ECOLOGICAL RISK ASSESSMENT OF CURRENT-USE PESTICIDES IN THE SIXAOLA WATERSHED, COSTA RICA

A Dissertation

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by

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AUTHORIZATION TO SUBMIT DISSERTATION

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ABSTRACT

Among the most important research priorities identified in tropical ecotoxicology is the need for risk assessment models specific to pesticide fate and toxicity in tropical watersheds. A number of different pesticides are applied in the Sixaola watershed, Costa Rica to produce export-quality plantains and bananas. Following an ecological risk assessment framework, the principal exposure pathways, environmental fate, and biological effect of current-use pesticides are integrated to provide an estimate of ecological risk to aquatic resources in the Sixaola watershed. Risk assessment of pesticide use in this region is essential for the identification of conservation or restoration priority areas, as well as for the development of better land management practices that address regional agriculture, conservation, and public health priorities.

As pesticide application practices have not been previously documented in the Sixaola watershed, the different pesticide application regimes used in banana and plantain production are presented and principal routes of human and ecological exposure are identified. Annual application rates range from less than 3 kg a.i./ha to more than 45 kg a.i./ha, and principal routes of exposure are primarily related to gaps in agrochemical or pest knowledge and the lack of appropriate infrastructure. A study of soil characteristics, in farms representing the range pesticide application regimes in plantain, suggests that floodplain soil properties important for agricultural production and agrochemical fate or transport are primarily driven by clay mineralogy and hydrologic processes. However, these floodplain soils are extremely heterogeneous over both large and small temporal and spatial scales, and present a challenge in estimating pesticide movement to aquatic resources from agricultural areas.

A number of different pesticides were measured in regional aquatic resources using both water grab samples and passive samplers (SPMDs). Field experiments to calibrate SPMD pesticide uptake rates showed that biofouling was not an important factor in SPMD pesticide sequestration over time, although several different stream characteristics may be important in the interpretation of SPMD-derived stream pesticide concentrations. Field-measured pesticide concentrations are integrated with modeled pesticide concentrations, knowledge of soil and water properties, primary routes of exposure, and available toxicity datasets to provide an assessment of risk for aquatic resources in the Sixaola watershed based on the hazard quotient method. However, given the unknown effects of pesticide mixtures and climatic conditions on toxicity, the lack of extensive tropical species toxicity data, and the complex species interactions and dynamic hydrologic regimes present in tropical landscapes, this method may not provide the most protective or conservative approach for risk assessment in tropical environments.

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Chapter One

Pesticide Application Practices, Pest Knowledge, and Cost-Benefits of Plantain Production in the BriBri-Cabécar Indigenous Territories, Costa Rica*

Abstract

The use of pesticides in the cultivation of cash crops such as banana and plantain is increasing, in Costa Rica and worldwide. Agrochemical use and occupational and environmental exposures in export banana production have been documented in some parts of Central America. However, the extent of agrochemical use, agricultural pest knowledge, and economic components in plantain production are largely unknown in Costa Rica, especially in remote, high poverty areas such as the Bribri-Cabécar Indigenous Territories. Our objective was to integrate a rapid rural assessment of indigenous farmer pesticide application practices and pest knowledge with a cost-benefit analysis of plantain production in the BriBri-Cabécar Indigenous Territories, for the development of better agricultural management practices and improved regulatory infrastructure. Interviews conducted with 75 households in 5 indigenous communities showed that over 60% of participants grew plantain with agrochemicals. Of these plantain farmers, over 97% used the insecticide chlorpyrifos, and 84% applied nematicides, 64% herbicides, and 22% fungicides, with only 31% of participants reporting the use of some type of protective clothing during application. The banana weevil (*Cosmopolites sordidus* Germar) was ranked as the most important agricultural pest by 85% of participants, yet only 28% could associate the adult and larval form. A cost-benefit analysis conducted with a subset of 26 plantain farmers identified several national markets and one export market for plantain production in the Indigenous Territories. Yearly income averaged $6200/ha and yearly expenses averaged $1872/ha, with average cost-benefit ratio of 3.67 for plantain farmers. Farmers applied an average of 9.7 kg a.i./ha/yr of pesticide products and 375 kg/ha/yr of fertilizer, but those who sold their fruit to the national markets applied more nematicides, herbicides, and fertilizers than those who sold primarily to export markets, suggesting a lack of appropriate application knowedge. Results indicate that the quantity of agrochemicals applied in plantain cultivation are less than that applied in export banana, but the absence of appropriate agrochemical application practices in plantain cultivation may pose serious risks to human and environmental health. Culturally appropriate farmer education and certification programs are needed as well as the development of safe-handling practices, regulatory infrastructure, and adequate agrochemical storage, transport, and waste disposal facilities.

Introduction

Cash crops provide nations around the globe with important sources of foreign exchange, food security, employment, and infrastructure development (Barham et al. 1992, Fafchamps 1992, Carvalho 2006). Banana and plantain (*Musa* spp.) are two cash crops in Costa Rica that comprise over 25% of Costa Rica's foreign exchange (Hernandez et al. 2000), contributing to substantial income generation and employment opportunities in both local and national economic sectors. Costa Rica is currently the second largest exporter of bananas in the world, exporting 95% of over 2.2 million metric tons of bananas produced annually, and the fourth largest exporter of plantains in the world, exporting over 40% of 70,000 metric tons of plantain produced annually (FAO 2007).

Agricultural production worldwide has been accompanied by continuous growth in the number and quantity of agrochemicals applied to crops (Carvalho 2006). This trend is increasingly evident in Central America, where pesticide use has essentially doubled during the past 20 years (Wesseling et al. 2005), from an estimated 30,000 tons of active ingredients applied annually in the 1980s to over 57,000 tons by 1999 (Wesseling et al. 2001a). In the year 2000, Costa Rica ranked second in the world in the amount of pesticides applied per unit area, with an average of 52 kg a.i./ha, and fourth in the world in fertilizer use with 385 kg a.i./ha (World Resources Institute 2007). Currently, an estimated 280 different pesticides are imported into Costa Rica and sold under more than 2,000 different brand names (de la Cruz and Castillo 2003). In 1998, over 18,000 metric tons of formulated agrochemicals were imported into Costa Rica (de la Cruz and Castillo 2003), more than one-third of which are used on banana and plantain production (Castillo et al. 2000). The majority of imported chemicals are fungicides, followed by herbicides, and less frequently, insecticides and nematicides (de la Cruz and Castillo 2003). Pesticide use is associated with environmental contamination and human health problems worldwide (Lacher and Goldstein 1997, Dinham and Malik 2003, Maroni et al. 2006). A number of human and environmental poisonings have been documented in commercial banana plantations in Costa Rica and Central America (Castillo et al. 1997, Castillo et al. 2000, Sass 2000, Wesseling et al. 2001b, Wesseling et al. 2005). Although increased documentation and research on agrochemical use in banana plantations are still badly needed, the need is even greater for such information relevant to plantain cultivation. No studies are known regarding pesticide use on plantain farms in Costa Rica, despite the fact that export quality plantain production in Costa Rica roughly follows the same agrochemical regime as commercial banana.

Agricultural lands in the Sixaola River Valley, located in the Talamanca region of southeastern Costa Rica, provide 52% of the plantain, 90% of the organic banana, and 6% percent of the commercial banana production in Costa Rica (Municipality of Talamanca 2003). Both plantain and banana have had a profound impact on the economy and environment of this poorest region of Costa Rica, and currently constitute the primary source of income for area residents either as revenue directly generated from household farms or as wage labor on commercial plantations (Borge and Castillo 1997, Dahlquist et al. 2007). Commercial banana production is limited to approximately 3,000 ha along the lower portions of the Sixaola River, where bananas for export are grown on large-scale plantations with intensive use of agrochemicals. Commercial banana producers are large landowners who are required by the transnational companies purchasing and marketing their fruit to meet strict quality standards and use prescribed production practices, including the use of large quantities of agrochemical inputs (Hernandez et al. 2000). It is estimated that up to 45 kg a.i./ha/yr are applied on these commercial banana plantations (IRET 2000, de la Cruz and Castillo 2003).

Unlike banana, where the majority of fruit is exported, plantain in Costa Rica is grown for both national and international markets (FAO 2007). Upstream from the commercial banana plantations, export-quality plantain is grown with moderate to intensive agrochemical use in organized cooperatives of household-plantain farms based on technology and knowledge adopted from commercial banana production. It has been estimated that between 10 and 15 kg a.i./ha/yr of pesticides are applied in intensive export-plantain production (IRET 2000). Farthest upstream in the Bribri-Cabécar Indigenous Territories, banana and plantain are grown on small-scale household farms in a variety of different agricultural systems ranging from organic banana and plantain in mixed agroforestry systems, to monocultures with moderate agrochemical use (Dahlquist et al. 2007). Plantain has historically been part of subsistence production in the Bribri-Cabécar Indigenous Territories, and was not grown for export until the late 1980s (Villalobos and Borge 1998). With the highest concentration of poverty in Talamanca occurring within the indigenous territories (Municipality of Talamanca 2003), plantain quickly became an important cash crop and much needed source of income for indigenous farmers. In the Bribri-Cabécar Indigenous Territories, historical cropping systems such as the cultivation of basic grains, cacao agroforestry systems, and traditional fallows are rapidly being abandoned in favor of monoculture plantain cultivation for national and export markets (Dahlquist et al. 2007). During the past 20 years, plantain cultivation in Talamanca has increased from 1,270 ha of plantain in production in 1981 (Somarriba 1993) to over 6,600 ha in 2001 (Municipality of Talamanca 2003), representing a significant land-use change in the region.

Little is known about pest management and agrochemical use within the Bribri-Cabécar Indigenous Territories. No information exists on the intensity and frequency of pesticide applications, pesticide costs, market options, or farmer knowledge of agrochemical alternatives and pest biology. Farmers within the territories have few economic resources and poor access to health and educational facilities, including agricultural extension services. Legislation regulating pesticide use is absent within the Indigenous Territories. These factors have been associated with high incidence of environmental and human poisonings in other areas (Aragon et al. 2001, Hurtig et al. 2003, Konradsen et al. 2003, Karlsson 2004). Our objectives were to determine the extent of agrochemical use and pest management knowledge in banana and plantain cultivation as well as the costs and benefits of plantain production for the Bribri-Cabécar Indigenous farmers. This information is essential for any further research, conservation, or rural development efforts in the Indigenous Territories as well as for national and regional public health and agricultural management initiatives.

Methods

Our work integrates two different studies conducted within the Bribri-Cabécar Indigenous Territories from 2004 to 2006: a rapid rural appraisal of plantain and organic banana production and integrated pest management practices, and a cost-benefit analysis of plantain production. Both studies were based on participatory methods (Mikkelsen 1995) for integration into larger biophysical research projects on integrated pest management and ecological risk assessments for pesticide use.

2004 Rapid Rural Appraisal

A rapid rural appraisal (RRA) of 75 households was conducted in five banana- and plantain-growing communities (Shiroles, Amubri/Tsuidi, Sepéque, Gavilan Canta, and Boca Urén) within the Bribri-Cabécar Indigenous Territories from June-August 2004. Methods included semi-structured interviews, participant observation, transect walks, and informal discussions with key informants and farmers (Mikkelsen 1995). Organic banana farmers were included since organic banana is often grown in agroforestry systems that include plantain. In each of the five communities, 15 families that cultivated banana, plantain, or both were randomly selected and interviewed with the assistance of two local indigenous promoters. Interview questions covered subjects such as plantain and banana management and pest control techniques, farmers' knowledge and attitudes regarding the pest status of the banana weevil and the effectiveness of control methods, the amount, type, and frequency of pesticides used for plantain production, methods of pesticide handling and storage, protection used during application, health effects experienced, and why farmers chose to use or not use pesticides.

2006 Plantain Cost-Benefit Analysis

Twenty-six monoculture plantain farmers from the primary plantain-producing communities of Shiroles and Sepéque, who had been involved in an ongoing soil quality research project, participated in an intensive study of the costs and benefits of plantain production within the Indigenous Territories. With the aid of local agricultural extensionists, farmers were asked to report all sources of income from their plantain production, including the different national and export markets that they sell their fruit to each week. Farmers were then asked to list all costs associated with their plantain farms including the type and quantity of agrochemicals used, equipment rented, workers paid, and transportation costs. Comparisons of total income generated and total costs expended per hectare per year were then calculated with farmers to help them determine the financial status of their plantain production.

Data Analysis and Triangulation

For both datasets, interview data were coded and descriptive statistics were calculated. Where open-ended questions were used, responses were aggregated by topic and the percentage of participants mentioning each topic was calculated. A Kruskal-Wallis test of variance and simple linear regression were conducted to determine significant relationships and correlations among farmer demographics and pesticide use. One-way analyses of variance (ANOVA) at the 95% confidence level were used to test for significant differences among different farmer groups in the cost-benefit analysis. Amount of fertilizer was calculated based on the combined elemental composition of the two most widely used products, urea (46% N) and a complete N-P-K formula (10-30-10% respectively). Active ingredients for pesticides were calculated based on those product formulations available in the Bribri-Cabécar Indigenous Territories. The active ingredient value for insecticide-impregnated plastic bags was obtained from IRET (2000), and represents the amount of chlorpyrifos per hectare calculated by weight from the number of impregnated plastic bags on banana plants spaced at 2 m x 2 m per hectare. All data gained through literature review and interviews were triangulated through both participant observation and group discussions (Mikkelsen 1995). Participant observation included living with community members, informal conversations with indigenous farmers and other household members, participating in household and farming activities, and observations from personal experience through working in the indigenous territories (Dahlquist et al. 2007). Several group discussions for feedback were held after each study for reiteration and confirmation of gathered datasets.

Results and Discussion

Participant Demographics

Demographics for participants in the 2004 RRA are presented in Table 1. The average participant was 40 years old and possessed a US-equivalent education of 4th grade. Over half (53%) of participants had lived their entire life within the community where they were interviewed. Sixty percent of participants interviewed grew plantain in monoculture, with an average holding of 2.75 ha. The remaining 40% did not grow plantain or grew it in combination with certified organic banana in mixed agroforestry systems (averaging 1.5 ha), in which agrochemical use is technically not allowed. Plantain in these organic agroforestry systems is generally grown for local or household use as no market currently exists for organic plantain in Costa Rica. Twenty-four percent of respondents had both monoculture plantain farms as well as separate organic agroforestry banana or plantain farms. All participants combined represented a total of 123 ha in monoculture plantain and 70 ha in organic banana or mixed organic banana and plantain agroforestry systems, with overall farmer holdings in banana or plantain averaging 2.5 ha. Thirty-nine percent of participants were female landowners who cultivated an average of 2.10 ha of plantain or banana, compared to an average of 2.95 ha cultivated by male landowners.

In a follow-up cost-benefit study of BriBri-Cabécar farmers with monoculture plantain holdings, farm holdings were similar to those observed in the RRA study conducted two-years earlier, with participants reporting monoculture plantain farms ranging from 1 to 5 ha in size with an average farm size of 2.8 ha. This number and all of the information gained in the cost-benefit study are based on a specific "parcel" belonging to each farmer participant. However, it is important to note that this number does not always represent the total land holdings of participants, as many farmers have several different parcels of land under various cropping systems, including additional plantain, on different farms spread out across the indigenous territories. In the indigenous territories, individuals and families can have many parcels of land holdings scattered across the territories based on inherited land, or entire collective holdings, which if combined can be as much as 20 to 50 ha (Whelan 2005).

Agricultural Pest Knowledge

When asked to name the most important pest on their farm, over 85% of RRA participants placed the banana weevil (*Cosmopolites sordidus* Germar) as the first or second most important pest, and 57% of respondents ranked black sigatoka (*Mycosphaerella fijiensis*) as the first or second most important agricultural pest (Table 2). The banana weevil is also considered to be the most important insect pest of bananas and plantain throughout the tropics (Gold et al. 2001). Damage is caused by the larva, which tunnels within the corm and interferes with nutrient uptake. Banana weevil damage can reduce yield and plantation life, and heavy infestation can lead to crop failure in newly planted fields (Gold et al. 2001). Plants infected with the black sigatoka fungal pathogen develop necrotic lesions on leaf tissue that can cause immature ripening and crop losses of up to 50% (Stover and Simmonds 1987; Robinson 1996). Other pests that affect banana and plantain were described less frequently by participants, including Panama disease (causal agent *Fusarium oxisporum*), nematodes, palm weevils (*Rhynchophorus palmarum*), parrots, and thrips (*C. orchidii, C. signipennis*). The burrowing nematode (*Radopholus similis*) is considered the most damaging nematode pest of banana and plantain worldwide, causing annual yield losses of approximately 20% through destruction of the root system and subsequent toppling of infected plants (Marín et al. 2002), although other nematode pests can include root-knot nematodes (*Meloidogyne* spp.), lesion nematodes (*Pratylenchus* spp.), and the spiral nematode (*Heliotylenchus multicinctus*) (Robinson 1996).

In general, farmers mentioned larger, more visible pests more frequently and gave them a higher ranking compared to agricultural pests that are less visible, a phenomenon that has been observed in other pest knowledge studies (Joshi et al. 2000, Morales and Perfecto 2000). For example, only 10.7% of RRA participants mentioned nematodes and only 4% mentioned thrips, whereas almost all participants (94.7%) mentioned the banana weevil (Table 2). However, although the banana weevil was mentioned most frequently as the most important pest, only 28% of respondents associated the adult weevil with the larva (Table 3). To control for banana weevil, the most commonly used method, mentioned by 46.6% of participants, was application of nematicide/insecticides (Table 3). Cultural control methods were used by 16% of participants. Cultural control methods include the removal of debris and weeds from the base of the mat, deleafing and desuckering, removal of rotted stems, and weeding by machete. Pseudostem traps were used by 9.3% of participants and mentioned by another 22.6% (Table 3). These traps are constructed of two pieces of fresh banana or plantain stem cut lengthwise and then placed on top of each other in the field to attract weevils away from nearby plants (Gold et al. 2002). Pheromone traps were mentioned by 12% of participants. These traps contain a lure with the aggregation pheromone of the banana weevil, which is produced in Costa Rica (Ndiege et al. 1996). Pheromone traps were promoted by local organic banana organizations several years ago, but none of the participants were currently using pheromone traps. The jabillo or sandbox tree (*Hura crepitans* L.) was mentioned by 8% of participants. Jabillo latex has been used historically by the Bribri and Cabécar as a fish poison. It contains the piscicidal compound huratoxin (Sakata et al. 1971) and several other toxic compounds which could have insecticidal activity (Barbieri et al. 1983, Stirpe et al. 1983). The latex can be extracted from the bark and mixed with water to make a botanical insecticide, which is applied to the base of the banana mat as a drench. Its efficacy in banana weevil control is unknown, but it has been promoted in some communities as a locally available resource that is acceptable for organic banana production. However, participants who mentioned jabillo also commented that working with the latex is unattractive because of its skin and eye irritant properties.

Agrochemical Use in Plantain

Pesticide application reported in commercial banana plantations (Matlock and de la Cruz 2002, IRET 2000) was combined with pesticide application data from the rapid rural appraisal and plantain cost-benefit study to categorize the of range of pesticide application regimes on plantain and banana farms in Talamanca (Table 4). Compared to all plantain producers, commercial banana producers apply far more fungicides spending as much as $1,000 - $1,200 per hectare per month (Hernandez et al. 2000) to control black sigatoka, which accounts for up to 27% of production losses annually (Stover and Simmons 1987). Although fewer fungicide applications are used on plantain than banana in Talamanca, black sigatoka is still estimated to be responsible for more than 38% loss of production in plantain (Marin et al. 2002). The number of different pesticide application regimes in plantain production compared to that of commercial banana is a reflection of the variability in access to available plantain markets, agrochemicals, and financial resources. In Talamanca, the majority of intensive plantain, where pesticide applications are estimated to reach 15 kg a.i./ha/yr (IRET 2000), occurs outside the Indigenous Territories just upstream from commercial banana plantations in plantain cooperatives that sell export-quality fruit to multinational corporations. Within the BriBri-Cabécar Indigenous Territories individual agrochemical use greatly varies and some intensive plantain production can be found. In general, however, the majority of plantain production in the Indigenous Territories can be considered to be moderate to low-intensity, with most farmers applying only a few types of pesticides, less frequently, and primarily only when they can afford to do so (Table 4).

A comparison of fertilizer and pesticide use by monoculture plantain farmers in the Indigenous Territories interviewed in 2004 and 2006 is shown in Figure 1. The primary difference between studies is the increase in reported fertilizer and fungicide use. In addition to a probability of increased use during the two-year period, other reasons may account for the observed differences. A likely explanation is that the smaller 2006 study was conducted in two of the larger towns within a major plantain-growing region of the Bribri-Cabécar Indigenous Territories, which has a wealthier population, increased access to agrochemicals, and more available plantain markets compared to other more remote and relatively poorer areas of the territories that were included in the broader 2004 study.

Use of agrochemicals by RRA participants on monoculture plantain farms is reported in Table 5. Almost all participating farmers with monoculture plantain holdings reported using insecticide-impregnated plastic bags to cover their fruit during maturation. These ubiquitous bags can be seen throughout banana- and plantain-producing regions of Costa Rica, and are impregnated with 1% chlorpyrifos by weight to protect the fruit from cosmetic skin damage caused by thrips. As there are no facilities or infrastructure in place in the Bribri-Cabécar Indigenous Territories to accommodate the disposal of agrochemical waste such as used insecticide-impregnated bags and empty pesticide containers, participants were asked what they did with the used plastic bags. Almost 90% of respondents reported either burying or burning them after use (Table 5). However approximately 10% of respondents reported recycling the bags, which after triangulation with community groups proved to be an option that was only available for a few years in the late 1990s when for a short period of time bags were recycled by a now defunct cooperative of plantain farmers. Used plastic fruit bags are generally either burned or buried, but are often thrown out or washed out in rivers, while used pesticide containers are often rinsed out in the river and left in the field or reused within the household (Polidoro and Dahlquist, unpublished observation). The solid waste generated by the amount of plastic bags used in banana and plantain production is staggering, and is estimated to be 67 kg/ha per year (Russo and Hernandez 1995). Recycling options do exist in Costa Rica, but lack of transport and means for organized collection within the Indigenous Territories has prevented the used bags from getting to recycling plants.

After the insecticide-impregnated bags, nematicides are the most commonly used pesticide in indigenous plantain production, applied by about 85% of participants with monoculture plantain holdings (Table 5). Nematicides with insecticidal activity are applied primarily during planting by over 80% of respondents to control the banana weevil, and by over 50% of respondents when the plants are maturing. Thirty-one percent of participants reported applying nematicides, both during planting and afterwards around the base of the plant. The most commonly used nematicide is terbufos (Counter®), followed by oxamyl (Vydate®), and then ethoprofos (Mocap®). Herbicides, most commonly glyphosate (Round-up®) and more recently paraquat and diuron (combined in the product Biomorun®), are used by approximately 64% of participants with monoculture plantain. Many indigenous farmers also mentioned manually weeding their fields with machetes, and only applying herbicides once or twice a year when they could afford it. Fungicides to control black sigatoka were reported to be used by only 22% of participants, as they are relatively expensive for most small-scale farmers. Although a great number of fungicides exist in Costa Rica for use in commercial banana, the only fungicides mentioned to be available in the Indigenous Territories are propiconazole and more recently difenoconazole; both are commonly referred to as Tilt. Finally, only one-third of participants reported using some type of protective clothing during pesticide application. Protective clothing during application can be defined as the use of clothing that covers the body and is changed immediately after application, or the use of gloves or a mask. After triangulation with community members, this percentage may be inflated, as most indigenous plantain farmers in practice prefer not to apply their own pesticides if they can afford to pay other community members or "peons" who receive pay for offering this service.

When asked the open-ended question about what they thought about pesticides, over one-third of all RRA participants responded that they damage the land (Table 5), with other common responses being that pesticides do give a better product, or that they simply cannot use pesticides because of proximity to their own or their neighbor's certified organic banana holdings. Interestingly, over one-quarter of respondents chose not to answer this question. This may be due to the fact that pesticide use in the Bribri-Cabécar Indigenous Territories is still considered "taboo" or a forbidden subject, as indigenous leaders often assert that there is no pesticide use in the indigenous territories in order to maintain a public image based on exclusively organic production.

In a Kruskal-Wallis or Chi-Squared test of variance at the 95% confidence level, age and amount of land were significantly related ($p < 0.05$) to more pesticide use, with younger RRA participants and larger landowners using more agrochemicals than older or smaller landowner participants. However, no significant relationships were found among pesticide use and participants’ educational level, control methods used, gender, or banana weevil knowledge.

Costs and Benefits of Plantain Production

In the more detailed cost-benefit study of plantain market values and associated agrochemical use, all participating farmers reported selling their plantain to at least two different markets, with some farmers selling their fruit to as many as four different markets. Currently, there are five different options for selling plantain in the BriBri-Cabécar Indigenous Territories, including one option to sell to the export market and four different options for selling to national markets. In general, farmers aspire to sell their best fruit (based on maximum plantain finger length, bunch weight, and cosmetic appeal) to the export market because it commands the highest and most consistent price per plantain plant or fruit bunch. In each farm, however, bunches that do not meet length and weight requirements for the export market are sold to the next best national market buyer. The prices paid per metric ton of fruit in each of the different market options are shown in Table 6, and are ranked in order of highest to lowest fruit quality which is indicated by average bunch weight. Overall, 60% of participating farmers hereafter referred to as "export producers," primarily produce plantain for the export market, which requires them to box their own fruit for buyers to collect. These export producers then sell their "leftovers" or lower quality fruit to one or more of the national markets depending on the fruit size and quality. The other 40% of participating farmers, referred to as "national producers," exclusively sell their fruit to the one or more national markets.

A breakdown of farm age, gross income, expenses, and agrochemical use is shown in Table 7. Participating cost-benefit study farmers reported a wide-range of different farm ages, as indicated by the age of planting material or plantain root stock. However, export producers as a group tended to have slightly younger-aged farms compared to national producers. Yearly gross income from all markets averaged $6,307/ha for all producers. Although not significantly different, national producers averaged a slightly higher yearly income ($6,505/ha) compared to export producers ($6,183/ha). Average yearly expenses include costs of agrochemical inputs, hired labor, transportation, rental equipment, and fuel. For all producers, yearly agrochemical inputs alone averaged $380/ha for fertilizers and $368/ha for pesticide products. Total average yearly expenses were also similar between export ($1,840/ha) and national ($1,925/ha) producers, with national producers showing a slightly larger range of yearly expenses compared to export producers. For this reason, export producers showed a slightly higher, although not significantly different, benefit-cost ratio (3.73) than national producers (3.59). Export producers sold an average of 482 kg/ha/week of fruit, with approximately 59% of their production going to the export market. Similarly, national producers sold an average of 461 kg/ha/week to one or more of the available national market buyers.

Gaps in Agrochemical and Pest Knowledge

Although agrochemical use widely varied among farmers participating in both the RRA and cost-benefit study, plantain-producing farmers in the cost-benefit study reported applying an average of 375 kg/ha/yr of fertilizer and 9.7 kg a.i./ha/yr of pesticides (Table 7). As a group, national producers reported using more fertilizer and more pesticides per hectare per year than export producers. A closer examination of the frequency of applications and the amount of chemical used per application is shown in Figure 2. National producers applied fertilizers, nematicides, and herbicides more frequently throughout the year than export producers, and also applied significantly more nematicide and slightly more fungicide on their farms per application. However, for both national and export producers no relationships were observed among pesticide or fertilizer use and income gained or farm age, with only a very weak linear relationship ($R^2 = 0.35$) between higher total expenses and increased pesticide use. These higher application rates (quantity and/or frequency) of fertilizers, nematicides, and herbicides by national producers in the absence of any significant production or financial benefits, suggest a lack of knowledge on how much and how often to apply agrochemicals.

With the exception of those who have worked on commercial banana plantations or in plantain cooperatives outside the Indigenous Territories, the majority of indigenous farmers rely on knowledge gained from their neighbors or the fruit buyers for how to use and apply agrochemicals (Polidoro and Dahlquist, unpublished observation). In the Indigenous Territories, the fruit buyers or intermediaries not only buy farmers' plantains, but also provide farmers with tools and agrochemicals, later deducting them from the sale of plantain, enabling households with little or no resources to begin plantain production (Whelan 2005). Increased access to intermediaries, outside plantain markets, and agrochemical distributors within the two major towns in the indigenous territories has likely facilitated the transfer of agrochemical and pest management knowledge from the export plantain cooperatives to indigenous farmers. Export producers in the Bribri-Cabécar Indigenous Territories have the most direct link to this knowledge as they operate through contracts to regularly sell their fruit to specific intermediaries directly connected to the export-plantain cooperatives. By contrast, national producers and those plantain farmers not living within the major towns sell their fruit for the best price to whichever intermediary is available for any number of national markets, and appear to have less consistent agrochemical knowledge.

Nematicide use is particularly high in the Indigenous Territories, with some farmers applying nematicides up to six times a year, including during planting. Most indigenous farmers do not have any knowledge of nematodes and therefore cannot identify the signs of nematode damage, as only 10% of rapid rural appraisal participants even mentioned nematodes. Similarly, less than a third of farmers interviewed in 2004 were able to identify the banana weevil adult or associate it with its larvae with many indicating that they applied nematicides when they saw palm weevils, centipedes, or other arthropods. Other studies have also found that farmers who could not identify agricultural pests sprayed more often when they saw other insects (Dinham 2003). Thus, many indigenous farmers may be applying nematicides when they are not necessary. As opposed to commercial banana production where any over-application of agrochemicals is generally prescribed, over-application of agrochemicals in the Indigenous Territories is likely to be a consequence of the lack of appropriate pest or agrochemical use knowledge.

The apparent over and potentially unnecessary application of agrochemicals by some indigenous plantain farmers is just one area of agrochemical knowledge that warrants attention. In addition to the observation that the majority of indigenous farmers do not use any protective clothing during pesticide application, many application practices observed in the Indigenous Territories pose serious health risks to the applicators. A list of all agrochemicals used in banana and plantain production in Talamanca and their known health risks is shown in Table 8. Of most concern are the extremely toxic organophosphates and carbamates that are known for both chronic and acute poisonings (Wesseling et al. 2002, de Silva et al. 2006). Plantain farmers place chlorpyrifos-impregnated bags over large portions of their farm every week by hand, receiving prolonged organophosphate dermal and inhalation exposure. The nematicides terbufos and ethoprofos are granulated organophosphates that are applied to the soil with bare hands or from an empty tuna can without any form of protection or gloves (Polidoro and Dahlquist, unpublished observation). Oxamyl is a liquid-formulated carbamate that is mixed with water, usually in a 55-gallon drum, after which plantain seedlings are dipped by hand into the mixture and planted, or it is sprayed with a manual sprayer onto the stems of maturing plants to protect against banana weevil. Although not quantified, many farmers in the 2004 study reported symptoms of pesticide exposure including nausea, headache, and rash (Wesseling et al. 2002) when applying agrochemicals, particularly the chlorpyrifos-impregnated bags.

In Talamanca and around the world, damaged or leaky backpack sprayers constitute a major source of pesticide exposure to rural farmers (Mekonnen and Agonafir 2002, Matthews et al. 2003). As opposed to the application of fungicides by airplane in commercial banana plantations, a practice which potentially causes drift and runoff problems (Hernandez and Witter 1996), fungicides in the Indigenous Territories are applied by motorized backpack sprayer. With this technique, the applicator essentially sprays the fungicides directly overhead from side to side, receiving most likely some portion of the falling spray. In addition, farmers are generally unaware of re-entry times after spraying or alternatives to agrochemicals. Other potentially hazardous practices include the poor transport of agrochemicals and improper storage in households or in the field. Children may be the segment of the population most at risk (Cantor and Goldman 2002), as they often work with or around pesticides on farms with relatives, even though the minimum legal age to work with or apply pesticides is 18 years in Costa Rica (de la Cruz and Castillo 2003).

Conclusion

The range of pesticide application regimes in banana and plantain production in Talamanca reflects the variability in access to available plantain markets, agrochemicals, and resources. In the Indigenous Territories, plantain production is clearly providing a much needed source of income; however, increased agrochemical use in plantain was not found to be significantly related to increased production or income. The expansion of pesticide use in plantain production is cause for human and environmental concern. The lack of appropriate agrochemical knowledge and application practices, including the absence of protective clothing, poorly maintained equipment, and the potentially unnecessary over-application of agrochemicals, such as nematicides, may pose serious threats to human and environmental health. Although the overall environmental impact of pesticide applications in moderate to low intensity plantain production is probably less than that documented in commercial banana plantations (Hernandez and Witter 1996, Henriques et al. 1997, Hernandez et al. 2000), it is likely exacerbated by accidental over-applications and unregulated agrochemical use. With no known mechanisms or infrastructure in place to regulate the application, formulation, sale, transport, storage, or disposal of agrochemical products within the Indigenous Territories, there is cause for additional concern.

Additional research on pesticide routes of exposure, fate, transport, and toxicology is required in Talamanca as many area residents work directly with pesticides to maintain agricultural production on household or commercial farms, as well as rely on river and groundwater resources for consumption, fishing activities, and household use. The

Talamanca region of Costa Rica is renowned for its high biodiversity as evidenced by the number of nationally and internationally protected terrestrial, marine, and freshwater areas. Enforcement of existing agrochemical laws to protect human health and reduce environmental contamination is necessary. In the case of Talamanca, efforts should be increased to provide all plantain farmers with culturally appropriate agrochemical and agricultural pest information, including certification programs for pesticide applicators and farmer field schools that emphasize agricultural pest identification and signs of damage. Regional efforts should aim to extend infrastructure for safe agrochemical transport, storage, and appropriate waste disposal into all plantain-producing areas including the Bribri-Cabécar Indigenous Territories.

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References

Aragon, A., Aragon, C., Thorn, A. 2001. Pests, peasants, and pesticides on the Northern Nicaraguan Pacific Plain. International Journal of Occupational and Environmental Health 7: 295-302.

Barbieri, L., Falasca, A., Franceschi, C., Licastro, F., Rossi, C.A., Stirpe, F. 1983. Purification and properties of two lectins from the latex of the euphorbiaceous plants *Hura crepitans* L. (sand-box tree) and *Euphorbia characias* L. (Mediterranean spurge). Biochemical Journal 215: 433-439.

Barham, B., Clark, M., Katz, E., Schurman, R. 1992. Nontraditional agricultural exports in Latin America. Latin American Research Review 27:43-82.

Borge, C., Castillo, R. 1997. Cultura y Conservación en la Talamanca Indígena. EUNED, San Jose, Costa Rica.

Cantor, A., Goldman, L.R. 2002. International impacts of pesticides on children. International Journal of Occupational and Environmental Health 8: 60-63.

Carvalho, F.P. 2006. Agriculture, pesticides, food security and food safety. Environmental Science and Policy 9: 685-692.

Castillo, L.E., Ruepert, C., Solis, E. 2000. Pesticide residues in the aquatic environment of banana plantation areas in the north Atlantic zone of Costa Rica. Environmental Toxicology and Chemistry 19: 1942-1950.

Castillo, L.E., de la Cruz, E., Ruepert, C. 1997. Ecotoxicology and pesticides in tropical aquatic ecosystems of Central America. Environmental Toxicology and Chemistry 16: 41-51.

Dahlquist, R.M., Whelan, M.P., Winowiecki, L., Polidoro, B., Candela, S., Harvey, C.A., Wulforst, J.D., McDaniel, P.A., Bosque-Pérez, N.A. 2007. Incorporating livelihoods in biodiversity conservation: a case study of cacao agroforestry systems in Talamanca, Costa Rica. Biodiversity and Conservation 16: 2311-2333.

de la Cruz, E., Castillo, L.E. 2003. The use of pesticides in Costa Rica and their impact on coastal ecosystems. In: Taylor, M.D., Klaine, S.J., Carvalho, F.P., Barcelo, D., Everaats, J. (Eds.), Pesticide Residues in Coastal Tropical Ecosystems: Distribution, Fate and Effects. Taylor and Francis, London, pp. 338-373.

de Silva, H.J., Smarawickrema, N.A., Wickremasinghe, A.R. 2006. Toxicity due to organophosphorus compounds: what about chronic exposure? Transactions of the Royal Society for Tropical Medicine and Hygiene 100: 803-806.

Dinham, B. 2003. Growing vegetables in developing countries for local urban populations and export markets: problems confronting small-scale producers. Pesticide Management Science 59: 575-582.

Dinham, B. Malik, S., 2003. Pesticides and human rights. International Journal of Occupational and Environmental Health 9: 40-52.

Fafchamps, M. 1992. Cash crop production, food price volatility, and rural market integration in the third world. American Journal of Agricultural Economics 74: 90-99.

FAO. 2007. http://faostat.fao.org, accessed Jan 20, 2007.

Gold, C.S., Okech, S.H., Nokoe, S. 2002. Evaluation of pseudostem trapping as a control measure against banana weevil, *Cosmopolites sordidus* (Coleoptera: Curculionidae) in Uganda. Bulletin of Entomology Research 92: 35-44.

Gold, C.S., Pena, J.E., Karamura, E.B. 2001. Biology and integrated pest management for the banana weevil *Cosmopolites sordidus* Germar (Coleoptera: Curculionidae). Integrated Pest Management Review 6: 79-155.

Henriques, W., Jeffers, R.D., Lacher, T.E., Kendall, R.J. 1997. Agrochemical use on banana plantations in Latin America: Perspectives on ecological risk. Environmental Toxicology and Chemistry 16: 91-99.

Hernandez, C., Witter, S.G., Hall, C.A.S., Fridgen, C. 2000. The Costa Rican banana industry: Can it be sustainable? In: Hall, C.A.S., Van Laake, P., Perez, C.L., Leclerc, G (Eds.), Quantifying Sustainable Development. Academic Press, San Diego pp. 563-593.

Hernandez, C.E., Witter, S.G. 1996. Evaluating and managing the environmental impact of banana production in Costa Rica: A systems approach. Ambio 25: 171-178.

Hurtig, A.K., San Sebastian, M., Soto, A., Zambrano, D., Guerrero, W. 2003. Pesticide use among farmers in the Amazon basin of Ecuador. Archives of Environmental Health 58: 223-228.

IRET (Regional Institute for Studies of Toxic Substances). 2000. Reducción del escurrimiento de plaguicidas al mar caribe: Informe Nacional: Costa Rica GEF/11000-99-04/PNUMA. Dec. 2000.

Joshi, R.C., Matchoc, O.R.O., Bahatan, R.G., Dela Peña, F.A. 2000. Farmers' knowledge, attitudes and practices of rice crop and pest management at Ifugao Rice Terraces, Philippines. International Journal of Pest Management 46: 43-48.

Karlsson, S.I. 2004. Agricultural pesticides in developing countries - a multilevel governance challenge. Environment 46: 22-41.

Konradsen, F., van de Hoek, W., Cole, D.C., Hutchinson, G., Daisley, H., Singh, S., Eddleston, M. 2003. Reducing acute poisoning in developing countries-options for restricting the availability of pesticides. Toxicology 192: 249-261.

Lacher, T.E., Goldstein, M.I. 1997. Tropical ecotoxicology: status and needs. Environmental Toxicology and Chemistry 16: 100-111.

Marin, D. H., Romero, R.A., Guzman, M., Sutton, T.B. 2003. Black Sigatoka: An increasing threat to banana cultivation. Plant Disease 87: 208-222.

Marín, D.H., Sutton, T.B., Barker, K.R. 2002. Dissemination of bananas in Latin America and the Caribbean and its relationship to the occurrence of *Radopholus similis*. Manejo Integrado de Plagas y Agroecología 66: 62-75.

Maroni, M., Fanetti, A.C., Metruccio, F. 2006. Risk assessment and management of occupational exposure to pesticides in agriculture. La Medicina del Lavoro 96: 430-437.

Matlock, R.B and de la Cruz, R. 2002. An inventory of parasitic Hymenoptera in banana plantations under two pesticide regimes. Agriculture, Ecosystems and Environment 93: 147-164.

Matthews, G., Wiles, T., Baleguel, P. 2003. A survey of pesticide application in Cameroon. Crop Protection 22: 707-714.

Mekonnen, Y., Agonafir, T. 2002. Pesticide sprayers' knowledge, attitude and practice of pesticide use on agricultural farms of Ethiopia. Occupational Medicine 52: 311-315.

Mikkelsen B. 1995. Methods for development work and research: a guide for practitioners. Sage Publications, London.

Morales H., Perfecto, I. 2000. Traditional knowledge and pest management in the Guatemalan highlands. Agriculture and Human Values 17: 49–63.

Municipality of Talamanca. 2003. Plan Local de Desarrollo: 2003-2013. Municipality of Talamanca, Bribri, Costa Rica.

Ndiege, I.O., Jayaraman, S., Oehlschlager, A.C., Gonzalez, L., Alpizar, D., Fallas, M. 1996. Convenient synthesis and field activity of a male-produced aggregation pheromone of *Cosmopolites sordidus*. Naturwissenschaften 83: 280-282.

Robinson, J.C. 1996. Bananas and plantains. CAB International, Wallingford, U.K.

Russo, R.O., Hernandez, C. 1995. The environmental impact of banana production can be diminished by proper treatment of wastes. Journal of Sustainable Agriculture 5: 5-13.

Sakata, K., Kawazu, K., Mitsui, T. 1971. Studies on a piscicidal constituent of *Hura crepitans* Part I. Isolation and characterization of huratoxin and its piscicidal activity. Agricultural and Biological Chemistry 35: 1084-1091.

Sass, R. 2000. Agricultural "killing fields": the poisoning of Costa Rican banana workers. International Journal of Health Services 30: 491-514.

Stirpe, F., Gasperi-Campani, A., Barbieri, L., Falasca, A., Abbondanza, A., Stevens, W.A. 1983. Ribosome-inactivating proteins from the seeds of *Saponaria officinalis* L. (soapwort), of *Agrostemma githago* L. (corn cockle) and of *Asparagus officinalis* L.

(asparagus), and from the latex of *Hura crepitans* L. (sandbox tree). Biochemical Journal 216: 617-625.

Somarriba, E. 1993. Allocation of farm area to crops in an unstable Costa Rican agricultural community. Ph.D. thesis, University of Michigan, Ann Arbor.

Stover, R.H., Simmonds, N.W. 1987. Bananas. Longman Scientific and Technical, New York.

Villalobos, V., Borge, C. 1998. Talamanca en la Encrucijada (2nd Edition). Editorial Universidad Estatal a Distancia, San José, Costa Rica.

Wesseling, C., Corriols, M., Bravo, V. 2005. Acute pesticide poisoning and pesticide registration in Central America. Toxicology and Applied Pharmacology 207: S697-S705.

Wesseling, C., Keifer, M., Ahlbom, A., McConnell, R., Moon, J.D., Rosenstock, L., Hogstedt, C. 2002. Long-term neurobehavioral effects of mild poisonings with organophosphate and n-methyl carbamate pesticides among banana workers. International Journal of Occupational and Environmental Health 8: 27-35.

Wesseling, C., Aragón, A., Castillo, L.E., Corriols, M., Chaverri, F., de la Cruz, E., Keifer, M., Monge, P., Partanen, T., Ruepert, C., van Wendal de Joode, B. 2001a. Hazardous pesticides in Central America. International Journal of Occupational and Environmental Health 7: 287-294.

Wesseling, C., van Wendel de Joode, B., Monge, P. 2001b. Pesticide related illness among banana workers in Costa Rica: a comparison between 1993 and 1996. International Journal of Occupational and Environmental Health 7: 90-97.

Whelan, M.P. 2005. Reading the Talamanca landscape: land use and livelihoods in the Bribri and Cabécar indigenous territories. M.Sc. Thesis, Centro Agronómico de Investigación y Enseñanza (CATIE), Turrialba, Costa Rica.

World Resources Institute. 2007. http://www.wri.org, accessed Jan. 20, 2007.

Table 1. Demographic and land-holding characteristics of rapid rural appraisal participants within the Bribri-Cabécar Indigenous Territories (N=75)

	Individuals (%)
Female	38.6
Male	61.4
Age Group (years)	
0-20	6.7
21-30	18.7
31-40	32.0
41-50	17.3
51-60	17.3
60+	8.0
Education Level	
no school	22.2
primary school	62.5
high school	14.6
Monoculture Plantain Holdings	
< 2 hectares	32.0
2-5 hectares	24.0
> 5 hectares	4.0
none	40.0
Agroforestry Banana and/or Plantain	
< 2 hectares	52.0
2-5 hectares	9.3
> 5 hectares	1.3
none	37.3

Table 2. Ranking of agricultural pests by rapid rural assessment participants (N=75)

Pest	**Spanish name**	**Latin name**	**Individuals that mentioned the pest (%)**	**1st most important pest ranked by individuals (%)**	**2nd most important pest ranked by individuals (%)**	**3rd most important pest ranked by individuals (%)**
Banana weevil	Picudo negro	*Cosmopolites sordidus*	94.7	68	18.6	5.3
Black sigatoka	Sigatoka negra	*Mycosphaerella fijiensis*	78.6	28	29.3	12
Panama disease	Mal de Pamana	*Fusarium oxysporum* f. sp*. cubense*	22.7	2.7	6.7	4
Palm weevil	Picudo del coco; picudo del palmito; picudo grande	*Rhynchophorus palmarum*	21.3	5.3	2.7	2.7
Nematodes	Nematodos	*Radopholus, Meloidogyne, etc.*	10.7	4	2.7	2.7
Leaf cutter ants	Hormigas, zompopos	*Atta cephalotes,* others	6.9	0	2.7	0
Parrots	Loros	*Aratinga finschi, Amazona farinosa,* others	6.7	0	1.4	1.4
Erwinia	Erwinia	*Erwinia chrysanthemi*	5.3	0	0	1.4
Thrips	Trips	*Chaetanaphothrips orchidii, C. signipennis*	4	0	1.4	1.4
Moko	Moko	*Pseudomonas solanacearum*	2.7	1.4	0	0
Sugarcane weevil	Picudo amarillo, picudo rayado	*Metamasius hemipterus*	10.7	0	0	0
Small banana weevil	Picudo pequeño, picudo chiquito	*Polytus mellerborgii*	6.7	0	0	0
Lepidoptera defoliators	Gusanos	*Caligo memmon, C. teucer,* others	1.4	0	0	0
Bees	Abeja conga	*Trigona corvina, T. trinidadensis silvestriana*	1.4	0	0	0

Table 3. Rapid rural appraisal of participant banana weevil knowledge and methods of control (N=75)

	Individuals (%)
Understand Banana Weevil Life Cycle	
Yes	28.0
No	53.3
Not sure	18.6
Banana Weevil Control Methods	
Nematicides	46.6
Cultural control	16.0
Pseudostem traps	9.3
Jabillo latex	5.3
Nothing	32.0
Other Methods Known But Not Used	
Pseudostem traps	22.6
Pesticides	14.6
Pheromone traps	12.0
Cultural control	4.0
Jabillo latex	2.6
None known	44.0

Table 4. Summary of pesticide use regimes in banana and plantain production in Talamanca, Costa Rica

	Intensive Banana	**Intensive Plantain**	**Moderate Intensity Plantain**	**Low-Intensity Plantain**	**Agroforestry Banana and Plantain**
Fungicides	**Rotation of Mancozeb, Tridemorph, Bitertanol, and Difenoconazole**	**Rotation of Mancozeb, Tridemorph, Bitertanol, and Difenoconazole**	**Propiconazole or Difenoconazole**	**None**	**None**
How Applied	Airplane	Motorized hand sprayer	Motorized hand sprayer		
Frequency	Every 8-15 days	3 to 6 times per year	1 to 3 times per year		
Nematicides	**Terbufos and Carbofuran**	**Terbufos or Ethoprofos and Oxamyl**	**Terbufos or Ethoprofos and Oxamyl**	**Terbufos or Ethoprofos**	**None**
How Applied	Manual hand pump	Manual hand pump	Manual hand pump or by hand	By hand	
Frequency	3 times a year (and during seeding)	3 times a year (and during seeding)	1 to 2 times a year (and during seeding)	Only during seeding	
Herbicides	**Glyphosate, Paraquat, Diuron**	**Glyphosate, Paraquat, Diuron**	**Glyphosate, Paraquat, Diuron**	**None**	**None**
How Applied	Manual hand pump	Manual hand pump	Manual hand pump		
Frequency	3 to 6 times per year	3 to 6 times per year	1 to 3 times per year		
Post-Harvest Fungicides	**Imazalil and Thiabendazole**	**Imazalil and Thiabendazole**	**None**	**None**	**None**
How Applied	In packing plant	In packing plant			
Frequency	3 to 7 times/week	3 to 7 times/week			
Insecticides	**Chlorpyrifos**	**Chlorpyrifos**	**Chlorpyrifos**	**Chlorpyrifos**	**None**
How Applied	Bagged fruit	Bagged fruit	Bagged fruit	Bagged fruit	
Frequency	3 to 7 times/week	1-3 times/week	1 time/week	1 time/2 weeks	
Total Active Ingredients	35-45 kg/ha/yr*	10-15 kg/ha/yr*	3-9 kg/ha/yr	<3 kg/ha/yr	None

* Source IRET 2000

Table 5. Characteristics of agrochemical use by rapid rural appraisal participants in monoculture plantain farms

Agrochemical Use (N=45)	**Individuals (%)**
Insecticide use (plastic fruit bags)	97.8
Nematicide use	84.4
Herbicide use	64.4
Fungicide use	22.2
Fertilizer use	66.7
Nematicide Use (N=38)	
Use during planting	81.5
Apply to plant during maturation	52.6
Use during and after planting	31.5
Use terbufos (Counter®)	42.1
Use oxamyl (Vydate®)	15.7
Use ethoprofos (Mocap®)	7.8
Use a combination of nematicides	34.2
Insecticide Bag Disposal (N=36)	
Buries	52.7
Burns	30.5
Either	5.5
Recycles	11.1
No use of protection (N=42)	69.0
What do you think about pesticides? (N=75)	
They damage the land	33.3
They give a better product	13.3
Certified organic, can’t use them	17.3
Too expensive	9.3
No comment	26.6

Table 6. Plantain market options in the Bribri-Cabécar Indigenous Territories in descending order from best fruit quality. Prices reflect 2006 market values using an exchange rate of 500 Costa Rican colones to the US dollar

Export Market	
Boxed Fruit	
average bunch weight (kg)	10
price per metric ton ($US)	270
National Markets	
Bagged bunch	
average bunch weight (kg)	10
price per metric ton ($US)	280
Non-bagged bunch	
average bunch weight (kg)	7
price per metric ton ($US)	230
Loose crate	
average bunch weight (kg)	5
price per metric ton ($US)	140
Peeled Fruit	
average bunch weight (kg)	4
price per metric ton ($US)	270

Table 7. Summary of benefits, costs, and agrochemical use in indigenous plantain production

All Producers (N=26)	Min	Max	Average	S.D.
Farm age (years)	2	18	5.0	3.24
Yearly gross income ($US/ha)	1848	12646	6307	2360
Yearly expenses ($US/ha)	810	3214	1872	675
Fertilizer product costs ($US/ha)	126	976	380	220
Pesticide products costs ($US/ha)	0	815	368	218
Benefit - Cost ratio	1.45	7.79	3.67	1.65
Fertilizer use (kg/ha/yr)	120	968	375	218
Fungicide use (kg a.i./ha/yr)	0.0	2.6	1.1	0.8
Nematicide use (kg a.i./ha/yr)	0.0	16.3	5.0	4.2
Herbicide use (kg a.i./ha/yr)	0.0	5.4	2.5	1.7
Insecticide use (kg a.i./ha/yr)	0.7	0.7	0.7	n/a
Total pesticide use (kg a.i./ha/yr)	0.7	24.4	9.7	5.4
Export Market Producers (N=16)				
Farm age in years	2	7	4.0	1.6
Yearly gross income ($US/ha)	3530	12646	6183	2371
Yearly expenses ($US/ha)	810	2827	1840	651
Benefit-Cost ratio	1.66	7.79	3.73	1.78
Export market supply (kg/ha/week)	153	490	284	97
National market supply (kg/ha/week)	35	470	198	153
Income from export market (%)	31	96	65	19
Fertilizer use (kg/ha/yr)	120	770	353	201
Pesticide use (kg a.i./ha/yr)	0.7	16.7	8.3	4.8
National Market Producers (N=10)				
Farm age (years)	2	18	6.6	4.5
Yearly gross income ($US/ha)	1848	9876	6505	2455
Yearly expenses ($US/ha)	1266	3214	1925	746
Benefit-Cost ratio	1.45	6.00	3.59	1.52
National market supply (kg/ha/week)	103	721	461	201
Fertilizer use (kg/ha/yr)	120	968	410	251
Pesticide use (kg a.i./ha/yr)	2.7	24.4	11.9	5.9

Table 8. Summary of applied agrochemicals in Talamanca, Costa Rica for banana and plantain

Active Ingredient	Common Name	Use	Chemical Class	WHO Class*	Other Risks **
Propiconazole	Tilt	Fungicide	Azole	II	DR[1]
Difenoconazole	Also called Tilt	Fungicide	Azole	III	Unknown
Mancozeb	Ditane	Fungicide	Dithiocarbamate	U	CA[1,3], DR[1], EN[4]
Bitertanol	Baycor	Fungicide	Azole	U	Unknown
Tridemorph	Calixan	Fungicide	Morpholine	U	Unknown
Terbufos	Counter	Nematicide	Organophosphate	IA	CO[5]
Ethoprofos	Mocap	Nematicide	Organophosphate	IB	CA[3], CO[5]
Oxamyl	Vydate	Nematicide	Carbamate	IB	CO[5]
Carbofuran	Furadan	Nematicide	Carbamate	IB	CO[5]
Glyphosate	Round-Up, Evigras, Biokim	Herbicide	Phosphonoglycine	U	Unknown
Diuron	Biomorun, Gramuron	Herbicide	Urea	U	CA[3], DR[1]
Paraquat	Gramuron, Biomorun	Herbicide	Bipyridylium	II	Unknown
Chlorpyrifos	Dursban, Lorsban	Insecticide	Organophosphate	II	CO[5], EN[4]
Imazalil		Post-Harvest Fungicide	Azole	II	CA[2], DR[1]
Thiabendazole		Post-Harvest Fungicide	Benzimidazole	U	CA[2], DR[1]

* World Health Organization Toxicity Classes: Extremely Hazardous (IA), Highly Hazardous (IB), Moderately Hazardous (II), Slightly Hazardous (III), and Unlikely Hazardous (U).

**Known Carcinogen (CA), Cholinesterase Inhibitor (CO), Developmental or Reproductive Toxin (DR), or Suspected Endocrine Disruptor (EN).

[1] USEPA Toxics Release Inventory List. U.S. Environmental Protection Agency, Washington DC.

[2] Office of Pesticide Programs List of Chemicals Evaluated for Carcinogenic Potential. U.S. Environmental Protection Agency, Washington DC.

[3] State of California Proposition 65 under the Safe Drinking Water and Toxic Enforcement Act of 1986.

[4] Keith, L.H. Environmental Endocrine Disruptors: A Handbook of Property Data, Wiley Interscience New York, 1997.

[5] The Pesticide Manual, 11th edition, C. D. S. Tomlin, Ed., British Crop Protection Council, Farnham, Surrey, UK, 1997.

Figure 1. Agrochemical use in plantain farms as reported by participants in the 2004 rapid rural appraisal compared to participants in the 2006 plantain cost-benefit study

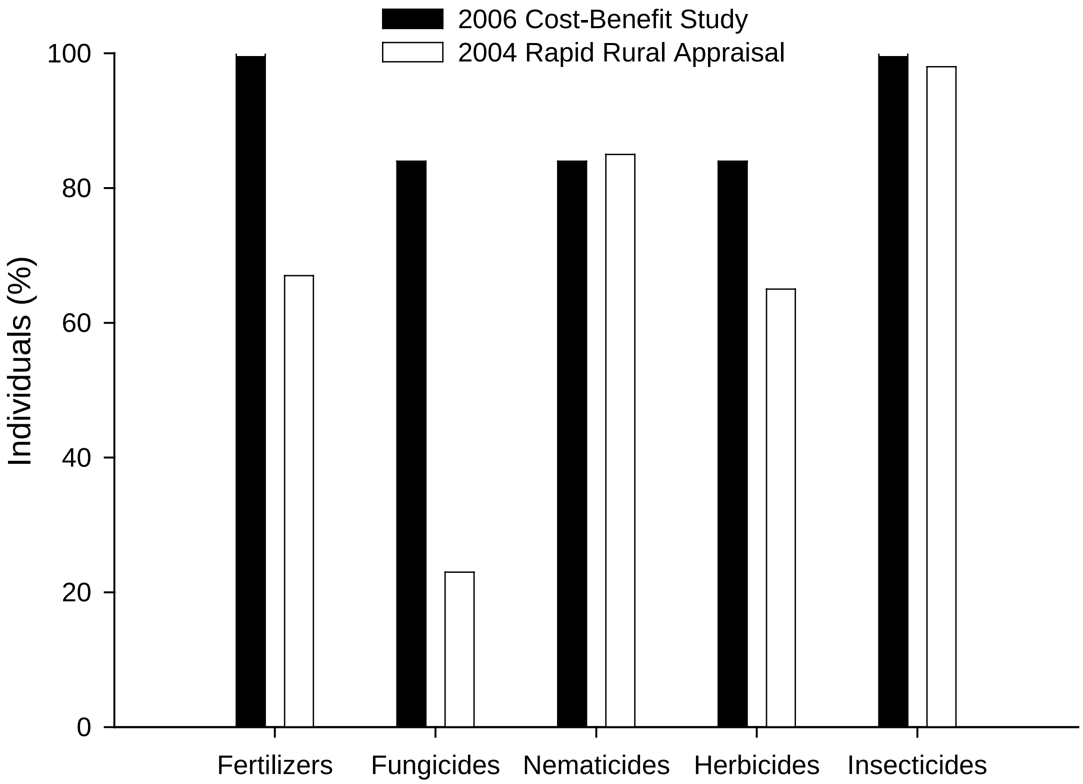
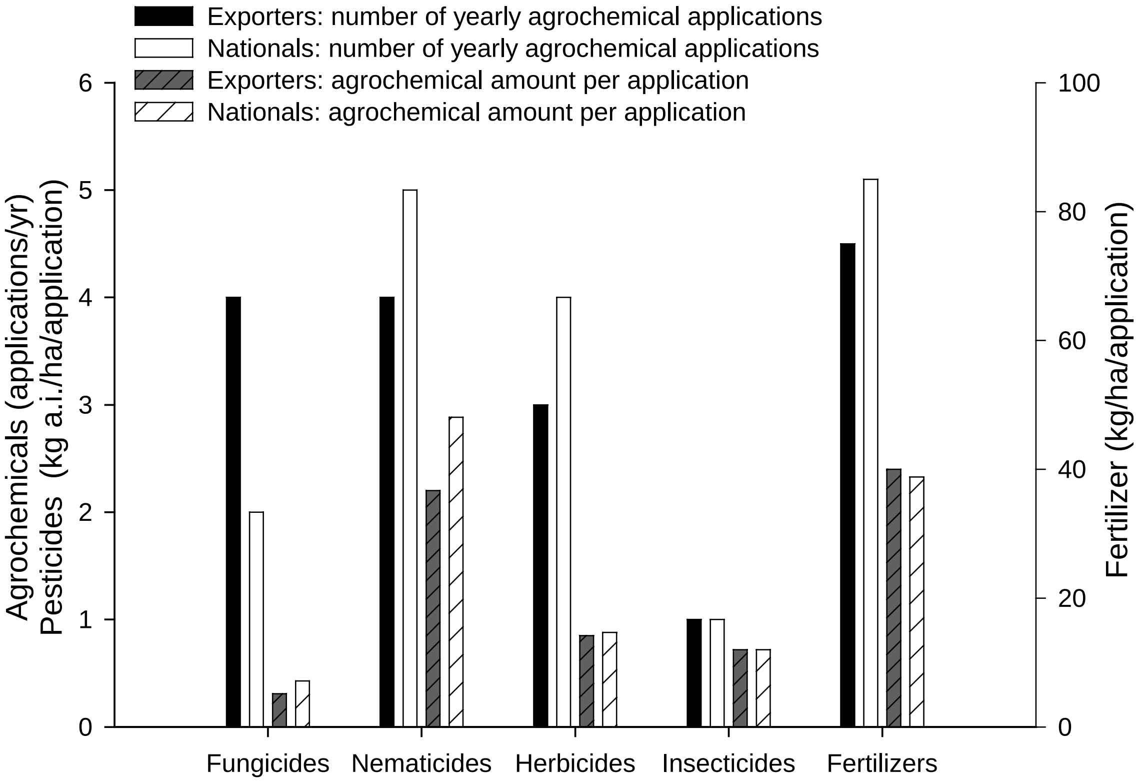


Figure 2. Median values of agrochemical applications per year and quantity per hectare applied during each application by exporters vs. national market producers



Chapter Two

Interpreting Floodplain Soil Variability at Different Scales: Implications for Agrochemical Modeling in Costa Rica

Abstract

Floodplain or alluvial soils are important areas for agricultural production worldwide. However, significant challenges exist in characterizing these highly variable soils for improved agricultural and land-use management at both the landscape and farm scale. In a tropical watershed located in southeastern Costa Rica, floodplain topsoils were collected at a coarse or landscape-level scale, and soil profile samples to a depth of 1-m at a fine or farm level scale. The objective was to understand the spatial and temporal variability of measured soil properties at these two different scales, and to identify general patterns in floodplain soil physiochemical properties that may be important for modeling pesticide fate and transport. Soil samples were analyzed for a suite of physiochemical properties including organic matter, texture, pH, acidity, cation exchange capacity (CEC), and extractable nutrients (Ca, Mg, K, P, Cu, Zn, Fe, Mn). Results indicate that fine-scale sites are spatially auto correlated when classified into 60-m distance classes from principal streams, with the highest ranges of measured values in Mn, K, OM, and percent sand or clay, and lowest ranges of values in pH, bulk density, CEC and Ca. However, all soil properties showed significantly different means ($p < 0.05$) among the 10 fine-scale sites and, with the exception of acidity and percent clay, showed significantly different means among different horizons. At the coarse scale, sampling sites were not spatially auto correlated when classified into 250-m distance classes from principal streams, and exhibited general trends of increasing organic matter and clay, and decreasing sand in downstream areas and in increasing distance from rivers. Although there were no clear observations of decreasing variability in individual soil properties with increased distance from rivers at either scale, principal component analyses (PCA) suggest that suites of soil properties are variable in different degrees and at different scales due to a complex array of both fast and slow landscape and soil-formation processes that produce both regular and random spatial and temporal variation. In sum, soil properties in this tropical

floodplain are largely driven by smectitic clay mineralogy and dynamic hydrologic processes. Using organic matter as a surrogate, pesticide concentrations will likely be higher in downstream areas of the Sixaola floodplain where finer sediments and higher applications occur. However, prediction of spatial distribution of pesticides at the landscape or coarse-scale would likely under or over estimate pesticide concentration for individual farm sites for any given point in time, while fine-scale or farm-level prediction is likely to produce more accurate results, but only over smaller or "faster" temporal scales. For these reasons, management goals must be clearly defined and based on the selection of appropriate spatial and temporal scales.

Introduction

All soils are inherently chaotic (Webster 2000). Soils by nature are heterogeneous with complex temporal and spatial variation of soil physical, chemical, and biological properties (Sommer 2006, Bruland and Richardson 2005, Burrough 1993). Alluvial soils in active floodplains are extremely variable both temporally and spatially as soil-forming material is continuously eroded and deposited in a dynamic environment. In alluvial soils, the stratification of different deposited sediments can vary spatially with sandy sediments overlying clays in one location or clays overlying sandy sediments in others (Iqbal et al. 2005). Regular changes in stream flow and variation in hydrologic conditions in active floodplains and riparian areas can also contribute to temporal changes in soil properties that can endure from minutes to millennia (McClain et al. 2003).

The characterization of soil spatial and temporal variability is essential for understanding the complex relationships among soil properties and environmental factors such as topography, vegetation, or hydrology (Yemefack et al. 2005, Goovaerts 1998), as well as for determination of appropriate agricultural and ecosystem management practices (Grunwald et al. 2007, Park and Vlek 2002, Bouma 1999). Examination of soil variability at a coarse or regional scale is important to understand widespread soil-forming factors (Yemefack et al. 2005), for application of landscape-level analyses, and for estimating soil properties when extensive sampling is not possible (Thompson et al. 2006, Chaplot et al. 2001). Similarly, characterizing soil variability at the fine or field scale has shown to be important for understanding fine-scale processes and nutrient cycles (Bruckner et al. 1999) as well as crop yield and precision agriculture for reduction of agrochemical loss (Yemefack et al. 2005, Earl et al. 2003).

Alluvial or floodplain soils are renowned for their high fertility (Ogden and Thoms 2002), exceptional biological diversity (Mouw and Alaback 2003, Naiman et al. 1993), and complex biogeochemical cycles (Neatrour et al. 2004, Tockner et al. 1999). Floodplains around the world have been highly altered by human activities (Thoms 2003), including agriculture. Agricultural production worldwide has been accompanied by continuous growth in the number and quantity of agrochemicals applied to crops (Carvalho 2006). As the impact of pesticides on biota and aquatic resources in both tropical and temperate zones is largely related to their interactions with soil constituents (Cheng 1990, Naidu et al. 1998), the need to estimate agrochemical fate and transport on floodplain soils is of major importance.

Alluvial soils of the Sixaola River floodplain in southeastern Costa Rica are important areas for the production of export-quality plantain and banana. Farms located on the Sixaola River floodplains yield 52% of the plantain, 90% of the organic banana, and 6% percent of the commercial banana produced in Costa Rica (Municipality of Talamanca 2003). Approximately 150 km^2 or 30% percent of the Sixaola Floodplain is cultivated with banana or plantain, where annual pesticide applications are estimated to be between 15 and 45 kg a.i./ha (IRET 2000, Chapter 1). Agrochemical fate and transport in the Sixaola floodplain is a concern as pesticide use is largely unregulated, and there is little knowledge of appropriate agrochemical application practices or available facilities for agrochemical storage or waste disposal (Chapter 1). Our objective was to characterize soil properties and their variability in tropical agricultural soils in the Sixaola floodplain at both coarse and fine spatial scales for the purpose of modeling pesticide fate and transport. It was hypothesized that the variability or range of values in measured soil properties would decrease with increasing soil depth and with increasing sampled distance from rivers on the floodplain. Characterization of soil properties at both fine and coarse scales and increased understanding of soil property patterns in the floodplain are essential steps for modeling agrochemical fate and transport in the region and for the development of improved agricultural management practices at both the landscape and farm-level.

Study Site Description

The Sixaola River watershed is located in the Talamanca region of southeastern Costa Rica on the Panama border (Figure 1). In the upper reaches of the Sixaola River, five tributaries (Rio Uren, Rio Lari, Rio Telire, Rio Yorkin, and Rio Coen) form an extensive floodplain before converging into the main stem of the Sixaola River, which eventually meets the Atlantic Ocean. The headwaters of the Sixaola River and its tributaries begin in the Talamanca Mountains that are largely covered by dense secondary tropical forest. In this region of Costa Rica, annual precipitation increases with altitude from approximately 2600 mm of rain on the lower reaches of the Sixaola River to over 5000 mm of rain in the surrounding mountainous areas (4000 m elevation) with evapotranspiration rates throughout the region estimated to be between 1565-1719 mm/yr (Kapp 1989). Average daily air temperatures in Talamanca range from 18° to 28°C, also reflecting the large variation in altitude. Soil temperatures at 60-cm depth are likely to be fairly constant throughout the year at 27°C (Appendix A). Changes in elevation occur rapidly over short distances, with foothill slopes beginning around 10% to 20%, and the highest, most remote areas having slopes of over 50% (Borge and Castillo 1997). Geology of the Talamanca region is complex, but principally characterized by andesitic and basaltic breccia and conglomerates, overlain or interlayered with marine sedimentary deposits of sandstone, limestone, carboniferous siltstone, and lutites. The floodplain soils along the Sixaola River are underlain by thick Quaternary alluvial deposits (Borge and Castillo 1997).

The floodplain of the Sixaola River begins at an elevation of approximately 300 m and ends at sea level at the Atlantic Ocean. The Sixaola River and its tributaries are extremely dynamic systems. The quick break in slope upon reaching the floodplain often results in fluvial deposition of gravel and boulder bedload and frequent changes in river course. Vegetation on the floodplain is primarily monoculture agriculture, with very little riparian buffer or remnant forest remaining. Due to the combined effect of floodplain deforestation and high annual rainfall in a large, confined watershed, the lower reaches of the Sixaola

River and its tributaries experience frequent annual floods, creating severe erosional events in some areas and extensive deposition of sediments in others. As there is no pronounced dry season in Talamanca and a shallow water table (approximately 1 m depth), these soils once completely wetted, are assumed to have a moisture suction normally above field capacity but below saturation (Kellman and Tackaberry 1997). Sixaola floodplain soils have been previously mapped at a scale of 1:200,000 and classified as Entisols or Inceptisols (Borge and Castillo 1997), with 70% of the Entisols classified as Typic Troporthents. The Inceptisols have been previously classified as Fluventic Humitropepts (30%), Aeric Tropaquepts (30%) or Typic Humitropepts (30%) (Kapp 1989). Previous studies of soils on the Sixaola floodplains (Nieuwenhuyse 1994) have shown the morphology and characteristics of these soils to be extremely variable due to the frequency of flooding and depositional events. Studies on the hydrological balance of these floodplain soils during a twenty-year period (1950-1969) depict an excess of water in the soil for an average of 8 months of the year, with only slight deficits during the months of September and October (Kapp 1989). In general, floodplain soils closest to the Sixaola River are described as well-drained, sandy soils with high base saturation. Floodplain soils farther from the river are described as loam or clay loam soils that are well drained, except for the Tropoaquepts, and have moderate base saturation (Kapp 1989).

Methods

Research Design and Sample Collection

All soil sampling occurred between April 2005 and January 2006 in monoculture banana or plantain farms on the Sixaola floodplain. Two spatial scales were selected for sampling and analysis: (i) landscape or coarse-scale analysis of floodplain topsoil properties and (ii) farm level or fine-scale analysis of floodplain soil properties by horizon to 1 meter depth. In the coarse-scale study, composite topsoil samples were collected from 47 monoculture banana or plantain farms located in floodplain soils of the Sixaola River or one of its major tributaries. For composite samples, 8 to 10 samples were collected from a depth of 0-10 cm, homogenized, and sub-sampled for subsequent analysis. Coarse-scale composite topsoil samples were analyzed for 14 soil properties: percent organic matter (OM), texture (percent sand, silt, and clay), pH, acidity (cmol(+)/kg), and extractable calcium (cmol(+)/kg Ca), magnesium (cmol(+)/kg Mg), potassium (cmol(+)/kg K), phosphorus (mg/kg P), copper (mg/kg Cu), zinc (mg/kg Zn), manganese (mg/kg Mn), and iron (mg/kg Fe).

From the 47 coarse-scale farm sites, 10 plantain farm sites within the largest section of the upper floodplain area were randomly selected for fine-scale sampling. Soil samples for fine-scale analysis were collected in a transect delineated perpendicular to a nearby principal stream or tributary in each of the 10 farms. Six to eight soils were excavated along the transect at intervals of 30 meters. No samples were composited. A total of 238 soil samples were collected from 65 soil profiles sampled by horizon to a depth of 100 to 110 cm. Bulk density samples were also collected from all horizons to a depth of 70 cm using a bulk density corer (300 cm^3 SST Core Sampler from AMS). Fine-scale soil samples were analyzed for 19 soil properties: percent OM, texture (percent sand, silt, and clay), pH, acidity (cmol/kg), cation exchange capacity (cmol/kg CEC), exchangeable (cmol/kg) Ca, Mg, K, and Na, and extractable (mg/kg) Ca, Mg, K, P, Cu, Zn, Mn, and Fe. All coarse-scale and fine-scale sampling sites were entered into a GarminV GPS unit with an estimated precision of less than +/- 8 meters.

<u>Laboratory Analysis</u>

All samples were air-dried and passed through a 2 mm sieve. Bulk density and gravimetric water content were determined by oven-drying bulk-density samples for 24 h at 105°C. Percent OM was determined by loss-on-ignition using the method and equation reported by Goldin (1987): %OM = (0.810*LOI) - 1.42 (in Bigham 1996). From the total 285 coarse and fine-scale samples, 52 samples were randomly selected for total carbon and nitrogen analyses. For carbon and nitrogen analyses, samples were oven-dried for 24 h at 105°C, with 1 g of each sample run on a CNS elemental analyzer at the Centro Agronómico Tropical de Investigación y Enseñanza (CATIE) in Turrialba, Costa Rica. From this subset of carbon samples a C: N ratio was calculated, and percent carbon (C) for all samples was estimated as %C = %OM*0.46, derived from simple linear regression (R^2=0.54).

All texture and nutrient analyses including pH, acidity, cation exchange capacity, base cations, and extractable metals were conducted by the soils laboratory at CATIE. Percent sand, silt, and clay were determined using the hydrometer method (Bouyoucos 1951). Cation-exchange capacity (CEC) and base cations were determined by ammonium acetate pH 7 method (SSSA 1996), with exchangeable Ca, Mg, K, and Na determined by atomic absorption spectrophotometry. Extractable Cu, Zn, Mn, Fe, K, and P were determined by Olsen extraction modified to pH 8.5 (Olsen and Sommers 1982, Diaz 1978) followed by atomic absorption for Cu, Zn, Mn, Fe, K, and colorimetry for P. Extractable Ca, Mg, and acidity were determined in 1 N potassium chloride extracts using atomic absorption (Diaz 1978). Soil pH was determined from a 1:1 ratio of soil in distilled water.

Mineralogical analyses were conducted on nine randomly selected soil samples by x-ray diffraction (Dixon and Schultz 2002). Three of the nine samples were composites from the coarse-scale study. The other six samples were fine-scale study samples where nine topsoil samples and nine subsoil samples were composited into six groups of three samples each. Soil samples were first treated for removal of any carbonates (none found), organic matter, and oxides. Clays were then isolated by dispersal, centrifuged, and treated for x-ray diffraction. Removal of free iron and aluminum with citrate-bicarbonate-dithionite (CBD) was conducted on three of the samples (SSSA 1996).

Geospatial and Statistical Analysis

Coarse-Scale Analysis

Descriptive statistics and Pearson correlation coefficients were calculated for the 47 coarse-scale composite topsoil samples. Raw data were tested for spatial autocorrelation using Moran's I statistic. Based on the parameters of inverse weighting and Euclidean distance without standardization of data or any selected distance lag, all measured soil variables were determined to be randomly distributed at the 95% confidence level ($p < 0.05$). Using ArcGIS, a trend surface analysis based on linear regression and a first-order polynomial was conducted for each measured soil property to explore any upstream or downstream patterns or trends. A digital stream layer of principal rivers and tributaries was then derived from a 90-m digital elevation model (DEM). To determine the effect of distance from streams on soil properties at the coarse scale, a sensitivity analysis for different distance classes was performed. The 47 sampling sites were mapped using equidistant buffers extending at least

1000 m from principal streams at different intervals of 100 m, 200 m, 250 m, 300 m, 400 m, 500 m, and 600 m. The 250-m buffer interval was selected as the most optimal distance class for subsequent analysis, as topsoil farm sites were the most equally distributed across the 250-m buffer intervals (i.e. in the 250-m buffer interval each distance class of 250 m, 500 m, 750 m, and 1000 m contained either 11 or 12 farm sites). Bar graphs of selected variables and box plots for each variable were plotted based on 250-m distance class. Scatter plots were created for variable pairs with the highest significant Pearson correlation coefficients. One-way analysis of variance (ANOVA) was conducted for each variable to determine if there were significant differences in the measured soil property mean among 250-m distance classes. Principal component analysis (PCA) using the correlation cross-products matrix (standardized variables) was performed to determine the different sources of variation among soil properties in coarse-scale distance classes as well as to reduce the number of measured soil properties to those that account for the majority of variation for subsequent multivariate analysis of variance (MANOVA) across 250-m distance classes.

Fine-Scale Analysis

Pearson correlation coefficients were calculated for soil property pairs. Descriptive statistics for the measured soil properties were calculated by horizon, with raw values depicted by horizon in box charts. Stratigraphic summaries of textural class and organic matter content displayed by horizon were constructed for each of the 10 farm sites by connecting corresponding horizons in farm-soil profiles. For each horizon, summarized textural class was determined based on the average concentration of sand and clay for that horizon number, which was often the same textural class as the majority of individual samples in the horizon. Classes of percent organic matter were determined by averaging individual samples represented in the horizon. Moran's I statistic was used to determine autocorrelation. When no standardization of values or zones of indifference were chosen, all measured variables showed a high ($p < 0.01$) degree of spatial autocorrelation across all variables and horizons based on Euclidean distance. Spatial autocorrelation is expected in fine-scale analysis as samples were collected in transects that map as clusters on the floodplain.

Using ArcGIS, a trend surface analysis based on linear regression and a first-order polynomial was conducted for selected soil properties in each horizon to explore any upstream or downstream trends in measured soil properties. To provide replicates for fine-scale analysis, the 65 soil profiles were grouped into three fine-scale distance classes established in the field during transect sampling. Soil profiles were grouped into distance classes of 60 m, 120 m, and 180 m based on estimated soil profile distances from an adjacent stream or tributary in each of the 10 fine-scale farm sites. Median values for soil properties by horizon and 60-m distance class are depicted in depth charts, and averaged values for selected soil properties depicted in bar graphs. Principal components analysis (PCA) using the correlation cross-products matrix was performed on first horizon samples and then on all fine-scale samples to characterize primary sources of variation at the fine-scale compared to coarse-scale samples, to compare variation across fine-scale distance classes, and to reduce the number of variables to those that account for the majority of variation for subsequent fine-scale distance analysis, including ANOVA and MANOVA.

Results

Floodplain soil characterization

Summary statistics and Pearson correlation coefficients for soil properties measured from coarse-scale topsoils are shown in Tables 1 and 2. Skewness and kurtosis values indicate that the data are fairly normally distributed, with the exception of a high kurtosis value and corresponding coefficient of variation (%CV) for acidity due to the inclusion of two or three high outlier values. With the exception of acidity, the coefficient of variation is highest for Mn as a result of the wide range of measured Mn, and lowest for pH, reflecting fairly uniform pH values across sampling sites. All coarse-scale topsoil samples could be classified into one of four soil textural classes: sandy loam, silt loam, loam, or clay loam. Two-thirds of the topsoil samples came from the upper floodplain of the Sixaola watershed. As a group, these upper watershed samples contained all of the soils classified as loam and the majority of samples classified as sandy loam or silt loam. The remaining third were collected from the lower or downstream section of the Sixaola floodplain and contained all of the samples classified as clay loam. Correlation coefficients indicate significant relationships among OM, textural class, and extractable Ca, Mg, P, Zn, and Mn. Extractable Cu is also significantly related to percent sand, silt, and clay (Table 2).

Box plots of selected fine-scale soil data by horizon are shown in Figure 2. Summary statistics by horizon and Pearson correlation coefficients for soil properties measured for fine-scale analysis are shown in Appendix B. Skewness and kurtosis values indicate that as a whole, measured soil properties are fairly normally distributed, with the exception of a few outlier values for K in horizon 4 and for Ca, P, and Mn in horizon 3. Based on the coefficient of variation (%CV) of soil properties in each horizon (Figure 3), soil properties for all horizons that showed less variation or more narrow ranges of values include bulk density (Pb), CEC, pH, and to some extent, both exchangeable and extractable Ca. Highest coefficients of variation are seen in Mn, K, OM, and percent sand or clay. Correlation coefficients for soil transect samples were similar to coarse-scale topsoil samples, with significant relationships among OM, textural class, base cations, P, Zn, and Mn. Stratigraphic cross sections of horizon morphology, textural class, and average OM content are shown for each of the 10 soil transects in Appendix C. Horizonation and textural class are extremely variable in these floodplain soils and as a result a representative profile could not be determined. Other studies have found that alluvial soils cannot be appropriately described by the method of soil diagnostic profiles due to the absence of soil genetic features combined with high horizontal and vertical variability (Mendonca Santos et al. 2000). Finally, clay mineralogical analyses were consistent with previous studies (Nieuwenhuyse 1994) and showed both surface and subsurface subset samples to be predominantly composed of smectite, with some vermiculite and kaolinite. A representative XRD trace is shown in Figure 4. Although not shown, the average C: N ratio for the soil subset samples is 8.75 with a standard deviation of 1.3.

Examples of mapped results for the trend surface analyses for both coarse-scale topsoil samples and fine-scale soil transect samples by horizon are shown in Appendix D. Only those soil properties that showed good trend agreement across both scales and horizons are reported. Horizon thickness, percent sand, and pH showed higher values upstream, while percent OM, percent clay, CEC, Mn, K, and P all showed higher values downstream. No measured soil properties showed clear trends in increasing lateral distance from streams. However, moderate agreement among scales and horizons is seen with Ca, Mg, and P where interpolated values increased with increasing lateral distance from principal streams.

Soil variation at two different scales

Coarse-scale

Average values and standard deviations for soil properties grouped into 250-m distance classes are shown in Table 3. Raw values in 250-m distance classes are plotted in box plots and scatter plots in Appendix E. Only four soil properties (percent OM, percent sand, percent clay, and Mn) showed clear linear relationships with increasing 250-m distance class from streams (R^2 values of 0.79, 0.88, 0.94 and 0.91, respectively, Appendix E). Percent OM, clay, and Mn all showed increasing values with increasing distance from streams, while percent sand decreased with increasing distance from streams. However, in a one-tailed ANOVA, only percent clay, showed a significantly different mean ($p < 0.05$) between the different 250-m distance classes. In a principal components analysis (PCA), 76% of the variance can be explained by 4 principal components. Bar charts depicting the loading or contribution of each soil property to the variation represented by each of the first four principal components are shown in Appendix F. Based on a contribution or loading greater than +/- 0.30, variation in the first principal component (PC1) is primarily explained by percent OM, percent sand, percent clay, Mn, and P. For the other components, PC2 is primarily explained by pH, extractable Ca, Mg, and Fe; PC3 by OM, Cu, and Zn; and PC4 by K. Box plots of coarse-scale sample scores grouped by 250-m distance class are shown for the first four principal components in Figure 5. Each of these soil property groups derived from PCA analysis were analyzed in a general multivariate analysis of variance (MANOVA). However, no multivariate relationships were found to be significant among 250-m distance classes at the 95% confidence level ($p<0.05$).

Fine-Scale

Relationships among exchangeable and extractable Ca, Mg, and K are shown in Appendix G. For purposes of comparison with coarse-scale analysis, exchangeable Ca, Mg, K, Na, and CEC were not used for further fine-scale sample analysis. Average values, standard deviations, and median values for soil properties by horizon in 60-m fine-scale distance classes are shown in Appendix H, with median values by horizon for percent organic matter, clay, and sand shown in Figure 6. Due to spatial autocorrelation, there is little observed difference among soil properties grouped by 60-m distance classes at the fine-scale.

However, all measured variables across the three 60-m distance classes decrease with depth, with the exception of pH, percent sand, and Cu. Percent sand and pH increase with depth, but Cu does not show a clear pattern of decreasing or increasing (Appendix H). In an unbalanced general linear model (crossed ANOVA based on 60-m distance class and horizon number as model variables), both pH and acidity showed significantly different means ($p < 0.05$) among the three 60-m distance classes, and all measured soil properties, except acidity and percent clay, again showed significantly different means among horizons.

For comparison with coarse-scale topsoil samples, a principal components analysis (PCA) was conducted on only the first horizon of the fine-scale analysis (n=65). In the PCA of first horizon samples, 80% of the variance can be explained by 4 principal components (Appendix I). Based on a loading greater than +/- 0.30, variation in the first principal component (PC1) is primarily explained by percent sand, percent silt, percent clay, and Ca. For the other components, PC2 is primarily explained by percent OM, pH, Mg, Zn, and Mn; PC3 by percent OM, percent silt, and Fe; and PC4 by K, P, and Mn. Box plots of first horizon sample scores within each 60m distance class are shown for the first four principal components in Appendix I. Various groups of first horizon soil properties derived from PCA analysis were analyzed in a general multivariate analysis of variance (MANOVA). No multivariate relationships in first horizon soil transect samples were found to be significant among 60-m distance classes at the 95% confidence level ($p<0.05$). Although no differences among soil properties by fine-scale distance class were seen, there were differences observed between fine-scale farm sites that had been flooded just before sampling in January of 2005 and those that had not. First horizon fine-scale PCA scores grouped by whether the site had been flooded or not in January 2005 are shown in Figure 7, with differences in measured topsoil properties shown in Table 4.

In a PCA of all fine-scale soil data to a 1-m depth, including horizon thickness, extractable Na, and CEC, 74% of the variance can be explained by four principal components. Bar charts depicting the contribution of each soil property to the variation represented by each of the first four principal components are shown in Appendix I. Based on a loading greater than +/- 0.30, variation in the first principal component (PC1) is primarily explained by percent sand, percent silt, CEC, and Mn. For the other components, PC2 is primarily explained by pH, Na, and K; PC3 by percent organic matter, pH, acidity, and Mg; and PC4 by percent OM, pH, P, Cu, and Fe. Box plots of sample scores by horizon are shown for the first four principal components in Figure 8. In an unbalanced general linear model (crossed ANOVA based on farm site and horizon as model variables), all soil properties showed significantly different means ($p< 0.05$) among the 10 farm sites, and with the exception of acidity and percent clay, showed significantly different means among horizons.

Discussion

Floodplain soil characterization

Based on the summary of measured soil properties and mineralogical analysis (Table 1, Figures 2 and 4), Sixaola floodplain soils exhibit some traits similar to soils described elsewhere as tropical smectitic soils. Tropical smectitic soils are medium to fine-textured alluvial soils with moderate to large amounts of clay (20% or more), moderate to high CEC (10-50 cmol/kg), high base saturation, low P-fixation capacity, high bulk density (1.2 - 2.0 g/cm^3), and high water-retention capacity (Juo and Franzluebbers 2003). In the wetter tropics, smectitic soils are high-base status Entisols or Inceptisols with calcium and magnesium as the dominant exchangeable cations and often have a field moisture capacity moisture content that ranges from 30-70% by weight. However, Sixaola floodplain soils overall appear to have higher sand content and lower clay content than the smectitic soils described by Juo and Franzluebber (2003). This difference most likely contributes to the lower and quite uniform bulk density value of 1 g/cm^3 observed in Sixaola floodplain soils. In general, soil textures on the Sixaola floodplain also tended to be coarser upstream and finer downstream, which reflects the higher stream gradient and depositional velocity upstream compared to the lower gradient and lower stream velocities found closer to the coast. Sand content also generally increased with depth while clay content decreased with depth. In the second horizon, average clay content slightly increased possibly indicating clay accumulation in some areas, which can be associated with the pedogenic processes of Bt horizon development (Buol et al. 2003).

The range of organic matter values and calculated carbon contents found in Sixaola floodplain soils are similar to those reported for Entisols (Psamments, Orthents and Fluvents) in Sumatra (van Noordwijk et al. 1997). However, organic matter values in Sixaola are higher than those reported for other tropical floodplains in drier climates such as the West African savannah (Ekwoanya and Ojanuga 2002) or in floodplains with distinct seasonal rainfall cycles such as the Amazon basin (Bernoux et al. 2001) or the Erbaifangzi floodplain in China (Bai et al. 2005). Although average organic matter contents in Sixaola floodplain soils gradually decreased with depth, the observed pattern was not always a linear decrease but could be rather variable in individual soil pits, similar to patterns reported by Bai et al. (2005) in a study of organic matter in floodplain soil profiles in China. Across both fine and coarse-scale datasets, percent organic matter in Sixaola floodplain soils was most significantly correlated ($p<0.05$) with Ca, Mg, Zn, and Mn, as organic matter can complex with Mn and Zn as well as other cations such as Ca and Mg (Havlin et al. 1999). Organic matter was significantly correlated, although to a slightly lesser degree, to percent clay and consequently, percent sand. Similarly, percent OM, along with clay, CEC, and Mn increased downstream in trend surface interpolation. Although percent clay is often a good predictor of soil carbon in many regions (Arrouays et al. 1995), other researchers have suggested that the type of clay is more critical to soil carbon than the amount of clay (Saggar et al. 1996, Torn et al. 1997). As isomorphic substitution and swelling characteristics of smectitic clays have been shown to enhance sorption of humic acids, organic matter, and other cations (Li et al. 2003, Kaiser and Guggenberger 2003), it is likely that clay mineralogy in Sixaola floodplain soils is an important driver of measured organic matter concentrations.

Quantities of exchangeable Ca, Mg, K, and Na are controlled in part by the cation exchange capacity (CEC) of a soil. All of these base cations, along with CEC, decrease with depth in Sixaola floodplain soils. The calcium content in soils is likely related to organic matter and clay type, as evidenced by decreasing organic matter and decreasing clay content with depth, since no carbonates were detected in these soils, and Ca and Mg are often the dominant exchangeable cations in smectites (Juo and Franzluebbers 2003). However, based on optimum soil nutrient levels recommended for banana or plantain cultivation (López et al. 2001), both exchangeable and extractable Ca are particularly high in these floodplain soils, while exchangeable and extractable Mg and K concentrations are relatively low, with an average Ca to Mg ratio of approximately 5:1. Clays saturated with Ca retain greater amounts of P, which can result in decreased availability of P in soils with a pH greater than 6.5 (Havelin 1999). Smectites in particular require greater than 70% saturation of Ca for adequate Ca availability (Havelin 1999), indicating that smectitic clays in the Sixaola floodplain are most likely well saturated with Ca. Banana and plantain are known to require relatively high amounts of K and P (Robinson 1996), and N-P-K fertilizer is regularly applied to these soils, which aids in fulfilling plant demand and amending the potential unavailability of phosphorus in the soil.

The high calcium content of Sixaola floodplain soils assists in the maintenance of a favorable pH and low acidity. The pH of Sixaola floodplain soils is consistently slightly acidic to neutral and well suited to the cultivation of a wide range of crops (Juo and Franzluebbers 2003). Soil pH values slightly increased with depth, potentially explaining significant correlations with extractable Fe, Mn, and Zn, in that all showed decreased concentrations with depth, possibly as a result of decreased solubility with increasing pH (Sparks 2003). In general, however, Sixaola floodplain soils are moderately deficient in extractable Zn for banana and plantain cultivation (NAMASOL 2000). Copper availability is also pH dependent, but in Sixaola soils Cu is not significantly related to pH nor does it exhibit the same decreasing trends with depth as Fe, Zn, or Mn. This is most likely explained by the historical application of copper sulfate in the region by large-scale banana plantations throughout the region from the 1900s to the 1950s (Thrupp 1991, Cordero and Ramírez 1979). Although Cu levels in Sixaola floodplain soils are not too far out of the range considered optimum for banana or plantain cultivation (López et al. 2001), the irregular patterns of extractable Cu concentration in Sixaola floodplain soils may be indicative the slow movement of copper in the soil profile as a result of historical application.

Soil Variation at Two Different Scales

Coarse-Scale

At the coarse-scale, where topsoil samples were grouped into 250-m distance classes, percent OM and clay increased with increasing distance class from principal streams, while percent sand decreased. This pattern most likely reflects depositional processes (Alexander and

Fielding 2006, Dollar 2004), in which flows from the Sixaola River deposit larger-grained sediments such as sand and gravel where highest velocities occur directly near the river, while finer-grained sediments would be deposited farther from the river with a corresponding decrease in flow velocity. High-flow events during regular annual flooding can redistribute organic carbon and organic matter through erosion, transport, and deposition (Martinelli et al. 2003, Smith et al. 2005). In the Amazon floodplain, for example, it is estimated that 150 million tons of sediment enter the principal rivers from floodplain soils while 200 million tons are then transferred from the river to the floodplain (Dunne et al. 1998). This redistribution of the soil through erosion, transport, and deposition of sediments caused by regular flooding events creates both spatial and temporal variation in soil properties that are likely related to flow velocity, flooding area, and flooding frequency (Alexander and Fielding 2006, Dollar 2004). For example, areas farthest from the river are flooded less often by Sixaola River during flooding events. Thus, higher clay and organic matter content farther from the stream may also simply be the result of less sand present, or may be indicative of increased landscape stability (Saldana et al. 1998), allowing for soil-forming processes related to accumulation of organic matter and subsoil clay accumulation to occur.

It was hypothesized that soil properties measured at the coarse-scale would show decreasing variability with increasing distance class, indicated by larger ranges or standard deviations of soil property values closer to streams, and more stable or smaller standard deviations for soil property values in areas farther from streams where less flooding events occur and more stable landscape processes may exist. However, there was no clear pattern of decreasing standard deviation for individual soil properties with increasing 250m distance class (Table 3). Instead the majority of soil properties measured showed highest standard deviations in the middle distance classes. For example, the standard deviation for organic matter, sand, and silt was highest at the 500-m interval, indicating the largest range of values occurring at this distance interval. This could be interpreted as soils in the 250-m distance interval are most likely always flooded and show consistently high sand deposition, while farms at the 1000-m interval are rarely flooded if at all, and have consistently less sand and more clay and more organic matter. However, in the middle distance classes, there is likely an interface where both flooding events and soil development processes are both operating. In which case, distances between 500 m and 750 m may represent a dynamic threshold where there are areas of frequent flooding events interspersed with areas of less frequent flooding and increased intervals of landscape stability for soil development processes to occur.

A principal components analysis (PCA) is one way in which measured individual soil properties can be reduced to a few components, each representing a group of weighted soil properties, to examine the relative contribution of a soil property group to the overall variation, in this case represented by the difference in Pearson's correlation coefficients (Table 2) for each soil property pair divided by the standard deviation (McCune and Grace 2002). In a PCA for coarse-scale topsoils, the first component is strongly influenced by percent OM, percent sand, percent clay, but many other soil properties also contribute fairly equally to the measured variation. For this reason, the slight increase in the explained variation at the 1000-m distance class observed in the box plot (Figure 5) for the first principal component is most likely due to the wider range of percent clay values observed at the 1000-m distance class. The second principal component, primarily explained by pH, extractable Ca, Mg, and Fe, shows higher case scores for farms located in the middle distance classes of 500m and 750m. The third principal component, represented primarily by organic matter, Cu, and Zn shows no difference in the explained variation among distance classes, while the fourth principal component, dominated by K, shows a decrease in median case scores with increasing distance class. In general, calculated farm scores do not show clear differences when grouped into coarse-scale distance classes for the first four principal component vectors. This indicates that the suites of soil properties, driving the random variability represented by principal component vectors, cannot be used to explain differences among sampled soils when grouped into coarse-scale distance classes.

At the coarse-scale, geostatistical analysis and the lack of autocorrelation both assume randomness in soil properties. However, soil variability can be both regular and random, with landscape pedology often focusing on the regular variability of soils and geostatistical techniques on what is assumed to be random variability (Sommer 2006). Several studies have found that appropriate spatial scales for measuring soil properties are not the same for all soil properties. For example, Iqbal et al. (2005) used structured semivariograms and autocorrelation to determine a sampling range of 400-m for soil textural properties, and 100-m for soil hydraulic properties in alluvial soils deposited by the Mississippi River. In addition, relationships among soil properties at different scales cannot often be revealed by linear correlation (Bourennane et al. 2003). For some soil properties there may not even be an appropriate scale. For example, Sobieraj et al. (2004) found little predictability for hydraulic conductivity (Ks) at sampling intervals as low as 25-m. Few soil studies incorporate temporal variation in soil properties (Sommer 2006), which is an obvious source of variation in dynamic floodplain environments. Soil classification does not account for temporal variation as discrete representation is used to explain soil properties. Although, soil classification combined with geostatistical tools, such as interpolation and kriging, can provide more continuous representation of soil variability, they also do not account for temporal variation (Heuvelink and Webster 2001). Most recently, geostatistics with space-time series analysis or spatial state -space approach based on observations and physical laws have been proposed as methods that incorporate both temporal and spatial variation in soils (Heuvelink and Webster 2001).

Fine-Scale

At the fine-scale, all soil properties were determined to be spatially auto correlated and thus not randomly distributed; therefore there were no significant relationships among soil properties and the three 60-m fine-scale distance classes (Figure 6). At this scale, the coefficient of variation (Figure 3) therefore provides an opportunity to examine the regular variability of soil properties with different population means at the fine-scale or farm level, as properties that show more variation are expected to be more sensitive to change than others that are more homogenous (Grunwald et al. 2007). Mg and K varied the most as they showed very high coefficients of variation throughout the soil profile, with organic matter and Zn showing moderately high coefficients of variation compared to the other measured soil properties. As previously mentioned, K is applied up to three times a year in banana and plantain as a part of N-P-K fertilizer. Fertilizer is generally applied to the base of the plant, where the solubility of K is generally related to concentration and dilution processes brought about by evaporation and precipitation. Exchangeable K on soil colloids, such as smectite, is related to the amount of exchangeable Ca (Havelin et al. 1999). The observed variation in K, is therefore likely due to the combined variation in fertilizer application, soil moisture conditions during sampling, as well as clay and Ca content. In general, K losses are highest in sandy soils that are subject to flooding (Havlin 1999), as in many areas of the Sixaola floodplain. Without lowering pH, soluble Mg can increase in waterlogged soils under poorly aerated or anaerobic conditions (Havlin et al. 1999). In the Sixaola floodplain, frequent flooding events combined with the heterogeneity of soils may create biogeochemical hotspots, where patches in the landscape show disproportionately high reaction rates compared to surrounding soils (McClain et al. 2003), such as anaerobic areas that increase soluble Mg. As soil water content can change rapidly on the floodplain, this spatial variation in soil conditions can also vary temporally to create what is known as hot moments, such as during flooding or during high precipitation and a water logging event (McClain et al. 2003), increasing soluble Mg for varying time intervals. Organic matter varies the most in the first and fourth horizon. First horizon variation may simply be related to field conditions during sampling, such as the amount of weeds present or differences in crop age. In the fourth horizon, variation of organic matter is likely related to the irregular horizonation in floodplain soils that exhibit buried horizons and fluvial deposits with varying textural classes and organic matter contents. Variation in Zn and organic matter may be somewhat complementary. Extractable Zn is highly pH dependent and increases with decreasing pH. However, given a stable pH, more than half of soil soluble Zn is thought to complex with organic matter (Havlin et al. 1999).

In principal component analysis of variation of the first horizon only, again there were no differences in variation across the three fine-scale distance classes. However, the first component (PC1) is primarily influenced by texture (sand, silt, and clay) and Ca. This is most likely due to the effect of flooding among fine-scale sites, as some farms were flooded just before sampling in January 2005, while others were not. Figure 7 shows this relationship best, where first horizon principal component scores are divided into fine-scale sites that had been specifically flooded or not-flooded in January 2005. In this regrouping of PCA scores, flooded sites account for the same or more of the variance explained by the first four principal components compared to those sites that had not been flooded in January 2005. This relationship is clearest in principal component two which is primarily explained by percent organic matter, pH, Mg, Zn, and Mn. Similarly, fine-scale sites not flooded in January 2005 averaged higher organic matter, Mg, Zn, and Mn and lower pH than flooded sites (Table 4).

Although the differences are not great, non-flooded sites also showed higher sand and lower clay in the first horizon compared to flooded farms. These results appear to conflict with what is observed at the coarse-scale, where areas that are flooded less frequently or are farther from streams have higher percent clay and lower percent sand in the first horizon. This spatial discrepancy may likely be explained by temporal variation at the fine-scale, as farms flooded in January of 2005 were not necessarily all of those closest to streams and are not necessarily flooded all the time. However, all farms were sampled between 6 to 12 months after the January 2005 flood event. Therefore, the flooded farms were likely at different stages of recovery from flooding during sampling, which could reflect different stages of organic matter decomposition and sediment stabilization. These "faster" scales of temporal variation reflected in fine-scale analysis are similar to those reported by Grunwald et al. (2007), where the variation in measured wetland soil properties, represented by semivariograms of principal components, identified spatial and temporal variation both of which operated at different scales: 1) labile fast response soil properties with fine-scale spatial autocorrelation, 2) stable, slow response soil properties with regional spatial autocorrelation, and 3) soil properties with intermediate response.

Horizonation in Sixaola floodplain soils is distinct as regular flooding events contribute to the erosion or deposition of different sediment layers with time. Across all soil transects at the fine-scale, all soil properties showed significant differences in means among horizons (Figure 2). When depicted by horizon, over 35% of total variance explained by the first principal component (Figure 8), represented primarily by percent sand, percent silt, CEC, and Mg, shows a clear decrease in variability with increasing depth or horizon. The first horizon would be expected to exhibit the most variability in these soil properties as it the most affected by dominant landscape processes and current agricultural practices. However, the lower soil horizons accounted for slightly more of the measured variability among horizons in principal components two, three, and four primarily due to component scores for pH, organic matter, and associated extractable nutrients such as Fe or P. Variation observed in these lower horizons is thus likely related to the influence of organic matter content, textural class, and groundwater depth on pH and extractable nutrients. In less weathered soils, such as those found on the Sixaola floodplain, nutrients come from organic matter as well as weatherable sand, silt, and clay minerals (Juo and Franzluebbers 2003). Thus, at lower horizons, the variability of pH and organic matter is likely due to the presence of different buried horizons and graded fluvial deposits (Yarie et al. 1998), as well as the effect of localized saturated or anaerobic conditions during groundwater fluctuations on enhanced or reduced biogeochemical activity (McClain et al. 2003) influencing nutrient availability and pH.

Implications for Agrochemical Modeling

There are a number of sources of variation in the prediction of pesticide behavior. Not only can soil properties and pesticide concentration vary both spatially and temporally, but many models developed to predict pesticide concentration in the environment are intended for use in temperate climates and may not be appropriate for tropical climates. The spatial distribution of pesticides in soil has been shown to vary widely based on the variation of soil characteristics and subsurface hydrologic flow patterns (Laabs et al. 2002, Lafrance and Banton 1995, Reichenberger et al. 2002, Stoorvogel et al. 1999, Witter et al. 2003). Specific properties of soils that are important for predicting pesticide sorption, desorption, and transport include organic carbon content, water content, pH, clay type and fraction, and redox potential (Cheng 1990). Although the organic matter contents of tropical soils are generally similar to those of the temperate regions, the kinds of clay minerals and amount of metal oxides are much more varied in tropical soils than in temperate zones (Racke et al. 1997). For these reasons, pesticide sorption models developed in temperate zones may not account for the potential influence of different variable charge clays on pesticide sorption in tropical soils. However, many studies have shown that preferential and macropore flow may be more important than all of these properties for predicting pesticide losses (Reichenberger et al. 2002, La France and Banton 1995), but these are difficult to predict as they tend to vary both spatially and temporally over small scales (Sobieraj et al. 2004, Mallants et al. 1996).

Pesticide concentration in soils can also vary both temporally and spatially based on the site, and the frequency and quantity of application relative to the different environmental degradation rates. Pesticides in soils and sediments are principally degraded by microbial activity, chemical hydrolysis or oxidation, photo degradation, and volatilization (Lalah et al. 2001). The rates of both organic matter decomposition and pesticide degradation have been shown to be greater in tropical soils compared to temperate soils due to increased microbial activity, photo degradation, and volatilization associated with increased temperatures (Lalah et al. 2001, Karpouzas and Walker 2000). Although pesticides are assumed to dissipate more rapidly in the tropics, actual degradation rates vary both temporally and spatially and are generally unavailable for conditions found in tropical climates (Stoorvogel et al. 1999). However, it has also been suggested that certain pesticides may be more toxic in tropical regions due to higher contaminant solubility, augmented biological uptake and bioconcentration, and lower dissolved oxygen at higher temperatures (Castillo et al. 1997).

Given the vast amount of uncertainty in predicting pesticide behavior in soils and in tropical zones, by convention soil organic matter or organic carbon content is the most commonly used parameter to estimate pesticide sorption in soils based on each pesticide's organic carbon partition coefficient (Farenhorst 2006, Bollag et al. 1992, Lafrance and Banton 1995). In this region of Costa Rica, the majority of applied pesticides are hydrophobic and would not be expected to leach into lower horizons. Rather, pesticides would be expected to move with organic matter and associated clay fractions during flooding events. Thus, for the purposes of discussion, organic matter can be used as a surrogate to predict pesticide behavior in soils on the Sixaola floodplain. At the landscape or coarse-scale, spatial distribution of pesticides in the soil would be estimated to be higher in the lower Sixaola floodplain, due to increased application rates, increased organic matter, and clay content. Temporal variation of pesticide content at the coarse-scale would be based on differences in application rates and large-scale flooding events. However, spatial distribution of pesticides on a farm or fine-scale would likely produce very different and perhaps conflicting results. For individual farms, predicted pesticide concentrations would be more accurate when current farm conditions matched those during sampling, and become less accurate over time as farm conditions changed (flooding, flood recovery, weed control, crop age, etc). Similarly, pesticide concentrations would also vary with depth in each farm, as in floodplain soils there can be considerable variation of soil organic matter, clay content, and associated contaminants in buried horizons (Witter et al. 2003). Given the variability of horizonation in floodplain soils it would be difficult to extrapolate results from farm or fine-scale variation to a larger scale. A landscape-level analysis based on pesticide concentrations predicted at the fine-scale would require the sampling of many more farms with results aggregated and interpolated to provide a continuous surface to reduce the effect of "faster" sources of fine-scale temporal variation. Either way, predicted pesticide concentration at the landscape or coarse-scale would likely under or over estimate pesticide concentration for individual farm sites for any given point in time. Thus, stakeholders must clearly define the aim and extent of environmental and agricultural management goals before attempting to predict pesticide concentration in soils in order to choose the appropriate spatial and temporal scales of analysis.

Summary and Conclusion

Soil properties in the Sixaola floodplain are largely controlled by clay mineralogy and particle transport. High annual precipitation and steep surrounding slopes create high velocity flows in the Sixaola River and its tributaries. These flows deposit a gradient of sand and loam-textured sediments to form soils that are well drained and rich in calcium-saturated smectitic clays and organic matter, which in turn provide nutrients and maintain optimum pH. General trends of erosion, deposition, and transport correspond to assumptions of flow velocity, where increased deposition of finer-grained sediments such as clay and organic matter occur in lower-velocity downstream areas and increased lateral distance from streams.

Coarse-scale trends in soil characteristics such as decreasing sand content and increasing clay and organic matter with increasing distance from streams are observed. However, variability of soil properties at the coarse-scale does not clearly decrease with increasing distance from streams. Rather, suites of soil properties at the coarse-scale exhibit varying degrees of spatial variation related to landscape position and temporal variation from the combined effect of regular flooding events and soil-forming processes during varying intervals of landscape stability. At a fine-scale, variation of soil properties is also both spatial and temporal, but as soil properties are spatially autocorrelated at this scale, decreased variation with increasing distance from streams is even more difficult to determine. Instead, temporal variation at finer or "faster" scales, such as recent flooding events and fertilizer application, as well as current crop age or field management at the time of sampling, become more important for the understanding of soil variation. Horizonation in Sixaola floodplain soils is distinct but extremely variable as a result of frequent fluvial erosion and depositional processes during flooding events. In general, a clear decrease in soil variability with depth is observed and primarily attributed to reduced variability in percent sand, silt, CEC, and Mg. In lower horizons, however, variation of organic matter and associated nutrients, likely from buried horizons, irregular fluvial deposits, and a fluctuating groundwater table presents the most important exception.

There is substantial uncertainty in the prediction of pesticide concentration in tropical soils. Increased knowledge of pesticide application practices combined with more site-specific soil and hydrologic characteristics is essential for the improved quantification of pesticides present in the environment. Using organic matter as a surrogate, pesticide concentrations will likely be higher in downstream areas of the Sixaola floodplain where finer sediments and higher applications occur. However, coarse-scale analysis is likely to be inaccurate for use at smaller scales. Fine-scale prediction of pesticide concentration on individual farms is likely to produce more accurate results over smaller or "faster" temporal scales. For these reasons, management goals must be clearly defined and based on the selection of appropriate spatial and temporal scales. Given the extreme spatial and temporal variability in floodplain soils, geostatistical tools that incorporate space-time series or spatial state-space approaches in combination with field observations and modeled soil-forming processes are needed to better account for both temporal and spatial variation at different scales.

References

Alexander, J., Fielding, C.R. 2006. Coarse-grained floodplain deposits in the seasonal tropics: Towards a better facies model. Journal of Sedimentary Research 76: 539-357.

Arouays, D., Vion, I., Kicin, L.J. 1995. Climate, organic matter and clay content relationship in the Pampa and Chaco soils, Argentina. Geoderma 83: 127-141.

Bai, J., Ouyang, H., Deng, W., Zhu, Y., Zhang, X., Wang, Q. 2005. Spatial distribution characteristics of organic matter and total nitrogen of marsh soils in river marginal wetlands. Geoderma 124: 181-192.

Baskaran, S., Kookana, R.S., Naidu, R. 2003. Contrasting behavior of chlorpyrifos and its primary metabolite, TCP (3,5,6-trichloro-2-pyridinol), with depth in soil profiles. Australian Journal of Soil Research 41: 749-760.

Bernoux, M., Graca, P.M.A., Cerri, C.C., Fearnside, P.M., Feigl, B.J., Piccolo, M.C. 2001. Carbon Storage in Biomass and Soils. In McClain, M.E, Victoria, R.L., Richely, J.E. (Eds), The Biogeochemistry of the Amazon Basin. Oxford University Press, New York.

Bigham, J.M. 1996. Methods of Soil Analysis. Part 3: Chemical Methods. Soil Science Society of America Book Series, No. 5. SSSA, Madison, Wisconsin.

Bollag, J.M, Myers, C.J., Minard, R.D. 1992. Biological and chemical interactions of pesticides with soil organic matter. The Science of the Total Environment 123/124: 205-217.

Borge, C., Castillo, R. 1997. Cultura y conservación en la Talamanca indígena. EUNED (Editorial Universidad Estatal a Distancia), San Jose, Costa Rica.

Boul, S.W., Southard, R.J., Graham, R.C., McDaniel, P.A. 2003. Soil Genesis and Classification, Fifth Ed. Iowa State Press, Iowa.

Bouma. J., Stoorvogel, J., Van Alphen, B.J., Booltink, H.W.G. 1999. Pedology, precision agriculture and the changing paradigm of agricultural research. Soil Science Society of America Journal 63: 1763-1768.

Bouyoucos, G.J. 1951.Recalibration of the hydrometer method for making mechanical analysis of soils. Agronomy Journal 43:434-438.

Brucker, A., Kandeler, E., Kampichler, C. 1999. Plot-scale spatial patterns of soil water content, pH, substrate-induced respiration and N mineralization in a temperate coniferous forest. Geoderma 93: 207-223.

Burrough, P.A. 1993. Soil variability: a late 20th century view. Soils Fertility 56: 529-562.

Castillo, L. E., de la Cruz, E., Ruepert, C. 1997. Ecotoxicology and pesticides in tropical aquatic ecosystems of Central America. Environmental Toxicology and Chemistry 16: 41-51.

Chaplot, V., Bernoux, M., Walter, C., Curmi, P., Herpin, U. 2001. Soil carbon storage prediction in temperate hydromorphic soils using a morphologic index and digital elevation model. Soil Science 166: 48-60.

Cheng, H.H. 1990. Pesticides in the soil environment: Processes, impacts and modeling. SSSA, Madison, Wisconsin.

Cordero, A., Ramirez, GF. 1979. Acumulamiento de cobre en los suelos del Pacifico sur de Costa Rica y sus efectos detrimentales en la agricultura. Agronomía Costarricense 3: 63-78.

Diaz Romeu, R., Hunter A. 1978. Metodología de muestreo de suelos, análisis químico de suelos, tejido vegetal e investigación en invernadero. CATIE, Turrialba, Costa Rica.

Dixon, J.B., Schulze, D.G. 2002. Soil Mineralogy with Environmental Applications. SSSA Book Series 7. Soil Science Society of America, Inc. Madison, Wisconsin.

Dollar, E.S.J. 2004. Fluvial geomorphology. Progress in Physical Geography 28: 405-450.

Donald, D.B., Hunter, F.G., Sverko, E., Hill, B.D., Syrgiannis, J. 2005. Mobilization of pesticides on an agricultural landscape flooded by a torrential storm. Environmental Toxicology and Chemistry 24: 2-10.

Dunne, T., Mertes, L., Meade, R.H., Richey, J.E., Fosberg, B.R. 1998. Exchanges of sediment between the flood plain and channel of the Amazon River in Brazil. Geological Society of America Bulletin 110: 450-467.

Earl, R., Taylor, J.C., Wood, G.A., Bradley, I., James, I.T., Waine, T., Welsh, J.P., Godwin, R.J., S.M. Knight. 2003. Soil factors and their influence on within-field crop variability, Part I: field observation of soil variation. Biosystems Engineering 84: 425-440.

Ekoanya, M.A., Ojanuga, A.G. 2002. Productivity assessment of upland and floodplain soils at Makurdi, Nigeria. Geoderma 108: 19-29.

Farenhorst, A. 2006. Importance of soil organic matter fractions in soil-landscape and regional assessments of pesticide sorption and leaching in soil. Soil Science Society of America Journal 70: 1005-1012.

Gevao, B., Jones, K.C., Semple, K.T., Craven, A., Burauel, P. 2003. Nonextractable pesticide residues in soil. Environmental Science and Technology 37: 138-144.

Goldin, A. 1987. Reassessing the use of loss-on-ignition for estimating organic matter content in non-calcareous soils. Communications in Soil Science and Plant Analysis 13: 1111-1116

Goovaerts, P. 1998. Geostatistical tools for characterizing the spatial variability of microbiological and physico-chemical soil properties. Biology and Fertility of Soils 27: 315-334.

Grunwald, S., Reddy, K.R., Prenger, J.P., Fisher, M.M. 2007. Modeling of the spatial variability of biogechemical soil properties in a freshwater ecosystem. Ecological Modelling 201: 521-535.

Havelin, J.L., Beaton, J.D., Tisdale, S.L., Nelson, W.L. 1999. Soil Fertility and Fertilizers: An Introduction to Nutrient Management. Prentice Hall, New Jersey.

Heuvelink, G.B.M., Webster, R. 2001. Modelling soil variation: past, present and future. Geoderma 100: 269-301.

Iqbal, J., Thomasson, J.A., Jenkins, J.N., Owens, P.R., Whisle, F.D. 2005. Spatial variability analysis of soil physical properties of alluvial soils. Soil Science Society of America Journal 69: 1338-1350.

Juo. A.S.R., Franzluebbers, K. 2003. Tropical Soils: Properties and Management for Sustainable Agriculture. Oxford University Press, New York.

Kaiser, K., Guggenberger, G. 2003. Mineral surfaces and soil organic matter. European Journal of Soil Science 54: 219-236.

Kapp, G.B. 1989. Perfil ambiental de la zona Baja de Talamanca, Costa Rica. Informe Técnico No.155, CATIE, Turrialba, Costa Rica.

Kellman, M., Tackaberry, R. 1997. Tropical Environments: The functioning and management of tropical ecosytems, Routledge, London.

Laabs, V., Amelung, W., Pinto, A., Zech, W. 2002. Fate of pesticides in tropical soils of Brazil under field conditions. Journal of Environmental Quality 31: 256-268.

Lafrance, P., Banton, O.1995. Implication of spatial variability of organic carbon on predicting pesticide mobility in soil. Geoderma 65: 331-338.

Lalah, J. O., Kaigwara, P. N., Getenga, Z., Mghenyi, J. M., Wandiga, S. O. 2001. The major environmental factors that influence rapid disappearance of pesticides from tropical soils in Kenya. Toxicological and Environmental Chemistry 81:161-197.

Li, H., Sheng, G., Teppen, B.J., Johnston, C.T., Boyd, S.A. 2003. Sorption and desorption of pesticides by clay minerals and humic acid-clay complexes. Soil Science Society of America Journal 67: 122-131.

López, A., Vargas, A., Espinosa, J., Vargas, R. 2001. Síntomas de deficiencias nutricionales y otros desordenes fisiológicos en le cultivo del banano (Musa AAA). CORBANA, San Jose, Costa Rica.

Martinelli, L.A., Victoria, R.L., de Camargo, P.B., de Cassia Piccolo, M., Mertes, L., Richey, J.E., Devol, A.H., Fosberg, B.R. 2003. Inland variability of carbon-nitrogen concentrations and delta C-13 in Amazon floodplain (varzea) vegetation and sediment. Hydrological Processes 17: 1419-1430.

McClain, M.E., Boyer, E.W., Dent, C. L., Gergel, S.E., Grimm, N.B., Groffman, P.M., Hart, S.C., McDowell, W.H., Pinay, G. 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. Ecosystems 6: 301-312.

McCune, B., Grace, J.B. 2002. Analysis of Ecological Communities. MJM Software Design, Gleneden Beach, Oregon.

Mallants, D., Mohanty, B.P., Jacques, D., Feyen, J. 1996. Spatial variability of hydraulic p roperties in a multi-layered soil profile. Soil Science 161: 167-181.

Mendonca Santos, M.L., Guenat, C., Bouzelboudjen, M., Golay, F. 2000. Three-dimensional GIS cartography applied to the study of the spatial variation of soil horizons in a Swiss floodplain. Geoderma 97: 351-366.

Mouw, J.E.B., Alaback, P.B. 2003. Putting floodplain hyperdiversity in a regional context: an assessment of terrestrial-floodplain connectivity in a montane environment. Journal of Biogeography 30: 87-103.

Naiman, R.J., Decamps, H., Pollack, M. 1993. The role of riparian corridors in maintaining regional biodiversity. Ecological Applications 3: 209-212.

NAMASOL. 2000. Perfil de la Propuesta de Protección y Manejo Sostenible de los Recursos Naturales Dentro de los Territorios Indígenas de Talamanca. Informe Proyecto Namasol, Talamanca Indigenous Territories, May 2000.

Neatrour, M.A., Webster, J.R., Benfield, E.F. 2004. The role of floods in particulate organic matter dynamics of a southern Appalachian river-floodplain ecosystem. Journal of the North American Benthic Society 23: 198-213.

Nieuwenhuyse, A. 1994. Los suelos de los sitios experimentales del proyecto agroforestal: Cantón de Talamanca, Costa Rica y distrito de Changuinola, Panamá. CATIE-GTZ, Guapiles.

Odgen R., Thoms, M.C. 2002. The importance of inundation to floodplain soil fertility in a large semi-arid river. Internationale Vereinigung fur Theoretishce und Angewandte Limnologie 28: 744-749.

Olsen, S.R., Sommers,L.E. 1982. Phosphorous. In Page, A.L., Miller, R.H., Keeney, D.R. (Eds) Methods of Soil Analysis Part 2: Chemical and Microbiological Properties, SSSA Madison, Wisconsin.

Park, S.J., Vlek, P.L.G. 2002. Environmental correlation of three-dimensional soil spatial variability: a comparison of three adaptive techniques. Geoderma 109: 117-140.

Paschke, A. 2003. Consideration of the physiochemical properties of sample matrices - an important step in sampling and sample preparation. Trends in Analytical Chemistry 22: 78-89.

Pionke, H.B., DeAngelis, R.J. 1980. Method for distributing pesticide loss in field runoff between the solution and adsorbed phase. In CREAMS, A Field Scale Model for Chemicals, Runoff, and Erosion from Agricultural Management Systems. USDA Conservation Resources Report 26, USDA, SEA, Washington, D.C.

Naidu, R., Kookana, R.S., Baskaran, S. 1998. Pesticide dynamics in the tropical soil-plant ecosystem: Potential impacts on soil and crop quality. ACIAR Proceedings 85: 171-183.

Racke, K. D. 2003. What do we know about the fate of pesticides in tropical ecosystems? In Coats, J. R., Yamamoto, H., (Eds), Environmental Fate and Effects of Pesticides, ACS Symposium Series 85, American Chemical Society, Washington, D.C.

Racke, K.D., Skidmore, M.W., Hamilton, D.J., Unsworth, J.B., Mayamoto, J., Cohen, S.Z. 1997. Pesticides report 38: Pesticide fate in tropical soils (Technical Report). Pure and Applied Chemistry 69: 1349-1371.

Reichenberger, S., Amelung, W., Laabs, V., Pinto, A., Totsche, K.U., Zech, W. 2002. Pesticide displacement along preferential flow pathways in a Brazilian oxisol. Geoderma 110: 63-86.

Robinson, J.C. 1996. Banana and Plantains. Cab International, UK.

Saggar, S., Parshotam, A., Sparling, G.P., Feltham, C.W., Hart, P.B.S. 1996. ^{14}C labeled ryegrass turnover and residence times in soils varying in clay content and mineralogy. Soil Biology and Biochemistry 28: 1677-1686.

Saldana, A., Stein, A., Zinck, J.A. 1998. Spatial variability of soil properties at different scales within three terraces of the Henares River (Spain). Catena 33: 139-153.

Smith, S.V., Sleezer, R.O., Renwick, W.H., Buddemeier, R.W. 2005. Fates of eroded soil organic carbon: Mississippi Basin case study. Ecological Applications 15: 1929-1940.

Sollins, P., Sancho, F.M., Mata, R., Sanford, R.L. Jr. 1994. Soils and soil process research. In McDade, L.A., Bawa, K.S., Hespenheide, H.A., Hartshorn, G.S. (Eds), La Selva: Ecology and Natural History of a Neotropical Rainforest, University of Chicago Press, Chicago.

Sommer, M. 2006. Influence of soil pattern on matter transport in and from terrestrial biogeosystems - A new concept for landscape pedology. Geoderma 133: 107-123.

Sparks, D. 2003. Environmental Soil Chemistry. Academic Press, San Diego.

Sposito, G. 1984. The Surface Chemistry of Soils. Oxford University Press, New York.

SSSA (Soil Science Society of America). 1996. Methods of Soil Analysis. SSSA Book Series 5, Part 3-Chemical Methods. Soil Science Society of America, Inc. Madison, Wisconsin.

Stoorvogel, J.J., Kooistra, L., Bouma, J. 1999. Spatial and temporal variation in nematicide leaching, management implications for a Costa Rican banana plantation. Assessment of Non-Point Source Pollution in the Vadose Zone, Geophysical Monograph 108 American Geophysical Union: 281-289.

Thompson, J.A., Pena-Yewtukhiw, E.M., Grove, J.H. 2006. Soil-landscape modeling across a physiographic region: Topographic patterns and model transportability. Geoderma 133: 57-70.

Thoms, M.C. 2003. Floodplain-river ecosystems: lateral connections and the implications of human interference. Geomorphology 56: 335-349.

Thrupp, L.A. 1991. Long-term losses from accumulation of pesticide residues: a case of persistent copper toxicity in soils of Costa Rica. Geoforum 22: 1-15

Tockner, K., Pennetzdorfer, D., Reiner, N., Schiemer, F., Ward, J.V. 1999. Hydrological connectivity, and the exchange of organic matter and nutrients in a dynamic river-floodplain system (Danube, Austria). Freshwater Biology 41: 521-535.

Torn, M.S., Tumbore, S.E., Chadwick, O.A., Vitousek, P.M. 1997. Mineral control of soil organic carbon storage and turnover. Nature 389: 170-173.

Webster. R. 2000. Is soil variability random? Geoderma 97: 149-163.

Witter, B., Winkler, M., Friese, K. 2003. Depth distribution of chlorinated and polycyclic hydrocarbons in floodplain soils of the River Elbe. Acta Hydrochimica et Hydrobiologica 31: 411-422.

Villalobos, V., Borge, C. 1998. Talamanca en la encrucijada, 1st ed. EUNED, San José, Costa Rica.

Villalobos, L.G. 1989. Determinación de las perdidas de aniones y cationes en el agua drenaje subterráneo en un suelo bananero. Masters Thesis, Facultad de Agronomía, Escuela de Fitotecnia, University of Costa Rica, San Jose.

Yarie, J., Viereck, L., van Cleve, K., Adams P. 1998. Flooding and ecosystem dynamics along the Tanana River. BioScience 48: 690-695.

Yemefack, M., Rossiter, D.G., Njomgang, R. 2005. Multi-scale characterization of soil variability within an agricultural landscape mosaic system in southern Cameroon. Geoderma 125: 117-143.

Table 1. Descriptive statistics for coarse-scale topsoils (0-10cm, N=47)

	% OM	% C	% sand	% silt	% clay	pH	Acidity cmol$^{(+)}$/kg	Ca cmol$^{(+)}$/kg	Mg cmol$^{(+)}$/kg	K cmol$^{(+)}$/kg	P mg/kg	Cu mg/kg	Zn mg/kg	Mn mg/kg	Fe mg/kg
Min	1.28	0.56	4.50	17.00	4.00	5.01	0.05	12.26	2.93	0.19	6.33	3.10	0.33	1.20	8.58
Mean	3.82	1.76	38.30	46.75	14.95	6.31	0.09	20.79	5.24	0.71	14.82	7.78	1.78	27.80	67.45
Median	3.33	1.53	37.00	47.50	11.50	6.23	0.05	20.82	5.42	0.61	13.00	6.40	1.50	13.80	66.80
Max	10.27	4.73	71.50	66.50	48.50	7.86	0.91	29.39	8.35	2.39	40.20	18.00	5.00	144.00	154.00
St Dev	1.97	0.91	18.54	12.31	10.36	0.51	0.13	4.28	1.23	0.45	7.40	3.70	1.15	32.20	29.69
Skewness	1.21	1.21	0.20	-0.55	1.42	0.77	5.64	0.24	0.14	2.08	1.87	0.98	1.28	1.88	0.66
Kurtosis	1.53	1.53	-1.14	-0.43	1.46	1.93	34.27	-0.52	-0.39	4.94	4.05	0.21	1.48	3.54	0.61
SE Mean	0.29	0.13	2.70	1.80	1.51	0.07	0.02	0.62	0.18	0.07	1.08	0.54	0.17	4.70	4.33
CV%	51.52	51.52	48.40	26.34	69.33	8.09	151.73	20.59	23.42	63.12	49.97	47.58	64.39	115.86	44.02

Table 2. Pearson's correlation coefficients for coarse scale topsoils ($p<0.05$ in **BOLD**, N=47)

	% OM	% sand	% silt	% clay	pH	Acidity	Ca	Mg	K	P	Cu	Zn	Mn
% sand	**-0.40**												
% silt	0.24	-0.85											
% clay	**0.44**	**-0.78**	**0.33**										
pH	-0.20	0.03	0.10	-0.17									
Acidity	0.18	-0.21	0.06	**0.29**	**-0.46**								
Ca	**0.44**	**-0.38**	**0.44**	0.15	**0.49**	-0.08							
Mg	**0.56**	**-0.35**	0.26	**0.32**	0.01	-0.07	**0.57**						
K	0.23	-0.23	0.14	0.23	-0.23	0.15	0.00	-0.03					
P	**0.43**	**-0.35**	0.07	**0.55**	**-0.46**	**0.48**	-0.09	0.11	**0.53**				
Cu	0.20	**-0.69**	**0.42**	**0.75**	-0.15	0.08	0.00	0.17	0.09	0.27			
Zn	**0.62**	-0.26	0.17	0.26	**-0.32**	**0.36**	**0.33**	**0.53**	**0.32**	**0.64**	0.01		
Mn	**0.44**	**-0.55**	0.26	**0.67**	**-0.44**	**0.42**	-0.04	0.04	**0.35**	**0.49**	**0.59**	0.19	
Fe	0.07	-0.11	0.00	0.19	**-0.66**	0.19	**-0.56**	-0.16	0.28	**0.40**	**0.31**	0.21	**0.32**

Table 3. Soil property averages and standard deviations for coarse-scale samples by 250m distance classes (N=47)

Average																
n	Distance	% OM	% C	% sand	% silt	% clay	pH	Acidity cmol(+) /kg	Ca cmol(+) /kg	Mg cmol(+) /kg	K cmol(+) /kg	P mg/kg	Cu mg/kg	Zn mg/kg	Mn mg/kg	Fe mg/kg
11	250	3.31	1.52	46.77	43.05	10.18	6.32	0.07	20.36	4.93	0.79	14.81	7.43	1.63	18.60	77.39
12	500	3.92	1.80	43.68	44.14	12.18	6.46	0.06	20.95	5.18	0.60	13.02	7.12	1.56	24.71	53.77
12	750	3.83	1.76	31.83	52.79	15.38	6.29	0.13	20.60	5.12	0.63	14.94	7.17	1.83	26.97	62.64
12	1000	4.19	1.92	31.63	46.72	21.66	6.16	0.10	21.22	5.71	0.83	16.50	9.37	2.10	40.15	76.84
St Dev																
n	Distance															
11	250	1.82	0.84	15.93	13.63	3.84	0.58	0.04	4.70	1.00	0.35	5.65	3.77	1.24	20.79	35.28
12	500	2.43	1.12	20.46	13.83	8.22	0.50	0.02	4.31	1.58	0.42	6.72	2.93	1.28	28.48	25.05
12	750	1.95	0.90	17.36	11.37	8.94	0.57	0.25	5.50	1.17	0.23	7.95	2.66	1.22	34.06	31.52
12	1000	1.74	0.80	16.99	9.15	14.42	0.41	0.09	2.70	1.09	0.69	9.23	4.99	0.89	41.36	22.58

Table 4. Comparison of first horizon soil properties in fine-scale farm sites flooded or not-flooded in January 2005 (N=65)

Average															
n		%OM	% sand	% silt	% clay	pH	Acidity cmol(+) /kg	Ca cmol(+) /kg	Mg cmol(+) /kg	K cmol(+) /kg	P mg/kg	Cu mg/kg	Zn mg/kg	Mn mg/kg	Fe mg/kg
33	Flooded	3.09	31.76	54.20	14.04	7.27	0.06	27.02	4.83	0.48	9.85	7.42	1.02	6.93	27.81
32	Not-Flooded	5.01	39.65	48.31	12.04	6.25	0.07	24.19	6.40	0.66	11.55	5.16	2.46	18.62	48.35
St Dev															
33	Flooded	1.56	18.97	13.51	7.71	0.51	0.01	3.74	1.45	0.25	3.60	3.15	0.55	5.11	15.70
32	Not-Flooded	2.88	15.20	12.30	4.55	0.32	0.03	3.72	1.32	0.55	5.24	2.35	1.38	15.24	21.89

Figure 1. Map of study area and location of soil sampling sites

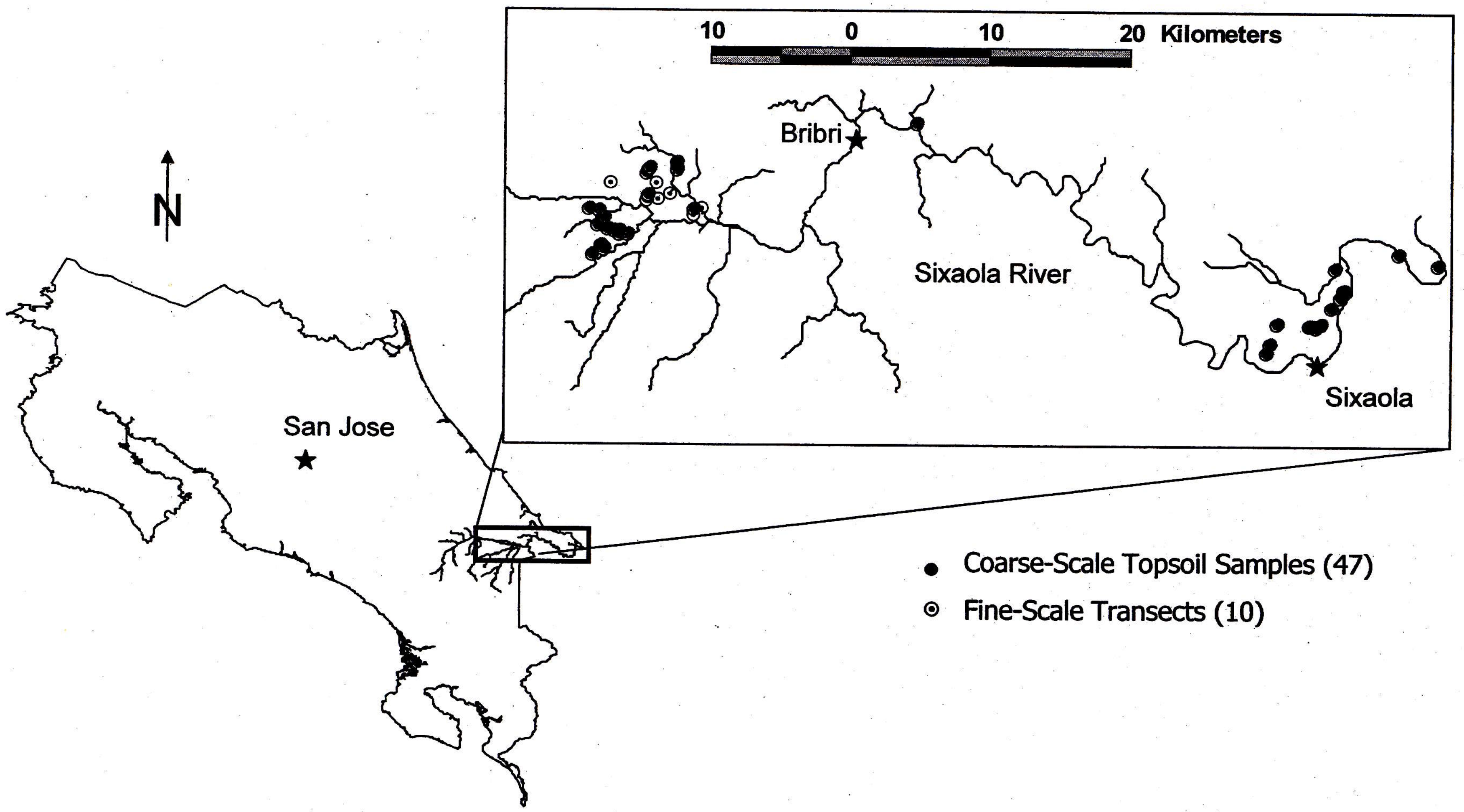
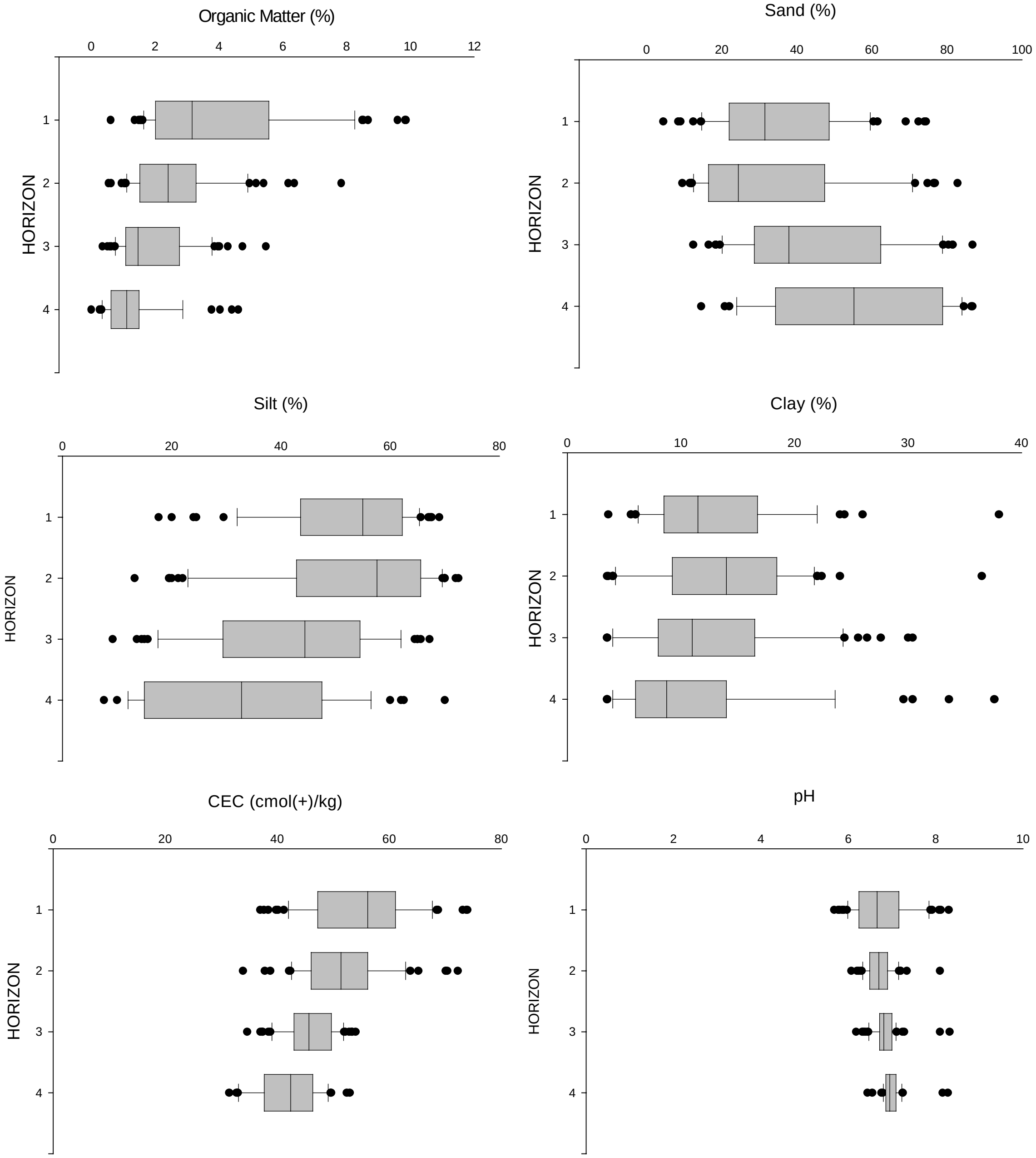
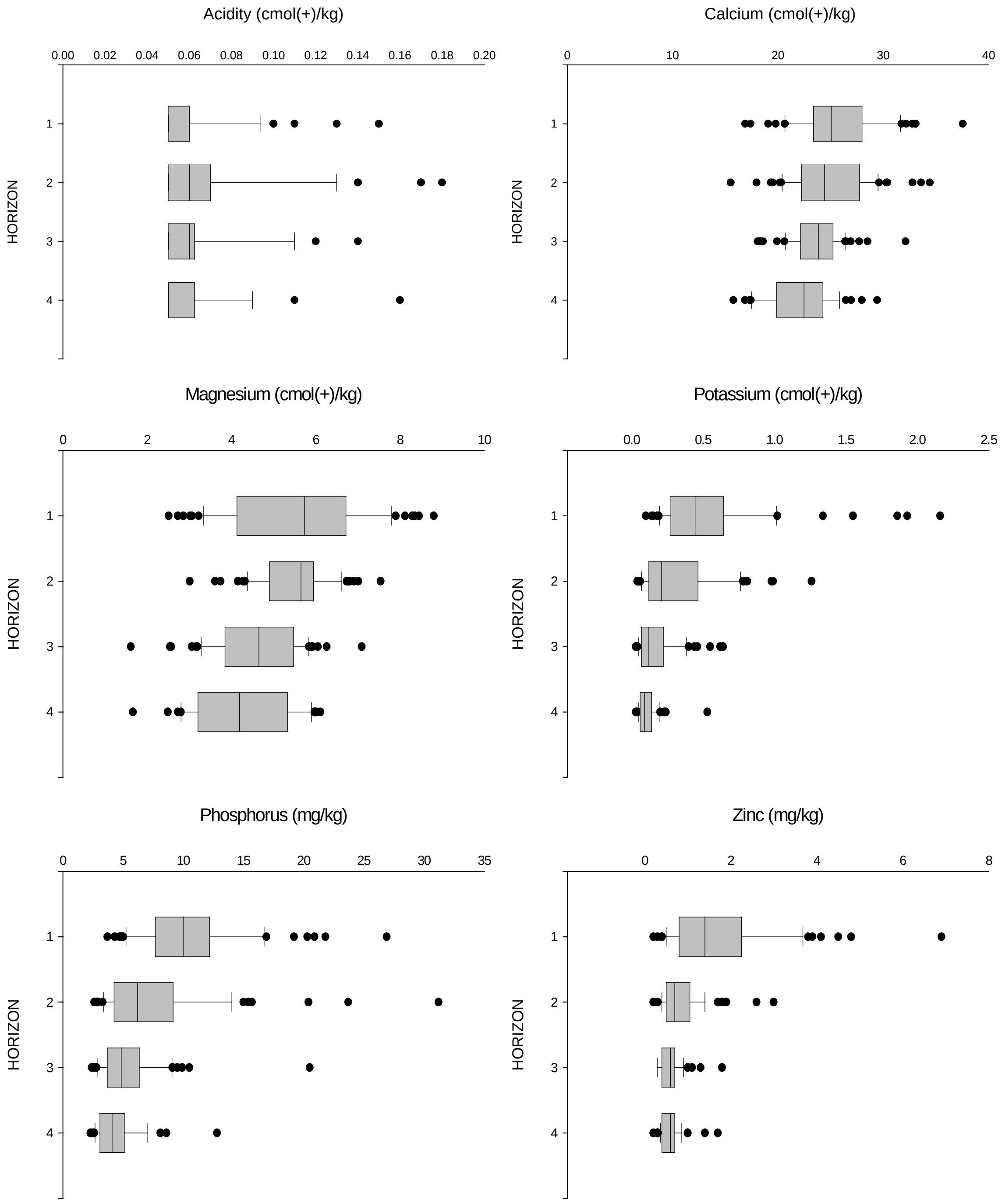
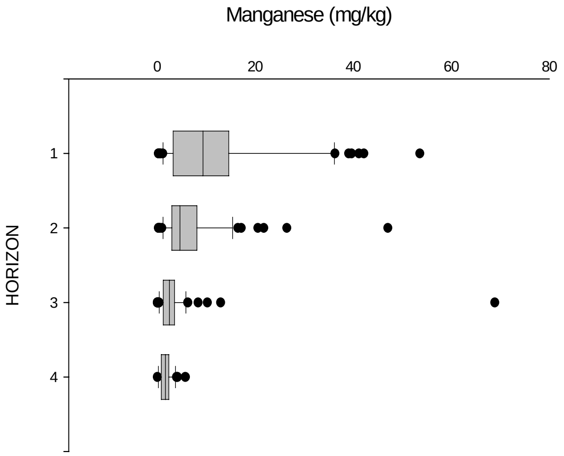
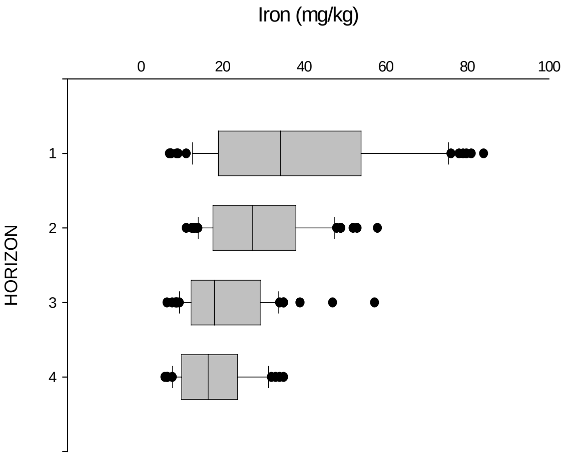


Figure 2. Box plots of 15 soil properties measured in fine-scale soil samples (N=238) by horizon




Acidity (cmol(+)/kg)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
HORIZON
1
2
3
4
Calcium (cmol(+)/kg)
0
10
20
30
40
HORIZON
1
2
3
4
Magnesium (cmol(+)/kg)
0
2
4
6
8
10
HORIZON
1
2
3
4
Potassium (cmol(+)/kg)
0.0
0.5
1.0
1.5
2.0
2.5
HORIZON
1
2
3
4
Phosphorus (mg/kg)
0
5
10
15
20
25
30
35
HORIZON
1
2
3
4
Zinc (mg/kg)
0
2
4
6
8
HORIZON
1
2
3
4


Manganese (mg/kg)
0
20
40
60
80
HORIZON
1
2
3
4


Iron (mg/kg)
0
20
40
60
80
100
HORIZON
1
2
3
4

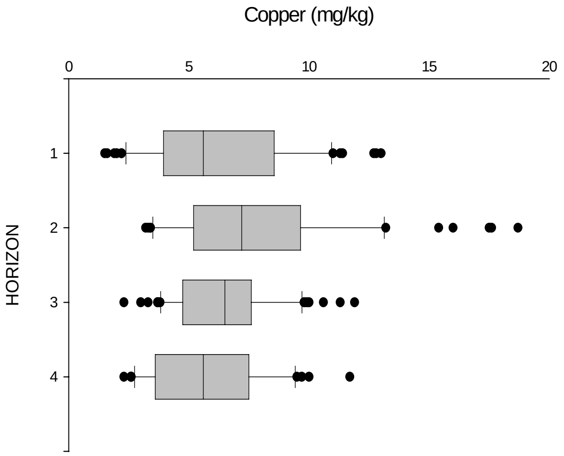

Copper (mg/kg)
0
5
10
15
20
HORIZON
1
2
3
4

Figure 3. Coefficient of variation (%CV) for fine-scale soil properties by horizon (N=65)

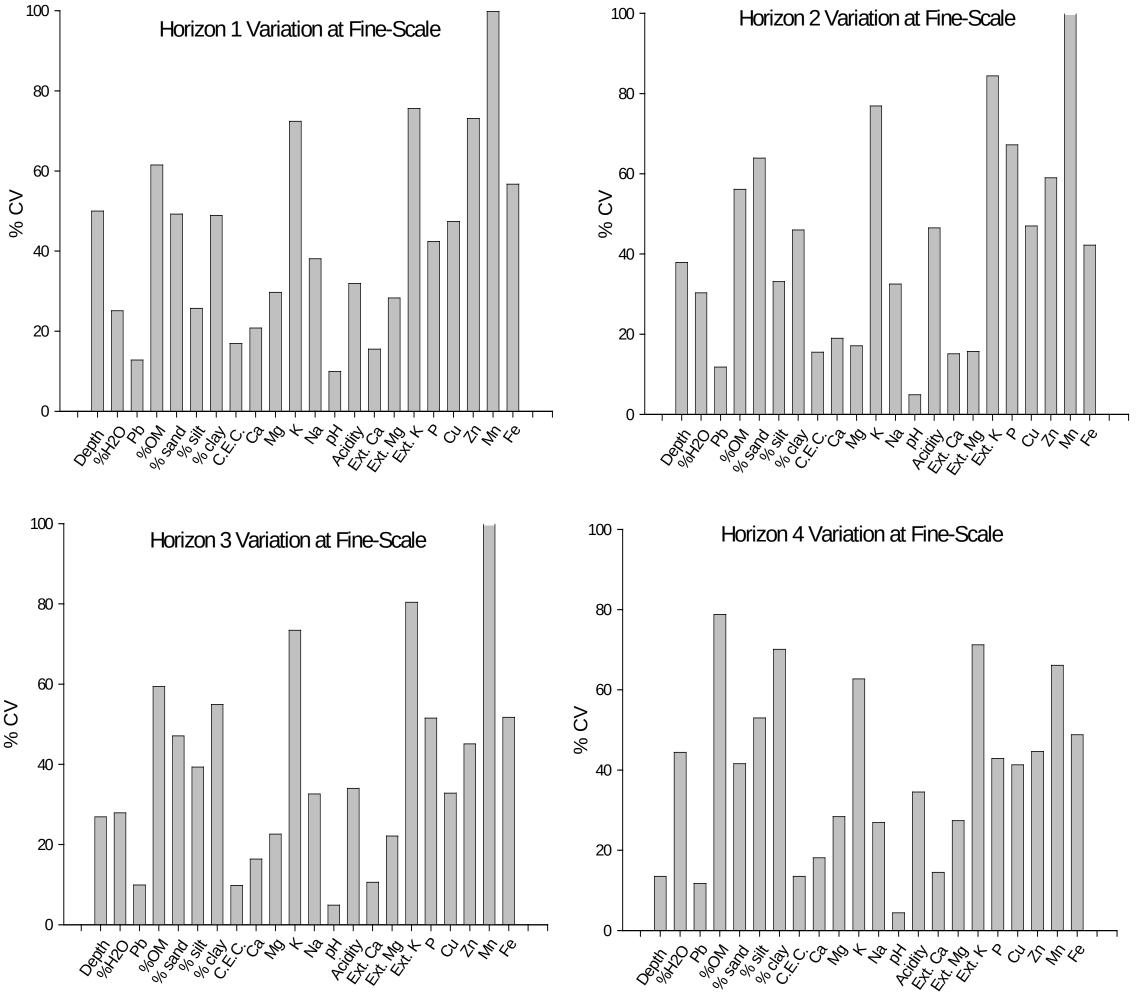
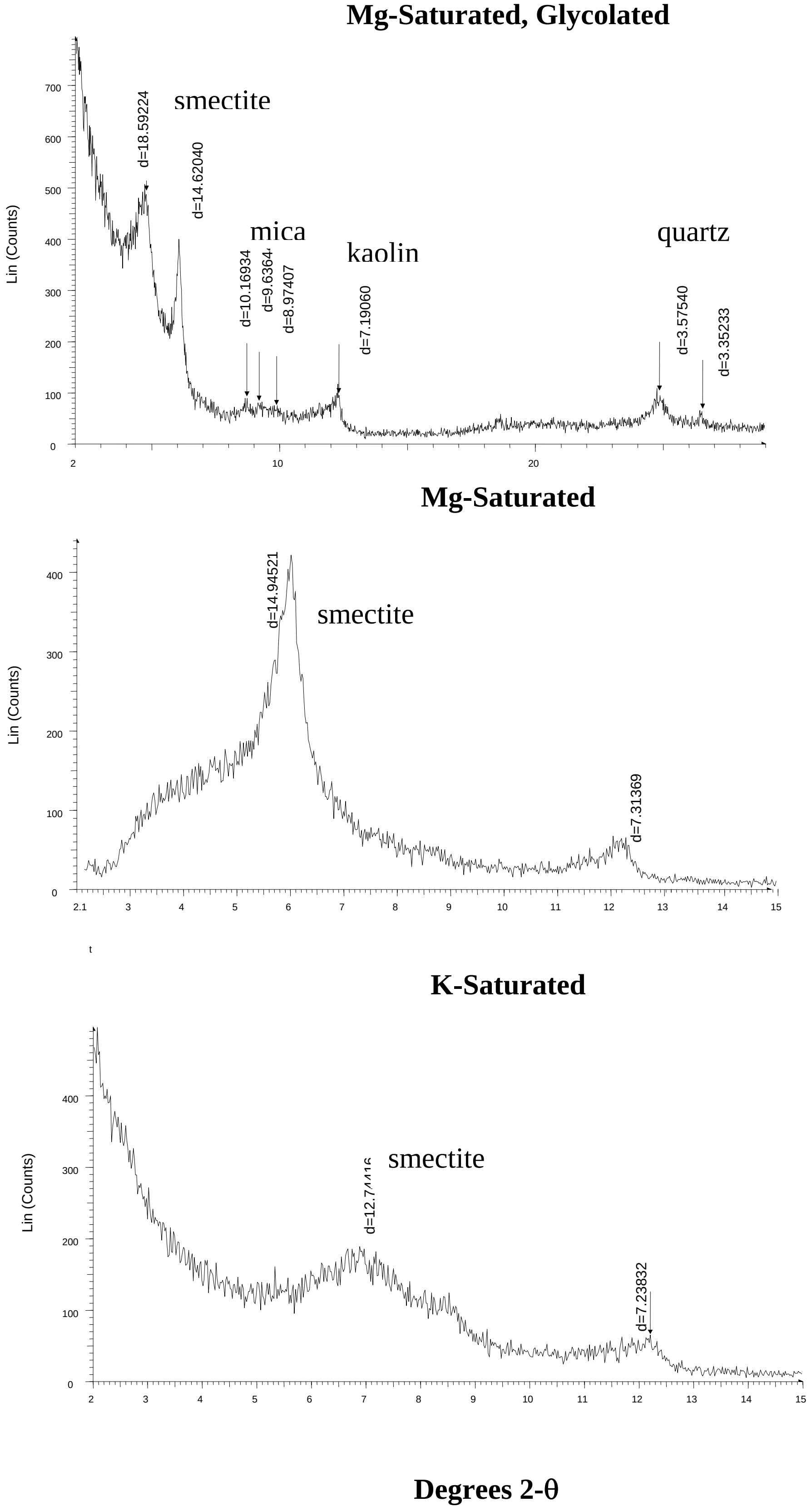


Figure 4. Representative XRD trace of soil mineralogical properties



Mg-Saturated, Glycolated

Mg-Saturated

K-Saturated

Degrees 2-θ

Figure 5. Box Plots of PCA scores by 250m distance class for first four principal components (eigenvalue, proportion of variance represented in parentheses).

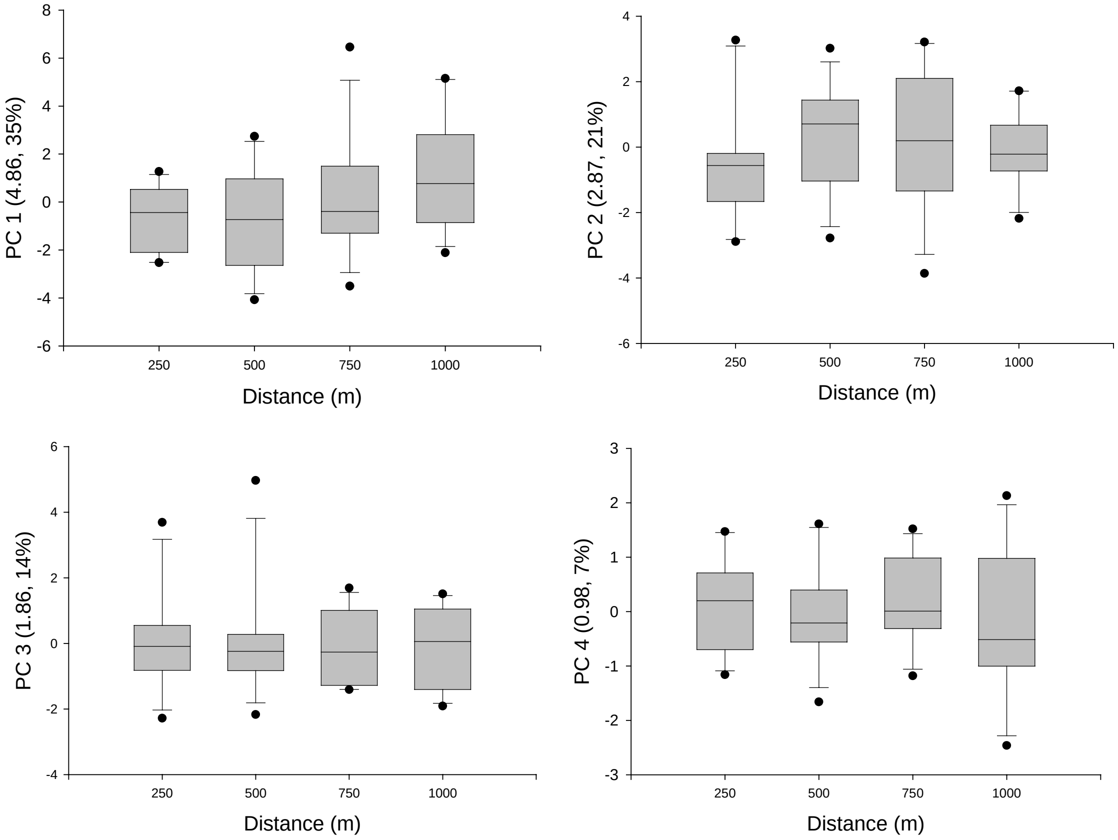
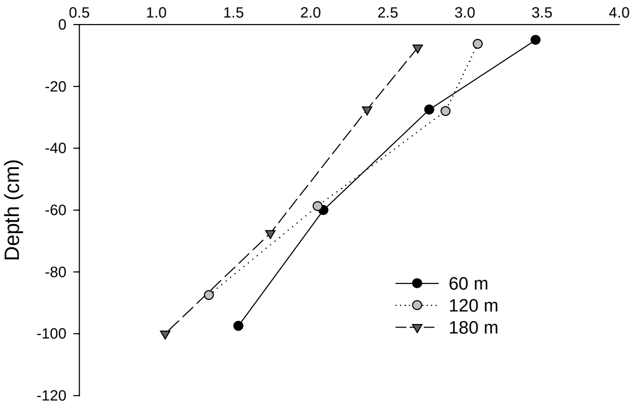
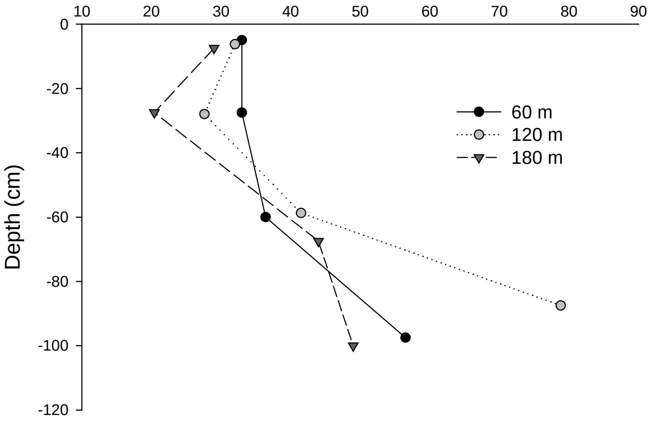


Figure 6. Median fine-scale percent organic matter, sand, and clay values in 60m, 120m 180m fine-scale distance classes by median horizon depth

Median %OM by Median Depth



Median %Sand by Median Depth



Median % Clay by Median Depth

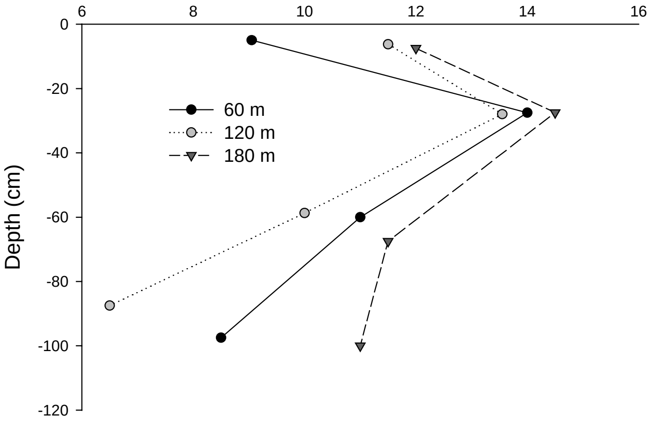


Figure 7. Box plots of PC values for first horizon of fine-scale samples by flooded or not-flooded in January 2005 (eigenvalue, proportion of variance represented in parentheses).

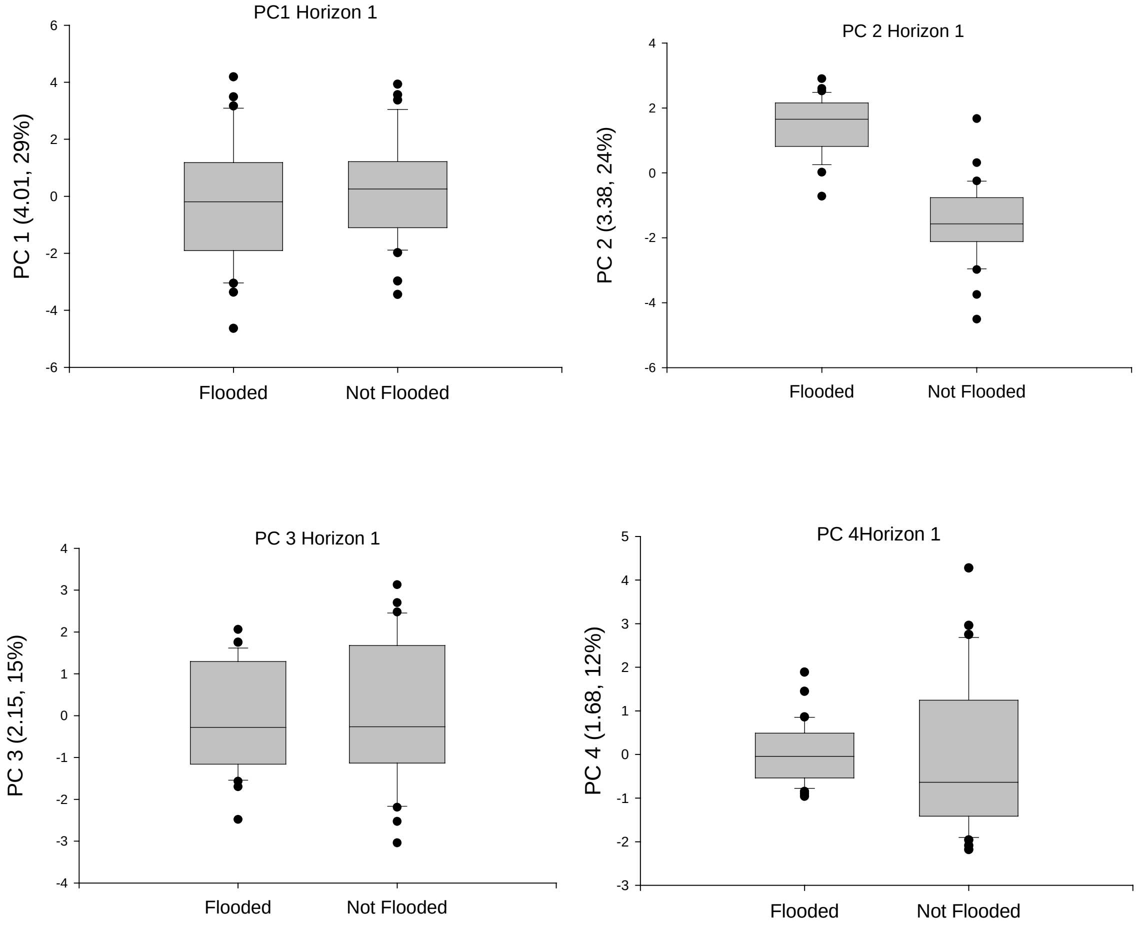
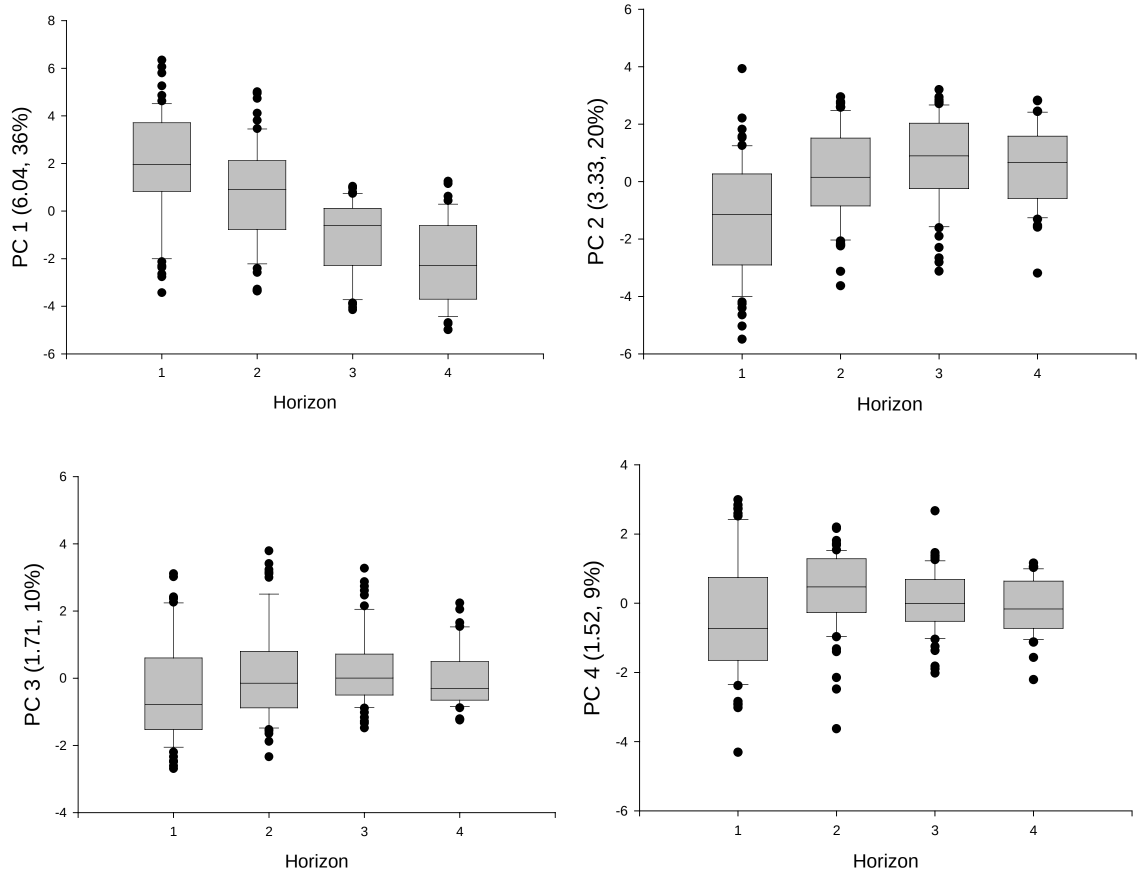


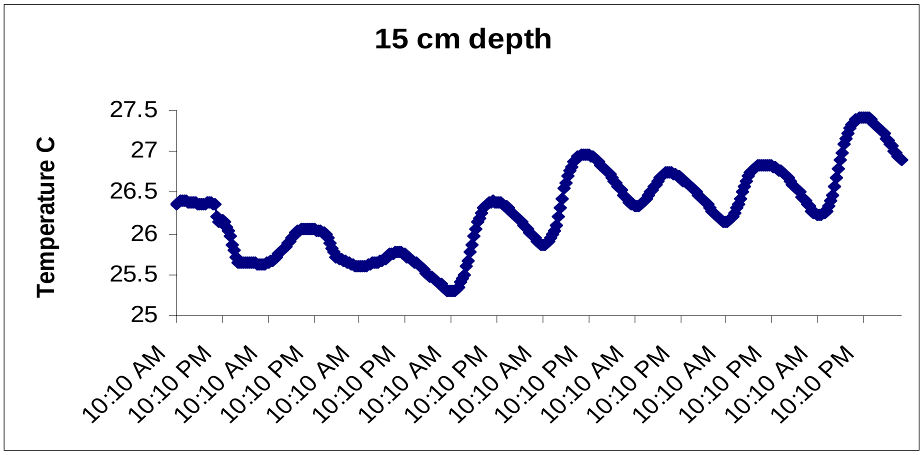
Figure 8. Box plots of first four principal components for all fine-scale samples by horizon (eigenvalue, proportion of variance represented in parentheses).

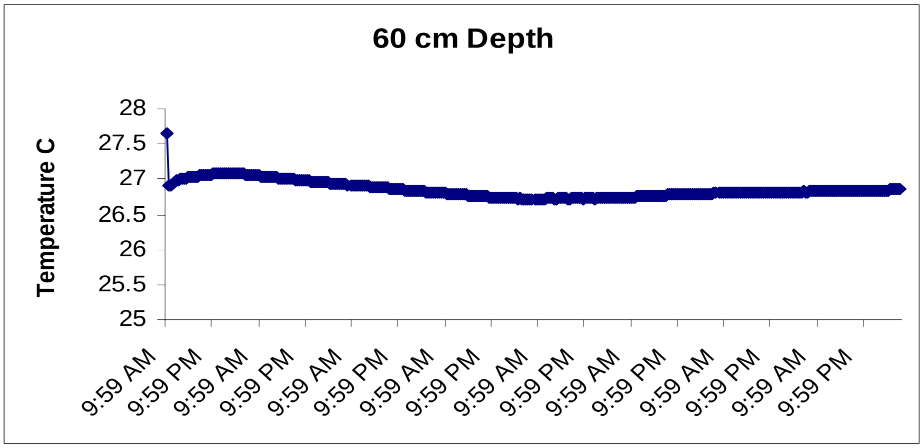


Chapter Two Appendices

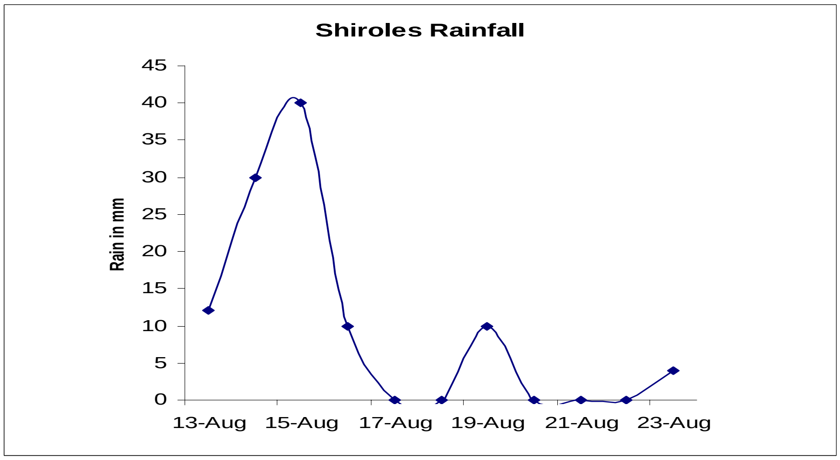
Appendix A: Soil Temperature

Soil temperatures measured with a HOBO water temp pro datalogger during the period of August 14 2006 (10am) through August 22 2006 (7:30am) at Fine-Scale Analysis Site number 4 (Finca Miguel) in Shiroles, Talamanca.





Rainfall in Shiroles during Temperature Sampling Period



Appendix B: Summary of Fine-Scale Soil Transect Samples (N=238)

HORIZON 1
(N=65)

								cmol (+)/kg						cmol (+)/kg					mg/kg			
	Depth cm	% H2O	Pb	% OM	% sand	% silt	% clay	C.E.C.	Ca	Mg	K	Na	pH	Acidity	Ext. Ca	Ext. Mg	Ext. K	P	Cu	Zn	Mn	Fe
Min	0.0	0.2	0.8	0.6	4.4	17.6	3.6	37.0	18.6	2.6	0.3	0.0	5.7	0.1	16.9	2.5	0.1	3.7	1.5	0.2	0.3	7.0
Mean	13.7	0.5	1.0	4.0	35.6	51.3	13.1	55.1	29.7	5.9	1.4	0.1	6.8	0.1	25.6	5.6	0.6	10.7	6.3	1.7	12.7	37.9
Median	12.0	0.5	1.0	3.2	31.5	55.0	11.5	56.1	28.8	5.8	1.1	0.1	6.7	0.1	25.1	5.7	0.5	10.0	5.6	1.4	9.4	34.2
Max	35.0	0.8	1.4	9.9	74.4	69.0	38.0	73.9	50.3	9.4	4.8	0.3	8.3	0.2	37.5	8.8	2.2	26.9	13.0	6.9	53.6	84.0
St Dev	6.9	0.1	0.1	2.5	17.5	13.2	6.4	9.3	6.2	1.8	1.0	0.0	0.7	0.0	4.0	1.6	0.4	4.5	3.0	1.3	12.7	21.5
Skewness	1.2	-0.1	0.7	0.9	0.5	-0.7	1.3	0.0	1.4	-0.1	2.0	1.1	0.5	2.4	0.4	-0.1	2.0	1.2	0.4	1.6	1.5	0.6
Kurtosis	1.8	-0.2	0.0	-0.3	-0.6	-0.3	2.2	-0.6	3.1	-0.9	4.1	4.4	0.7	6.5	0.5	-0.7	4.2	2.0	-0.6	3.6	1.4	-0.7
SE Mean	0.9	0.0	0.0	0.3	2.2	1.6	0.8	1.2	0.8	0.2	0.1	0.0	0.1	0.0	0.5	0.2	0.1	0.6	0.4	0.2	1.6	2.7
CV%	50.0	25.1	12.8	61.5	49.2	25.7	48.9	16.9	20.8	29.7	72.4	38.1	9.9	31.9	15.5	28.3	75.6	42.4	47.4	73.1	99.8	56.7

HORIZON 2
(N=65)

	Depth cm	% H2O	Pb	% OM	% sand	% silt	% clay	C.E.C.	Ca	Mg	K	Na	pH	Acidity	Ext. Ca	Ext. Mg	Ext. K	P	Cu	Zn	Mn	Fe
Min	5.0	0.2	0.8	0.5	9.5	13.2	3.5	33.9	17.1	3.3	0.1	0.1	6.1	0.1	15.5	3.0	0.0	2.6	3.2	0.2	0.3	11.1
Mean	43.2	0.5	1.0	2.7	34.2	52.1	13.7	51.7	27.2	5.6	0.8	0.1	6.7	0.1	24.8	5.5	0.3	7.6	8.0	0.9	6.9	28.4
Median	40.0	0.5	1.0	2.4	24.4	57.6	14.0	51.4	26.2	5.7	0.6	0.2	6.7	0.1	24.4	5.7	0.2	6.2	7.2	0.7	4.7	27.4
Max	95.0	0.9	1.4	7.8	82.8	72.5	36.5	72.2	43.8	7.7	3.1	0.3	8.1	0.2	34.4	7.5	1.3	31.2	18.7	3.0	47.1	58.0
St Dev	16.4	0.1	0.1	1.5	21.8	17.3	6.3	8.0	5.2	1.0	0.6	0.0	0.3	0.0	3.8	0.9	0.3	5.1	3.8	0.5	7.4	12.0
Skewness	0.5	0.3	0.3	1.1	0.8	-0.8	0.5	0.6	1.0	-0.2	1.4	-0.1	1.2	2.3	0.3	-0.4	1.3	2.4	1.0	2.0	3.2	0.5
Kurtosis	0.6	-0.1	0.2	1.3	-0.7	-0.7	1.2	0.4	1.3	-0.1	2.0	-0.6	3.7	4.3	0.0	0.4	1.5	7.6	0.7	5.4	13.8	-0.7
SE Mean	2.0	0.0	0.0	0.2	2.7	2.1	0.8	1.0	0.6	0.1	0.1	0.0	0.0	0.0	0.5	0.1	0.0	0.6	0.5	0.1	0.9	1.5
CV%	37.9	30.3	11.8	56.1	63.9	33.1	46.0	15.5	19.0	17.1	76.9	32.5	4.9	46.5	15.1	15.7	84.4	67.2	47.0	59.0	106.2	42.2

HORIZON 3
(N=62)

								cmol (+)/kg						cmol (+)/kg				mg/kg				
	Depth cm	% H2O	Pb	% OM	% sand	% silt	% clay	C.E.C.	Ca	Mg	K	Na	pH	Acidity	Ext. Ca	Ext. Mg	Ext. K	P	Cu	Zn	Mn	Fe
Min	15.0	0.2	0.8	0.4	12.4	9.2	3.5	34.6	17.7	1.8	0.1	0.1	6.2	0.1	18.1	1.6	0.0	2.4	2.3	0.3	0.1	6.4
Mean	83.7	0.4	1.0	2.0	45.2	41.8	13.0	45.9	25.6	4.6	0.5	0.2	6.9	0.1	23.7	4.6	0.2	5.5	6.5	0.6	4.0	20.5
Median	87.5	0.4	1.0	1.5	37.9	44.4	11.0	45.7	25.2	4.7	0.3	0.2	6.8	0.1	23.8	4.7	0.1	4.9	6.5	0.6	2.6	18.0
Max	120.0	0.7	1.3	5.5	86.8	67.2	30.4	54.0	49.8	7.2	1.7	0.3	8.3	0.1	32.1	7.1	0.6	20.5	11.9	1.8	68.9	57.3
St Dev	22.5	0.1	0.1	1.2	21.3	16.4	7.1	4.5	4.2	1.1	0.3	0.1	0.3	0.0	2.5	1.0	0.1	2.8	2.1	0.3	8.7	10.6
Skewness	-0.5	0.5	-0.2	1.0	0.5	-0.3	0.7	-0.3	3.4	-0.3	1.6	-0.3	1.9	1.8	0.1	-0.4	1.6	2.7	0.5	1.8	7.1	1.0
Kurtosis	0.0	-0.1	0.3	0.3	-1.1	-1.0	-0.2	-0.4	18.6	0.0	2.9	-0.7	7.7	2.3	1.5	0.3	2.3	12.2	-0.1	5.4	53.1	1.2
SE Mean	2.9	0.0	0.0	0.1	2.7	2.1	0.9	0.6	0.5	0.1	0.0	0.0	0.0	0.0	0.3	0.1	0.0	0.4	0.3	0.0	1.1	1.3
CV%	26.9	27.9	9.9	59.4	47.1	39.3	54.9	9.8	16.4	22.6	73.4	32.6	4.9	34.0	10.6	22.1	80.4	51.5	32.8	45.1	218.7	51.7

HORIZON 4
(N=46)

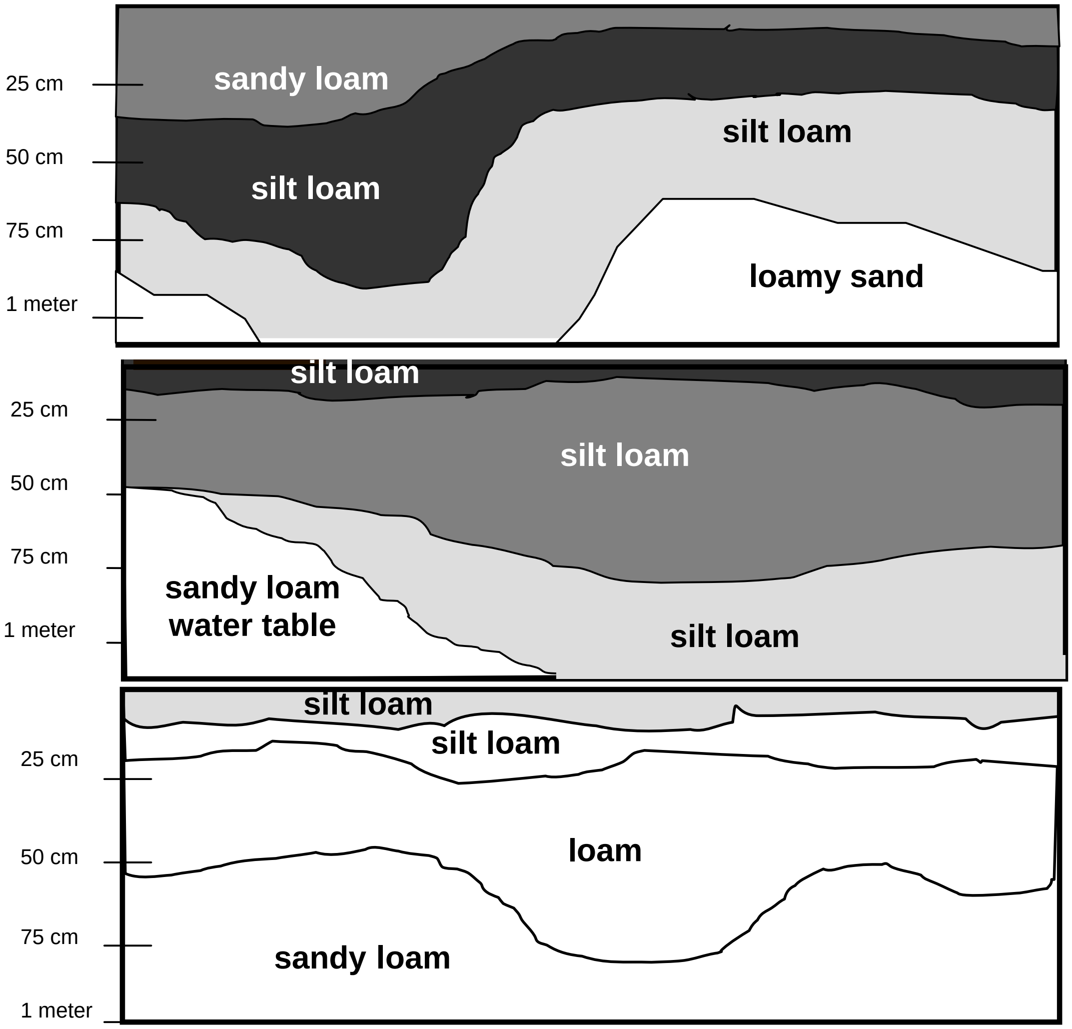
	Depth cm	% H2O	Pb	% OM	% sand	% silt	% clay	C.E.C.	Ca	Mg	K	Na	pH	Acidity	Ext. Ca	Ext. Mg	Ext. K	P	Cu	Zn	Mn	Fe
Min	30.0	0.3	0.8	0.1	14.5	7.6	3.5	31.4	16.9	1.8	0.1	0.1	6.4	0.1	15.8	1.7	0.0	2.3	2.3	0.2	0.1	5.9
Mean	106.8	0.4	1.0	1.3	55.2	33.4	11.4	41.8	24.0	4.3	0.3	0.2	7.0	0.1	22.1	4.2	0.1	4.5	5.7	0.6	1.8	17.5
Median	110.0	0.3	1.0	1.1	55.3	32.8	8.8	42.4	23.5	4.2	0.3	0.2	7.0	0.1	22.5	4.2	0.1	4.2	5.6	0.6	1.8	16.5
Max	120.0	0.7	1.2	4.6	86.8	70.0	37.6	52.9	40.5	6.3	1.3	0.3	8.3	0.2	29.4	6.1	0.5	12.8	11.7	1.7	5.8	35.0
St Dev	14.4	0.2	0.1	1.0	23.0	17.7	8.0	5.6	4.3	1.2	0.2	0.1	0.3	0.0	3.2	1.2	0.1	1.9	2.3	0.3	1.2	8.6
Skewness	-2.1	1.8	0.0	1.8	-0.1	0.2	1.8	-0.1	1.5	0.1	3.1	0.0	2.6	3.0	0.0	0.0	3.2	2.0	0.5	2.1	1.0	0.5
Kurtosis	5.8	3.3	-0.7	3.5	-1.5	-1.3	3.1	-0.8	3.8	-1.1	14.4	-1.0	9.6	10.9	-0.6	-1.0	14.4	6.3	-0.5	6.4	1.4	-0.9
SE Mean	2.1	0.1	0.0	0.1	3.4	2.6	1.2	0.8	0.6	0.2	0.0	0.0	0.0	0.0	0.5	0.2	0.0	0.3	0.3	0.0	0.2	1.3
CV%	13.5	44.4	11.7	78.8	41.6	53.0	70.1	13.5	18.1	28.4	62.7	26.9	4.4	34.5	14.5	27.4	71.2	42.9	41.3	44.6	66.1	48.8

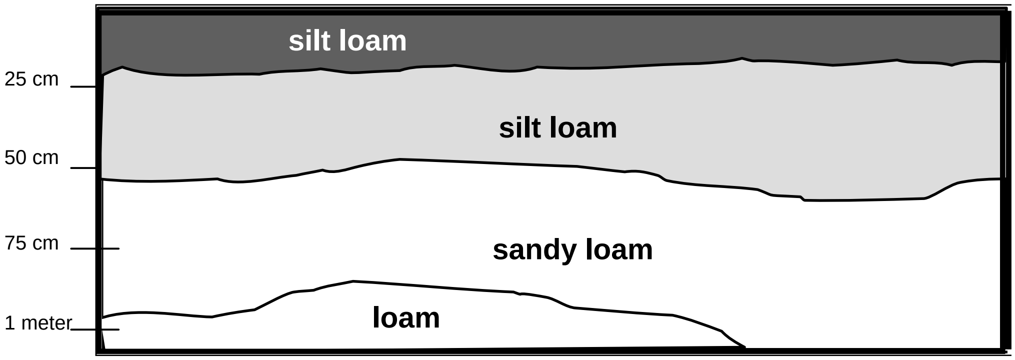
Pearson's correlation coefficients for fine-scale soil transect samples ($p<0.05$ in **BOLD** N=238)

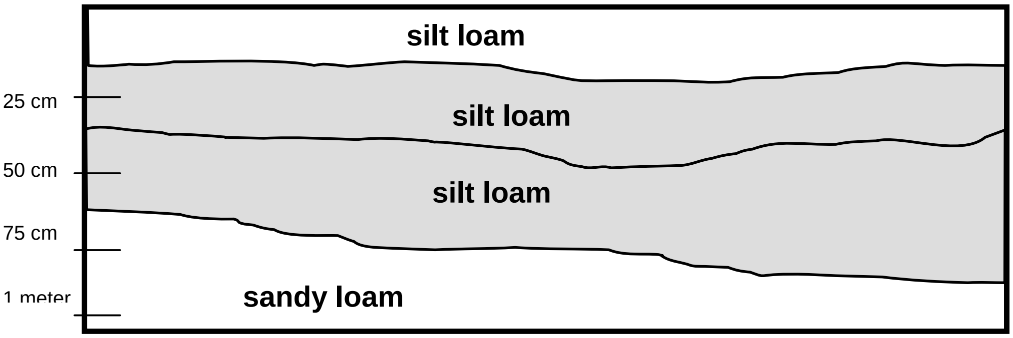
	%OM	% sand	% silt	% clay	C.E.C.	Exch. Ca	Exch. Mg	Exch. K	Exch. Na	pH	Acidity	Ext Ca	Ext Mg	Ext K	P	Cu	Zn	Mn
% sand	**-0.40**																	
% silt	**0.34**	**-0.97**																
% clay	**0.43**	**-0.75**	**0.56**															
C.E.C.	**0.75**	**-0.69**	**0.64**	**0.59**														
Exch. Ca	**0.50**	**-0.60**	**0.55**	**0.54**	**0.71**													
Exch. Mg	**0.65**	**-0.53**	**0.47**	**0.50**	**0.73**	**0.36**												
Exch. K	**0.24**	-0.11	0.11	0.07	**0.42**	**0.16**	**0.30**											
Exch. Na	-0.08	-0.17	0.09	**0.30**	**-0.13**	0.09	-0.12	**-0.68**										
pH	**-0.18**	-0.04	0.00	0.12	**-0.16**	**0.45**	**-0.38**	**-0.20**	0.26									
Acidity	0.09	**0.15**	**-0.16**	-0.08	-0.02	**-0.23**	0.11	-0.04	-0.01	**-0.39**								
Ext. Ca	**0.58**	**-0.71**	**0.64**	**0.65**	**0.79**	**0.92**	0.37	0.09	**0.20**	**0.34**	**-0.21**							
Ext. Mg	**0.65**	**-0.54**	**0.48**	**0.51**	**0.71**	**0.33**	**0.98**	**0.23**	-0.07	**-0.40**	**0.14**	**0.38**						
Ext. K	**0.26**	-0.09	0.09	0.07	**0.42**	**0.16**	**0.29**	**0.99**	**-0.66**	**-0.19**	-0.03	0.09	**0.23**					
P	**0.42**	-0.10	0.07	0.12	**0.47**	**0.27**	**0.38**	**0.58**	**-0.55**	**-0.18**	0.00	**0.24**	**0.35**	**0.58**				
Cu	-0.02	**-0.72**	**0.70**	**0.54**	**0.44**	**0.36**	**0.23**	0.06	**0.15**	0.09	**-0.23**	**0.48**	**0.23**	0.04	-0.07			
Zn	**0.54**	**-0.29**	**0.28**	**0.20**	**0.64**	**0.42**	**0.52**	**0.50**	**-0.33**	**-0.24**	-0.05	**0.34**	**0.45**	**0.49**	**0.45**	0.06		
Mn	**0.53**	**-0.22**	**0.24**	0.10	**0.48**	**0.16**	**0.41**	**0.22**	**-0.19**	**-0.45**	**0.16**	**0.21**	**0.40**	**0.23**	**0.24**	0.02	**0.46**	
Fe	0.06	**-0.23**	**0.30**	-0.04	**0.29**	0.02	**0.25**	**0.46**	**-0.42**	**-0.49**	0.00	-0.05	**0.20**	**0.43**	**0.26**	**0.24**	**0.50**	**0.39**

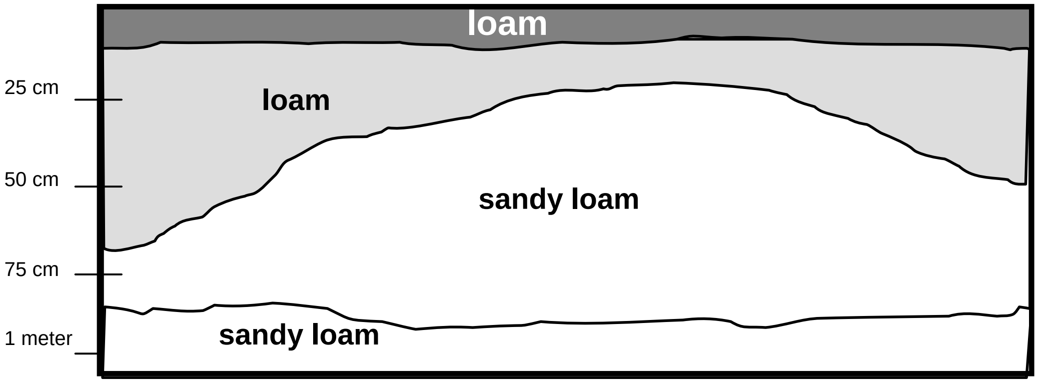
Appendix C: Soil Transect Stratigraphy of
Fine-Scale Farm Sites 1-10
Y axis represents depth of horizon
X axis represents increasing distance from stream (<200m)

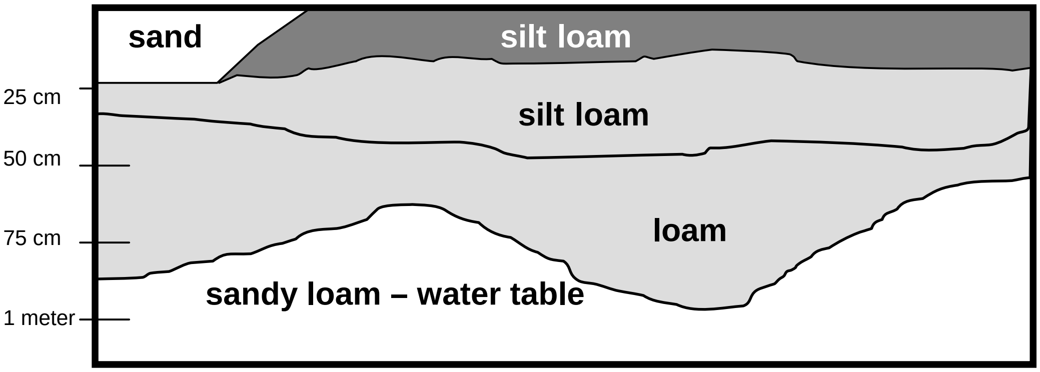
■ > 7% OM
▒ 4-7% OM
░ 2-4% OM
□ < 2% OM

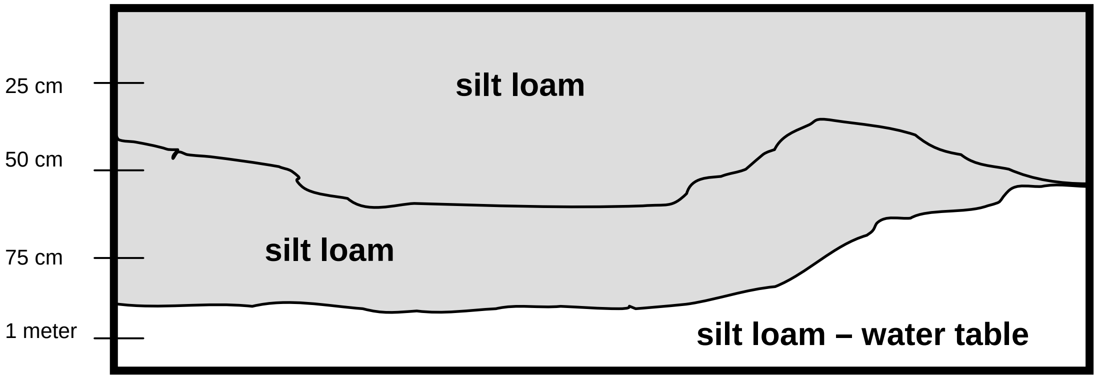


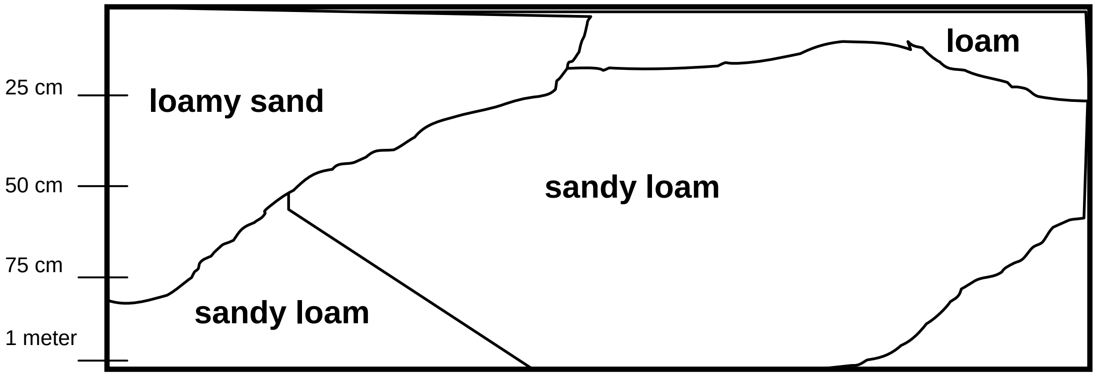

silt loam
25 cm
silt loam
50 cm
75 cm
sandy loam
1 meter
loam

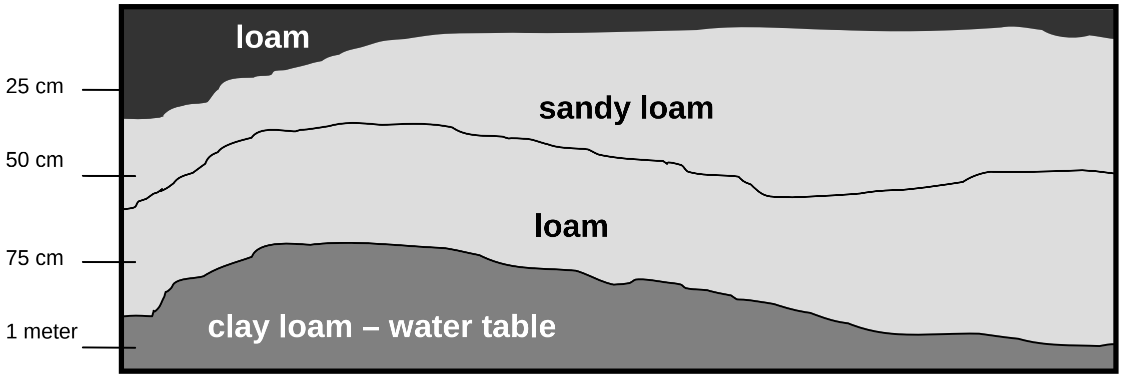

silt loam
25 cm
silt loam
50 cm
silt loam
75 cm
1 meter
sandy loam


loam
25 cm
loam
50 cm
sandy loam
75 cm
1 meter
sandy loam


sand
silt loam
25 cm
silt loam
50 cm
75 cm
loam
1 meter
sandy loam – water table

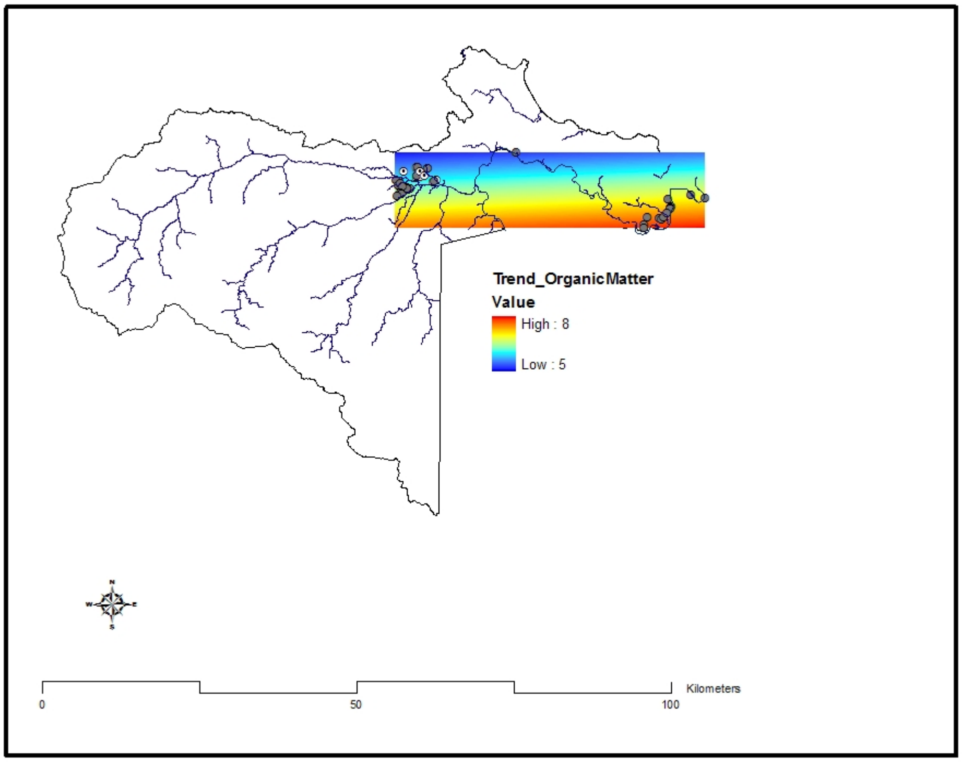

25 cm
50 cm
75 cm
1 meter
silt loam
silt loam
silt loam – water table


loam
25 cm
loamy sand
50 cm
sandy loam
75 cm
sandy loam
1 meter

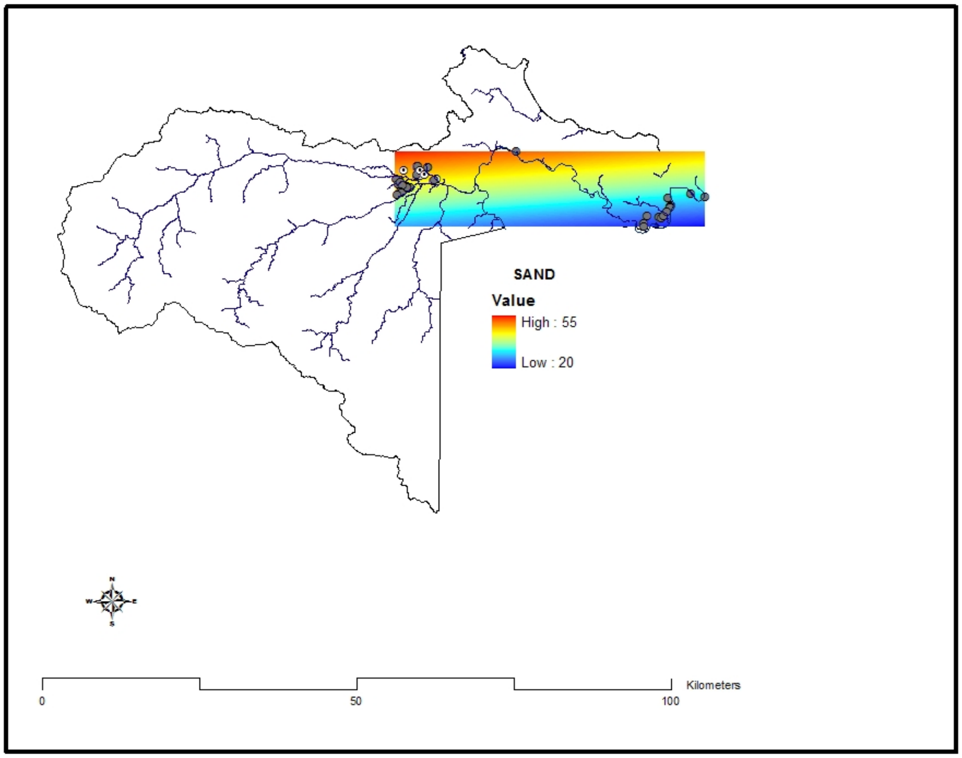

loam
25 cm
sandy loam
50 cm
loam
75 cm
1 meter
clay loam – water table

Appendix D: Trend Surface Analyses

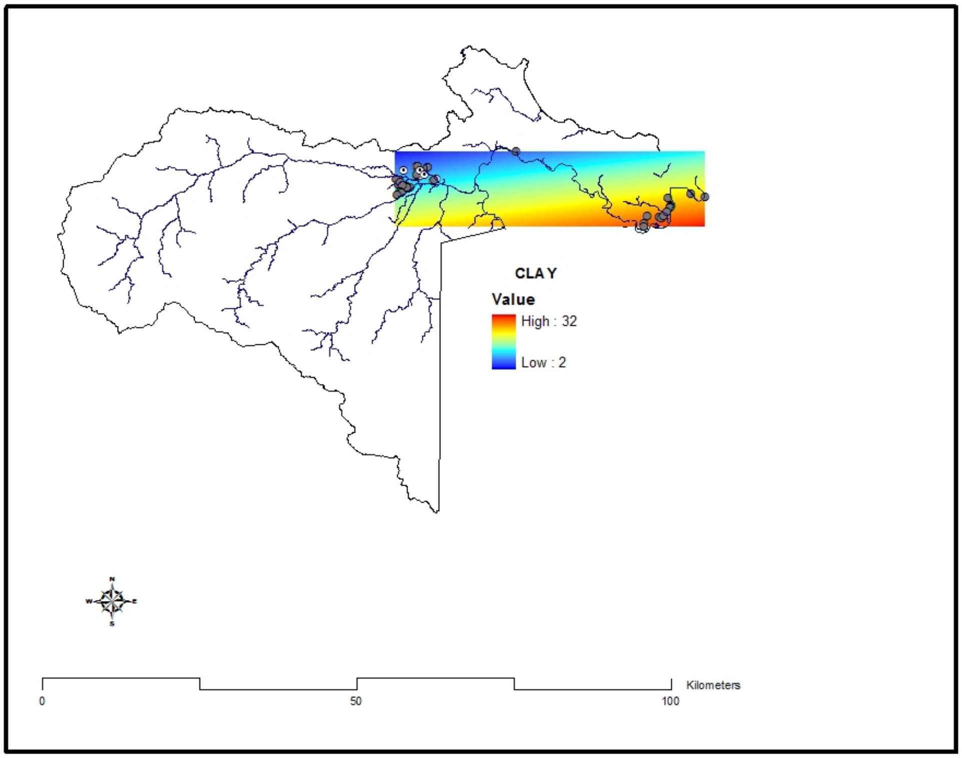
Example 1: Percent Organic Matter



Example 2: Percent Sand

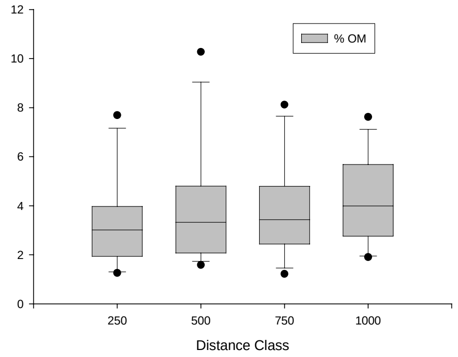


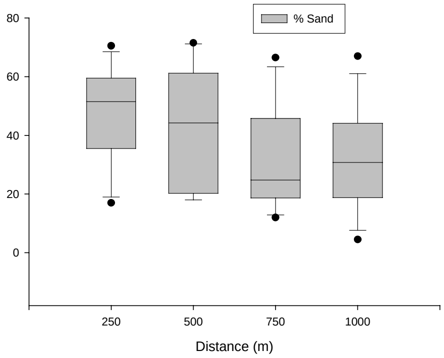
Example 3: Percent Clay

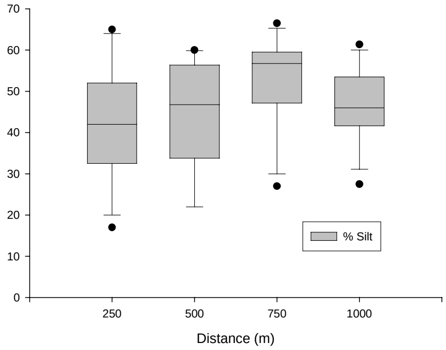


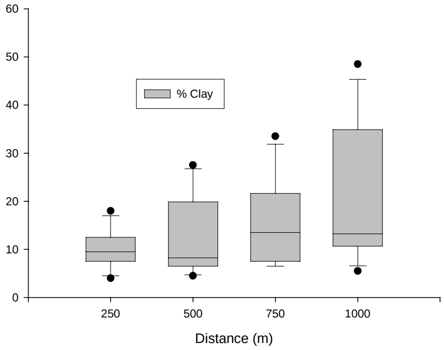
Appendix E: Coarse-Scale Box Plots and Scatter Plots

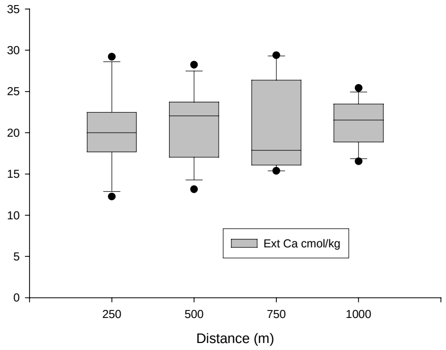
Box plots of coarse-scale raw values by 250m distance class.

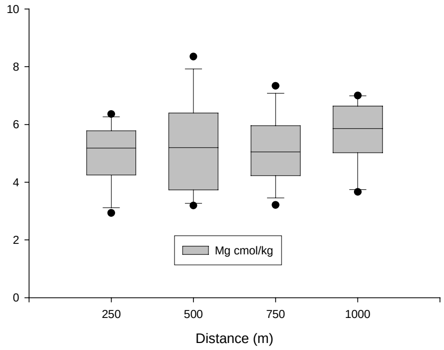


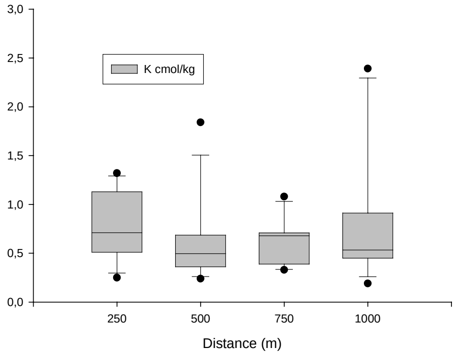


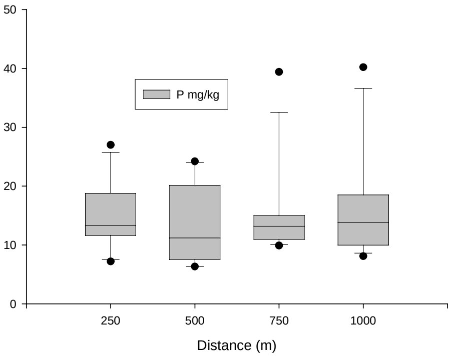


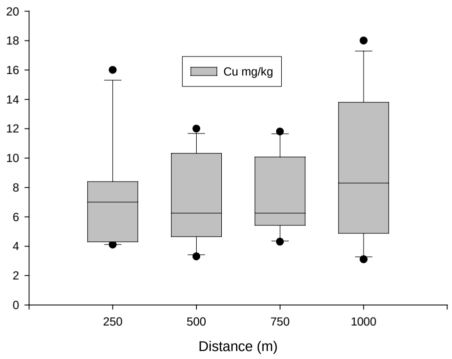


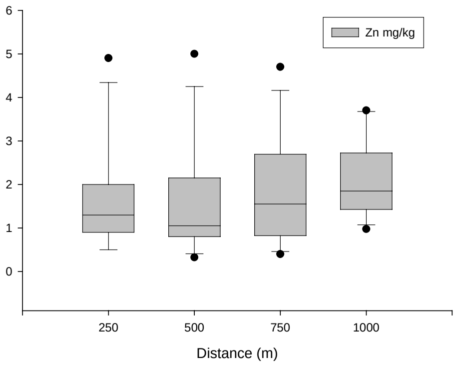


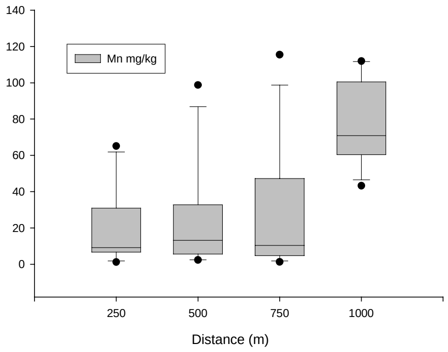


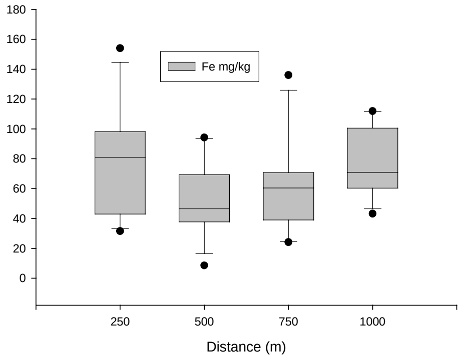




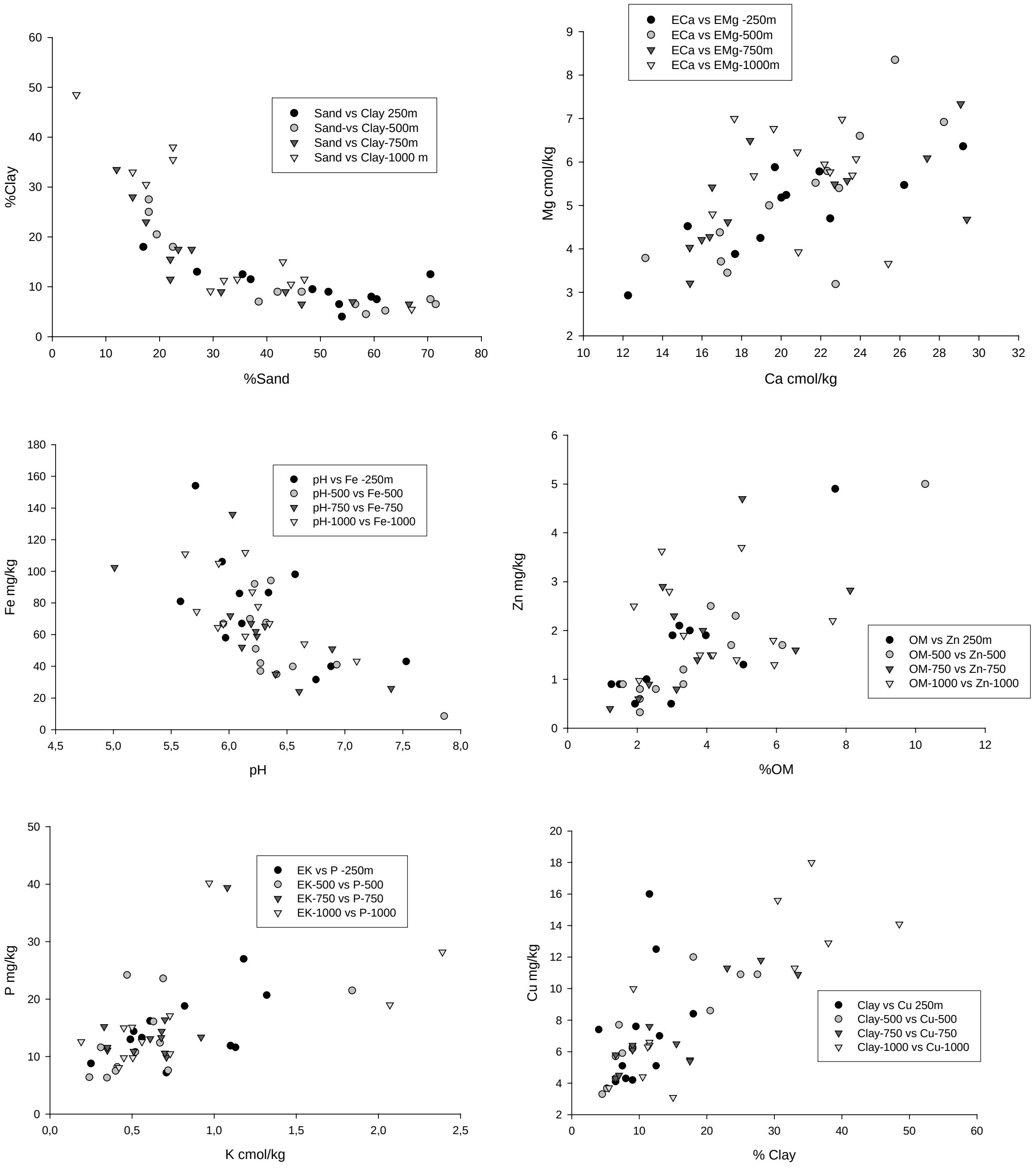

20
18
16
14
12
10
8
6
4
2
0
Cu mg/kg
250
500
750
1000
Distance (m)

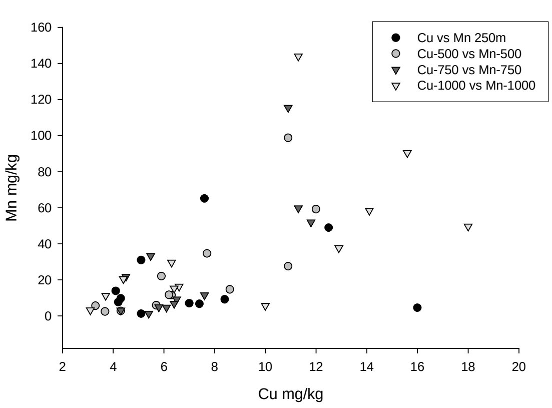

6
5
4
3
2
1
0
Zn mg/kg
250
500
750
1000
Distance (m)

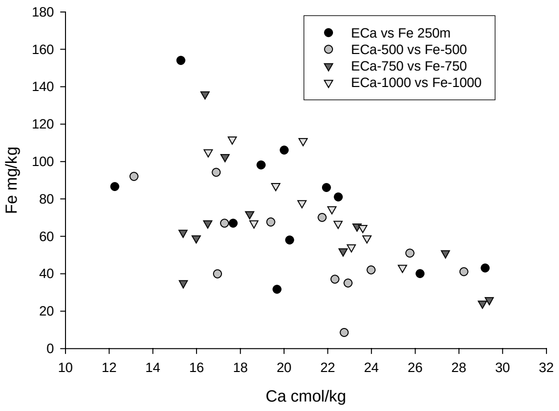

140
120
100
80
60
40
20
0
Mn mg/kg
250
500
750
1000
Distance (m)


180
160
140
120
100
80
60
40
20
0
Fe mg/kg
250
500
750
1000
Distance (m)

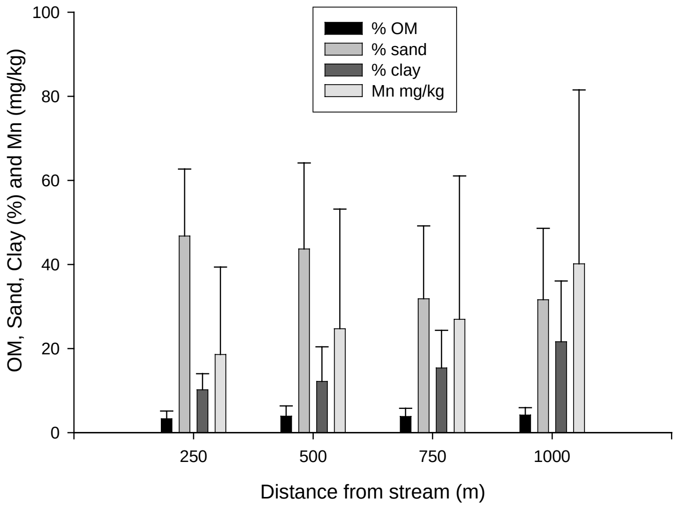
Scatter plots of selected correlated relationships (significant Pearsons) by 250m distance class







Linear relationships for averaged soil properties: R^2 Values: OM (0.79), Sand (0.88), Clay (0.94), and Mn (0.91)

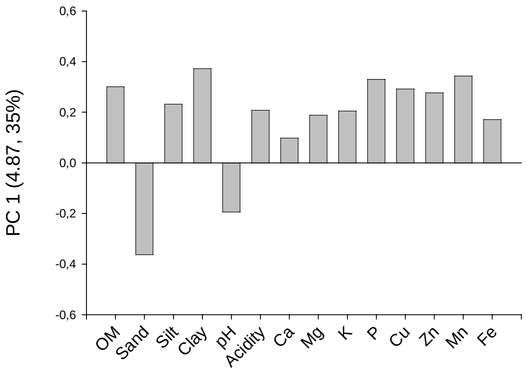


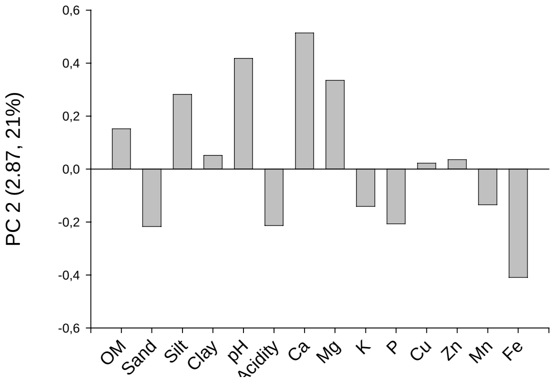
Appendix F: Coarse Scale Principal Components Analysis (PCA)

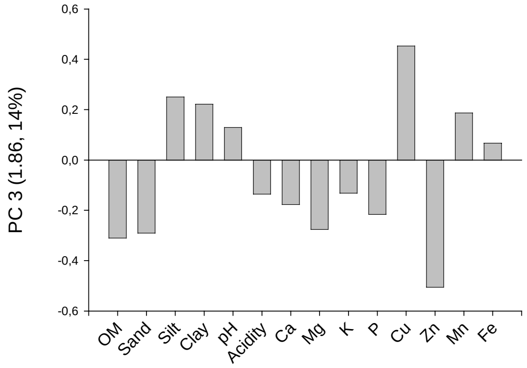
First four principal components for coarse scale topsoil samples (N= 47)

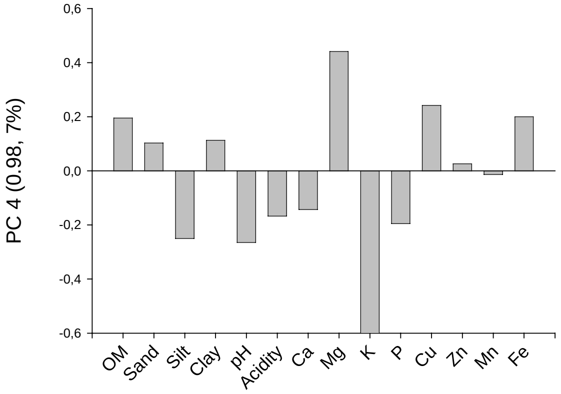
	Eigenvalue	% Proportion	% Cumulative
PC1	4,87	35	35
PC2	2,87	21	55
PC3	1,86	14	69
PC4	0,98	7	76

Contribution of coarse-scale soil properties (loadings) to variation represented by the first four principal components (eigenvalue, proportion of variance represented in parentheses).

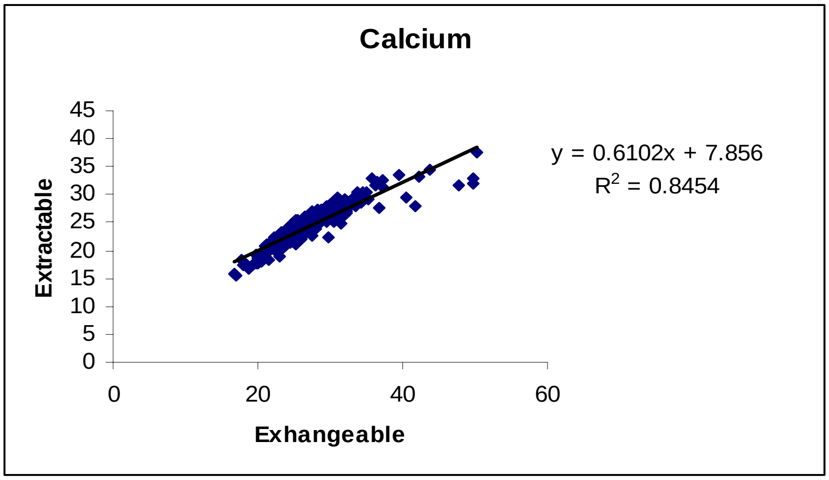


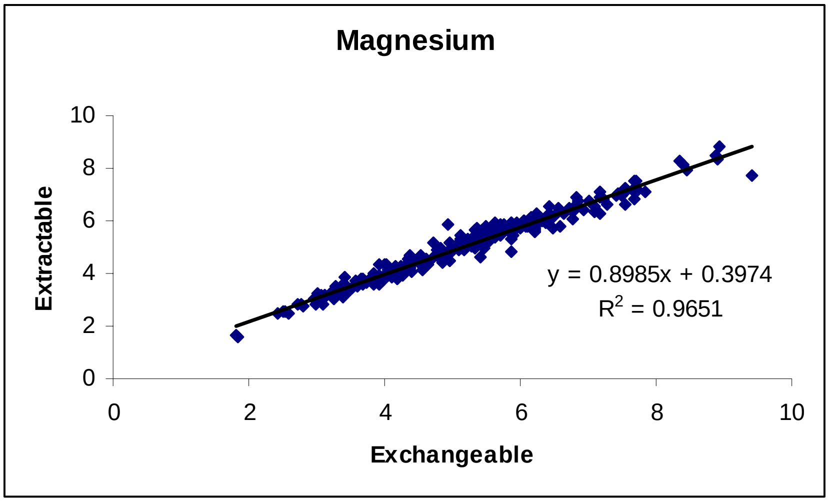


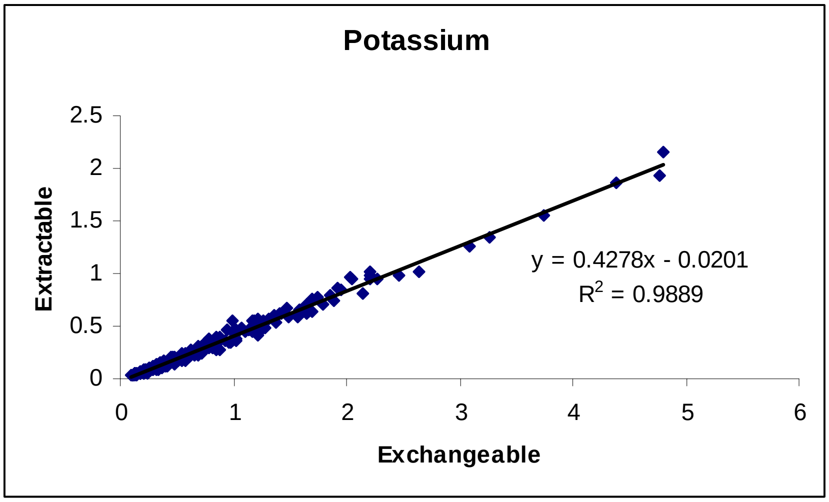




Appendix G: Relationship between Extractable and Exchangeable Cations in Fine-Scale Soil Samples







Appendix H: Fine-Scale Distance Class Averages and Median Values

Average values and standard deviation of fine-scale analysis by 60m distance class (N=238)

Horizon 1

AVERAGE

						cmol (+) /kg		cmol (+) /kg				mg/kg				
n	Distance	%OM	% sand	% silt	% clay	C.E.C.	pH	Acidity	Ca	Mg	K	P	Cu	Zn	Mn	Fe
24	60	4.31	38.40	49.29	12.31	55.56	6.88	0.06	26.00	5.54	0.51	9.95	5.78	1.76	11.41	33.13
22	120	4.11	35.44	50.85	13.71	54.23	6.66	0.07	25.20	5.63	0.58	10.95	6.45	1.65	13.27	41.72
19	180	3.61	32.41	54.36	13.24	55.61	6.74	0.06	25.65	5.67	0.62	11.32	6.80	1.78	13.62	39.58

ST DEV

n	Distance	%OM	% sand	% silt	% clay	C.E.C.	pH	Acidity	Ca	Mg	K	P	Cu	Zn	Mn	Fe
24	60	2.64	19.99	15.38	6.62	11.11	0.76	0.01	4.05	1.77	0.42	4.29	3.02	1.62	12.98	19.05
22	120	2.58	17.82	12.65	7.27	8.91	0.64	0.03	4.54	1.46	0.43	4.53	2.98	1.05	11.95	23.41
19	180	2.22	13.84	10.55	5.10	7.55	0.59	0.01	3.26	1.57	0.45	4.95	3.01	1.02	13.58	22.13

Horizon 2

AVERAGE

n	Distance	%OM	% sand	% silt	% clay	C.E.C.	pH	Acidity	Ca	Mg	K	P	Cu	Zn	Mn	Fe
24	60	2.77	38.3	48.6	13.1	51.7	6.77	0.08	24.9	5.43	0.29	6.51	8.01	0.85	6.16	27.8
22	120	2.87	36.4	49.9	13.8	51.9	6.64	0.07	24.5	5.46	0.38	8.61	7.09	0.92	7.99	28.2
19	180	2.37	26.4	59.1	14.5	51.6	6.72	0.06	25.2	5.63	0.3	7.76	9.03	0.83	6.66	29.3

ST DEV

n	Distance	%OM	% sand	% silt	% clay	C.E.C.	pH	Acidity	Ca	Mg	K	P	Cu	Zn	Mn	Fe
24	60	1.37	23.2	17.5	7.86	9.42	0.4	0.04	4.41	0.75	0.29	3.22	3.92	0.6	6.4	13.6
22	120	1.92	23.8	18.6	6.36	8.41	0.26	0.02	3.72	0.95	0.27	5.31	3.69	0.56	9.78	12.4
19	180	1.09	16.0	13.8	3.85	5.7	0.3	0.02	2.97	0.92	0.25	6.59	3.54	0.31	5.1	9.56

Horizon 3

						cmol (+) /kg		cmol (+) /kg						mg/kg		
n	AVERAGE	%OM	% sand	% silt	% clay	C.E.C.	pH	Acidity	Ca	Mg	K	P	Cu	Zn	Mn	Fe
24	60	2.08	44.7	42	13.3	46.2	6.89	0.06	24.1	4.55	0.17	4.97	6.6	0.66	5.71	21
20	120	2.04	45.1	41.3	13.6	45.9	6.8	0.07	23.6	4.48	0.2	5.72	6.03	0.58	3.36	20.1
19	180	1.74	45.8	42.2	12	45.4	6.86	0.06	23.4	4.86	0.16	5.86	6.73	0.56	2.53	20.3

ST DEV

n	Distance	%OM	% sand	% silt	% clay	C.E.C.	pH	Acidity	Ca	Mg	K	P	Cu	Zn	Mn	Fe
24	60	1.11	21.6	17.5	7.22	5.34	0.35	0.02	3.13	0.82	0.14	1.76	2.48	0.38	14	12.2
20	120	1.28	20.4	14.4	8.61	4.6	0.42	0.03	2.28	1.23	0.15	2.19	1.61	0.2	2.98	10.3
19	180	1.14	23.0	17.9	5.35	3.34	0.2	0.01	1.88	1.02	0.14	4.19	2.15	0.16	1.52	9.16

Horizon 4

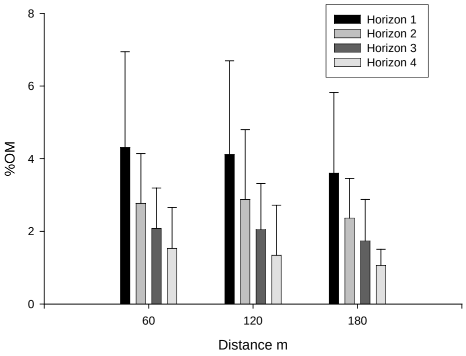
AVERAGE

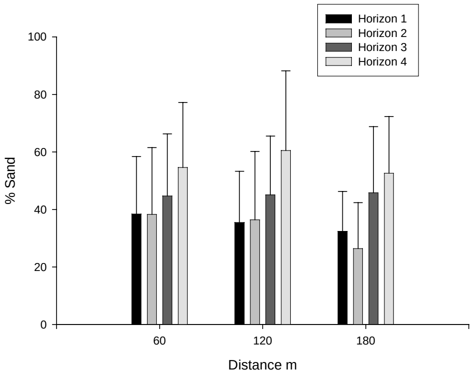
n	Distance	%OM	% sand	% silt	% clay	C.E.C.	pH	Acidity	Ca	Mg	K	P	Cu	Zn	Mn	Fe
17	60	1.6	54.6	33.2	12.2	42.0	7.1	0.06	22.8	3.9	0.1	5.2	5.4	0.6	1.7	16.2
13	120	1.3	60.5	28.3	11.1	40.5	6.9	0.07	21.0	4.2	0.1	4.6	5.2	0.6	1.8	16.3
15	180	1.1	52.6	36.7	10.7	42.3	7.0	0.05	21.9	4.7	0.1	3.8	6.3	0.6	2.0	19.7

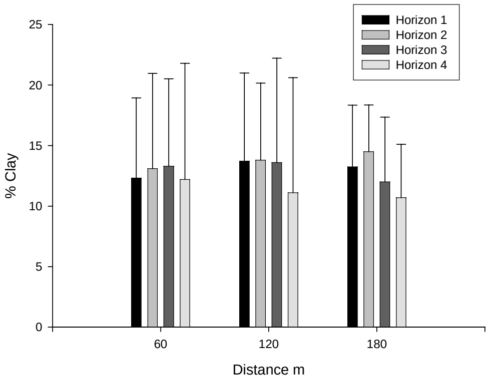
ST DEV

n	Distance	%OM	% sand	% silt	% clay	C.E.C.	pH	Acidity	Ca	Mg	K	P	Cu	Zn	Mn	Fe
17	60	1.1	22.6	16.2	9.6	5.5	0.5	0.03	3.5	1.1	0.1	2.8	2.2	0.3	1.5	8.3
13	120	1.4	27.7	21.1	9.5	6.7	0.2	0.02	3.5	1.2	0.1	1.2	2.7	0.2	1.1	9.3
15	180	0.4	19.7	16.1	4.4	4.9	0.1	0.01	2.3	1.1	0.0	1.0	2.2	0.3	1.1	8.5

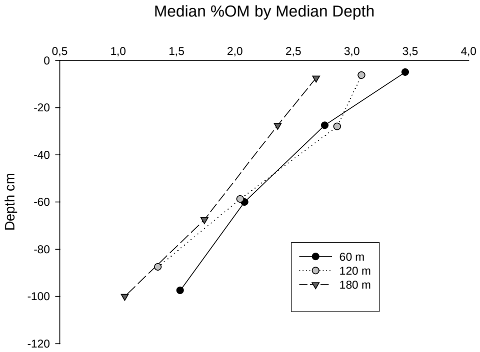
Average percent organic matter, sand and clay of fine-scale soil samples by horizon and 60m distance class

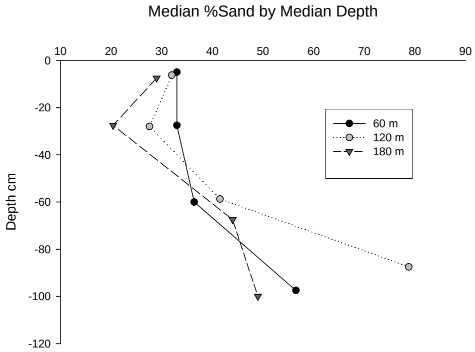


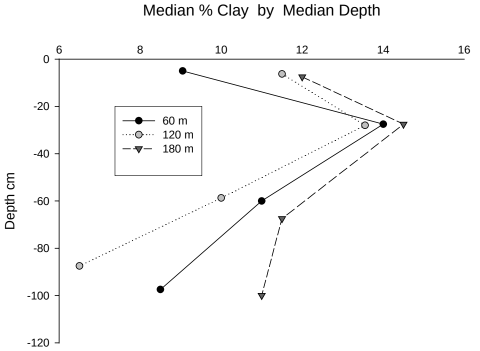


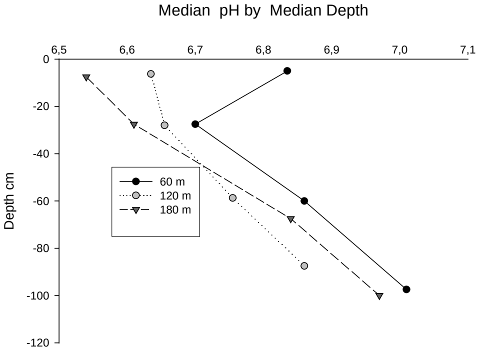


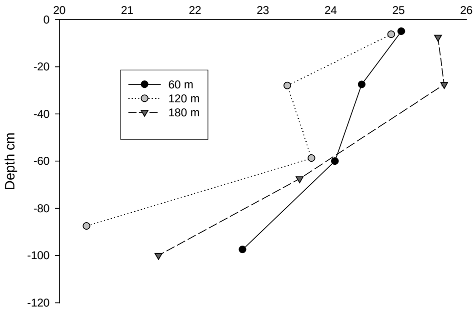
Median soil property values in 60m, 120m 180m fine-scale distance classes by median horizon depth

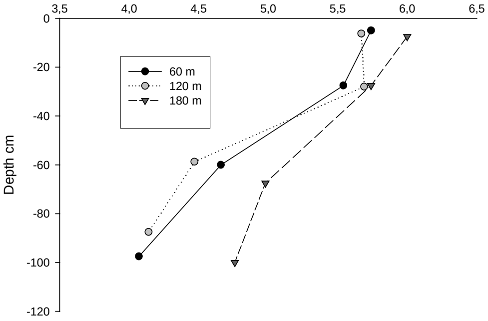

Median %OM by Median Depth

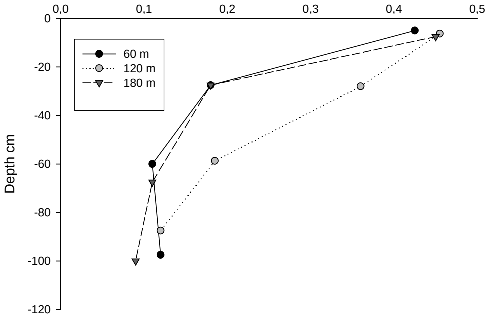

Median %Sand by Median Depth

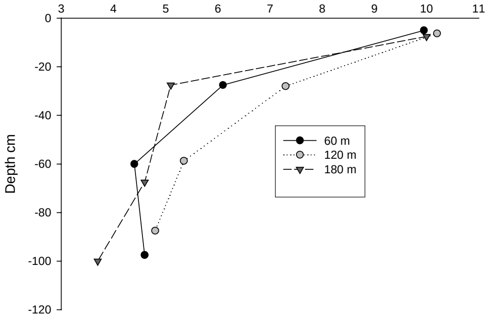

Median % Clay by Median Depth

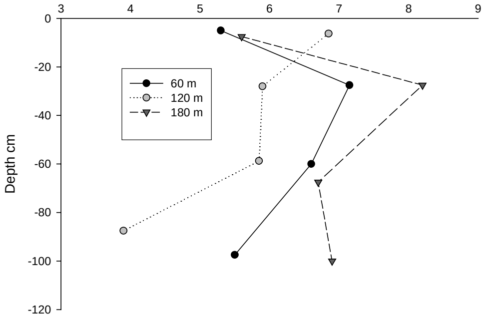

Median pH by Median Depth

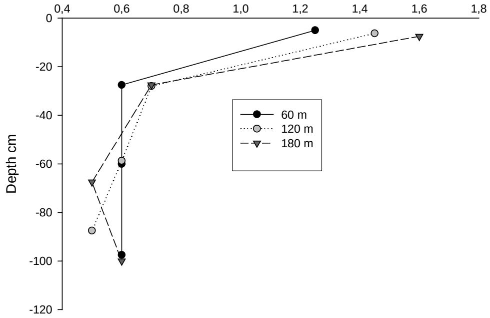

Median Calcium by Median Depth

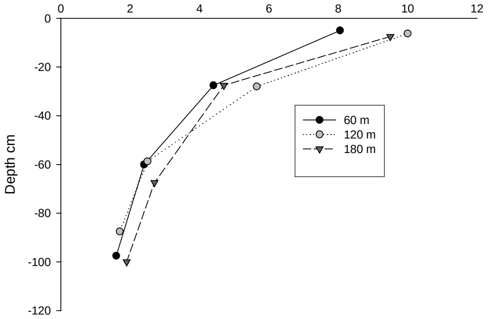

Median Magnesium by Median Depth

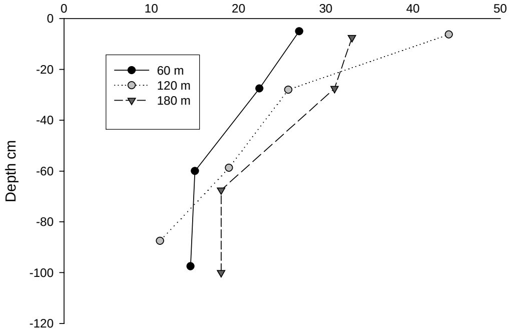

Median Potassium by Median Depth


Median Phosphorus by Median Depth


Median Copper by Median Depth


Median Zinc by Median Depth


Median Manganese by Median Depth

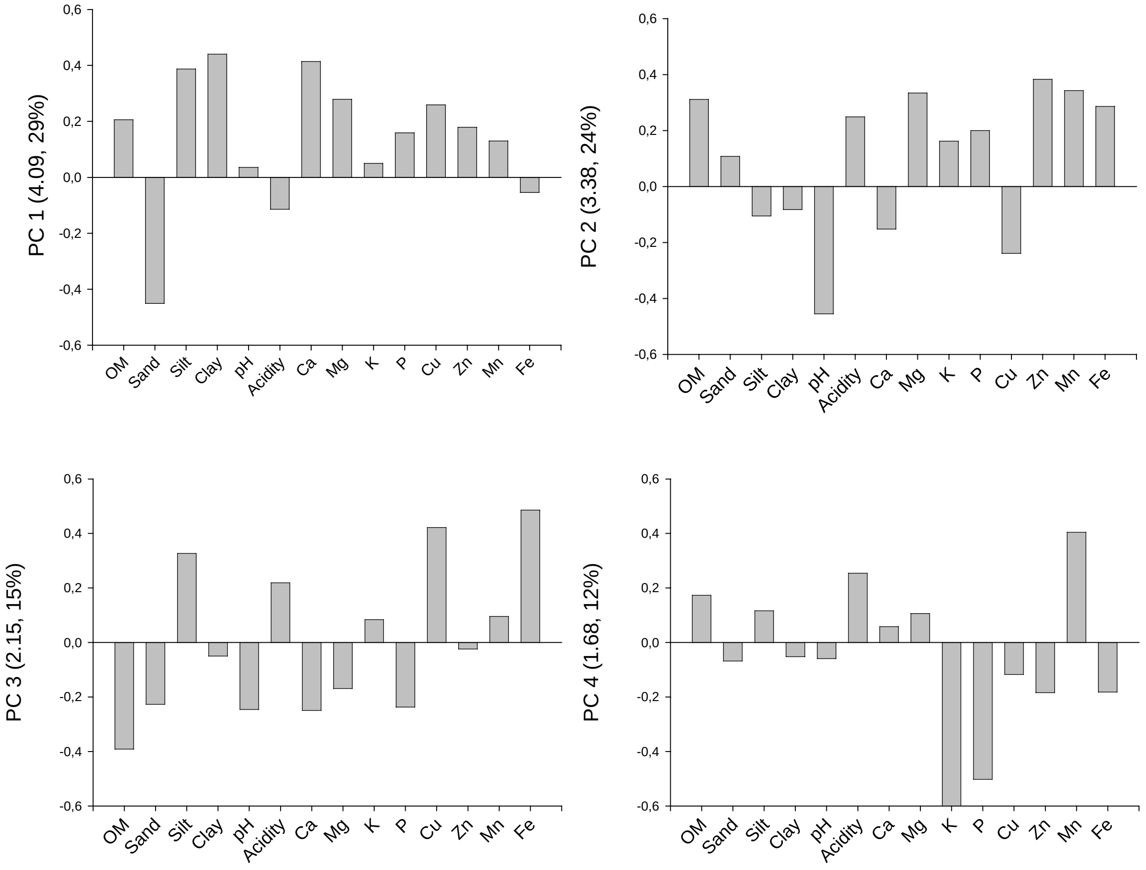

Median Iron by Median Depth

Appendix I: Fine-Scale Principal Components Analysis (PCA)

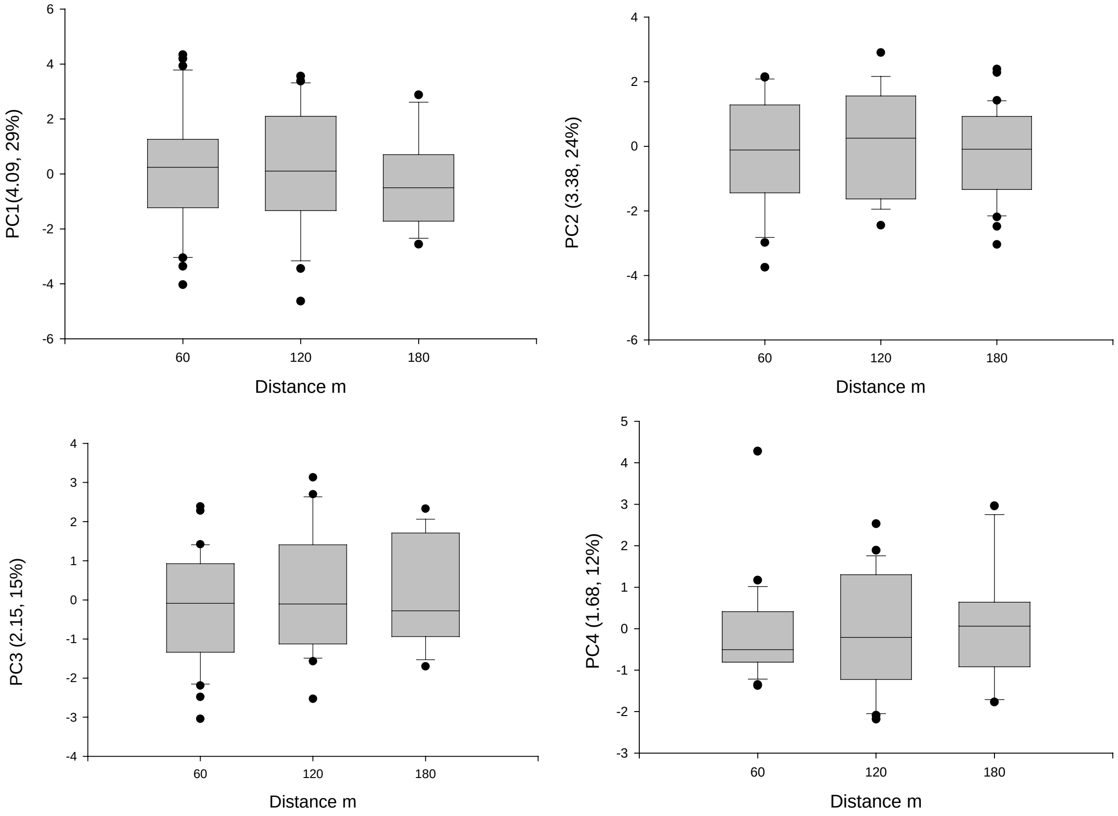
First four principal components for first horizon of fine-scale samples (N=65).

	Eigenvalue	% Proportion	% Cumulative
PC1	4,01	29	29
PC2	3,38	24	53
PC3	2,15	15	68
PC4	1,68	12	80

Contribution of first horizon of fine-scale soil properties (loadings) to variation represented by the first four principal components (eigenvalue, proportion of variance represented in parentheses).



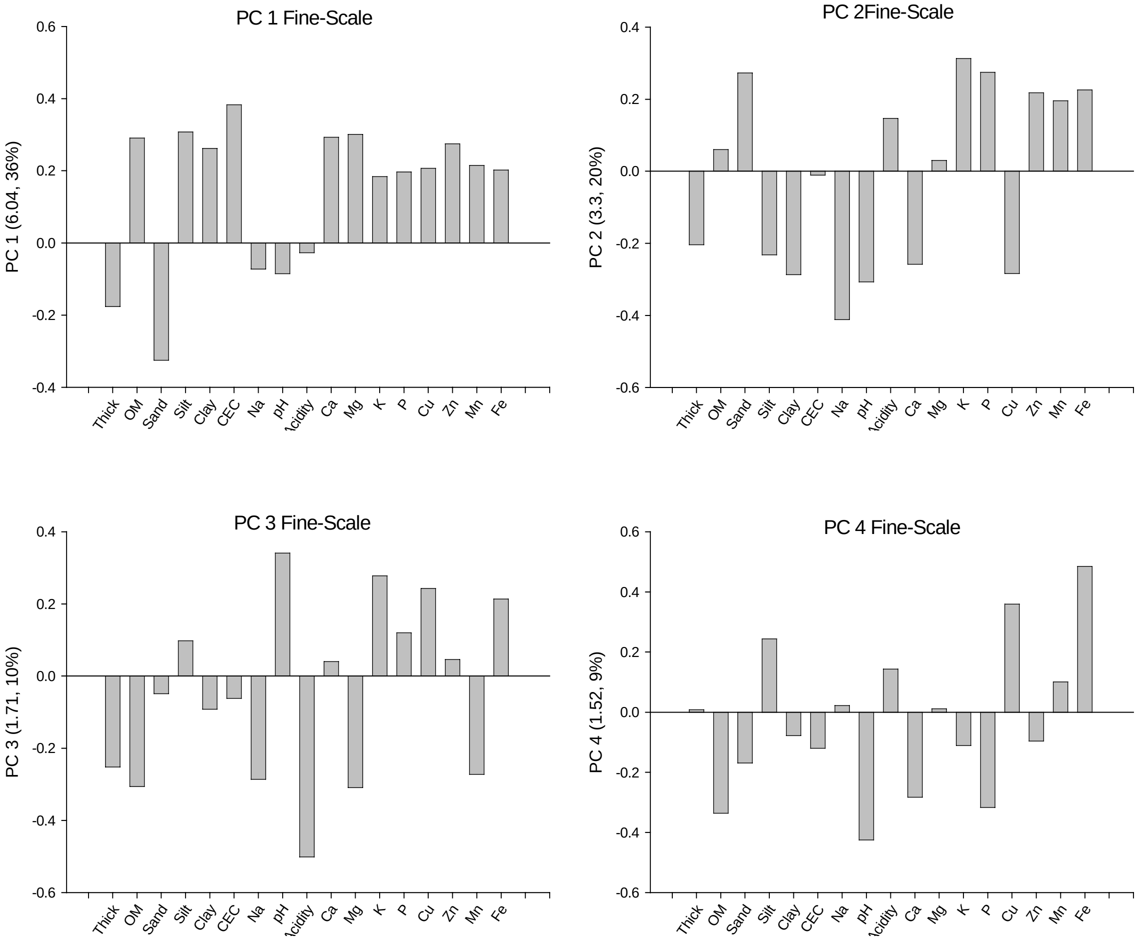
Box plots of PC values for first horizon of fine-scale samples by 60m distance class (N=65)



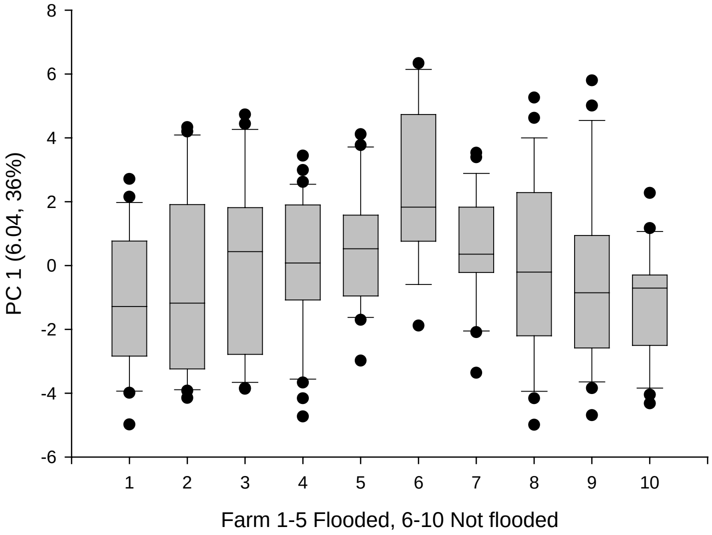
Principal components for all fine-scale soil transect data (N=238)

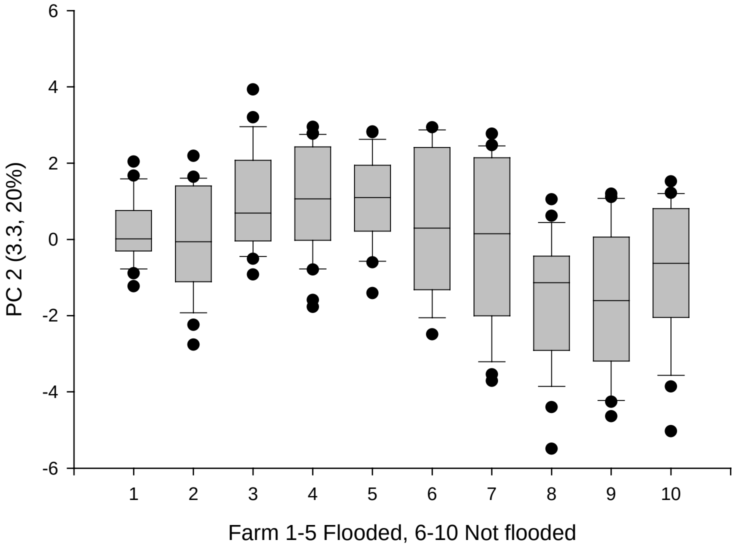
	Eigenvalue	% Proportion	% Cumulative
PC1	6,04	36	36
PC2	3,33	20	55
PC3	1,71	10	65
PC4	1,52	9	74

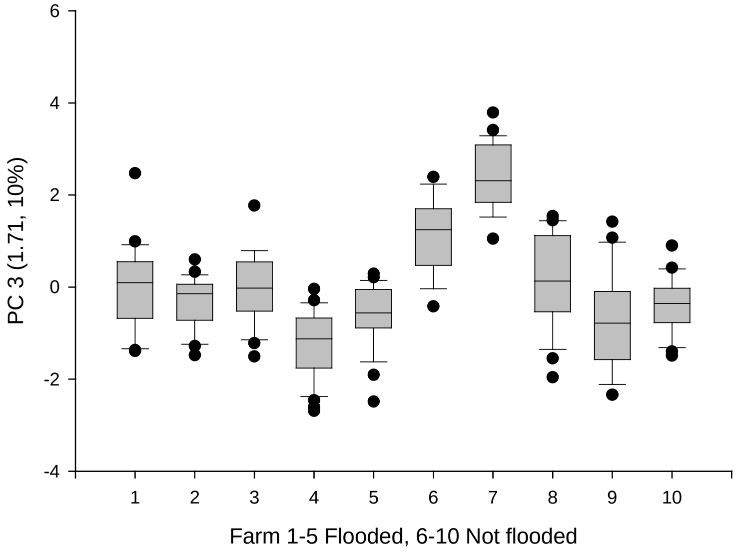
Contribution of fine-scale soil properties (loadings) to variation represented by the first four principal components. (Thick = horizon thickness)

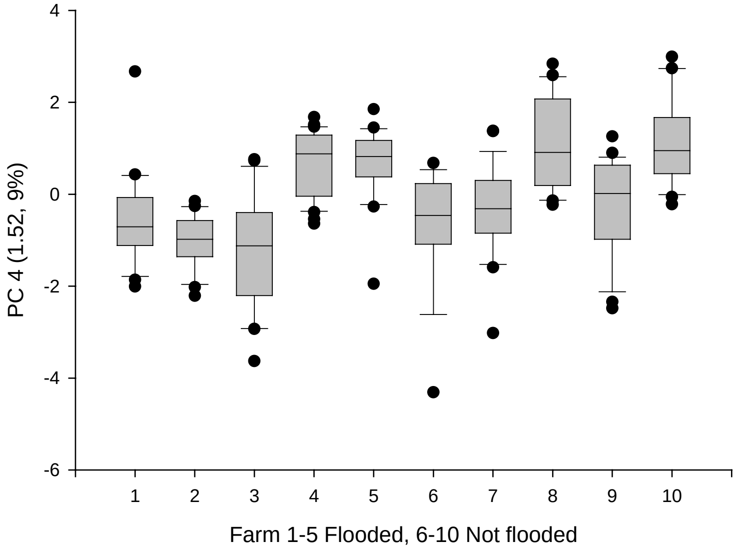


Box plots of first four principal components for fine-scale samples by farm site.






6
4
2
0
-2
-4
PC 3 (1.71, 10%)
1
2
3
4
5
6
7
8
9
10
Farm 1-5 Flooded, 6-10 Not flooded


4
2
0
-2
-4
-6
PC 4 (1.52, 9%)
1
2
3
4
5
6
7
8
9
10
Farm 1-5 Flooded, 6-10 Not flooded

Chapter Three

Pesticide Sequestration in Passive Samplers (SPMDs): Biofouling and Deployment Time in a Tropical Watershed

Abstract

Field-deployed passive samplers such as semi-permeable membrane devices (SPMDs) provide an informative and cost-effective approach in the monitoring of contaminants. However, sequestration of contaminants in passive samplers can vary based on a number of environmental factors including water flow, biofouling, and deployment time. In three one-month long trials, SPMDs were concurrently deployed for 4, 15, and 28 d in three different stream sites in an extensive agricultural area in south-eastern Costa Rica in order to determine the effects of biofouling on pesticide sequestration over time. Water, bottom sediment, and suspended sediment grab samples were also collected at corresponding time intervals during each month and several environmental variables were monitored daily. In all three sites, SPMD concentrations of the widely used insecticide chlorpyrifos increased with deployment time, with no significant relationship between membrane biofouling and pesticide uptake. Higher suspended solids concentrations combined with higher flow velocities and lower standing water conditions showed increased chlorpyrifos concentration in SPMDs in replicate sites. The longer exposure period of SPMDs also allowed for the detection of lower concentrations of chlorpyrifos, terbufos, and difenoconazole compared to water grab samples. In addition to flow and deployment time, several other environmental variables including stream turbidity, flow regime, and morphology may also be important for optimum SPMD deployment and data interpretation.

Introduction

The use of passive samplers, including semi-permeable membrane devices (SPMDs), is rapidly being adopted for a number of different uses in the environmental monitoring of hydrophobic organic compounds. Applications in both marine and freshwater environments have included screening for the presence or absence of environmental contaminants, contaminant speciation, monitoring of temporal pollution trends, monitoring of spatial distribution of pollutants and tracing of pollutant sources, contaminant fate in different environmental compartments, time-weighted average of aqueous concentrations, estimation of organism exposure, and the biomimetic extraction for toxicity assessment of aqueous contaminants (Vrana et al. 2005).

The SPMD design was first published in 1990 (Huckins et al. 1990), and since then nearly 300 studies have been reported (CERC 2007, Vrana et al. 2005), with only a handful conducted in tropical areas. SPMDs are constructed of lay-flat tubing of low-density polyethylene (LDPE) filled with high-molecular weight and high purity triolein. LDPE is a non-porous material with transient cavities of 1 nm, effectively sequestering compounds with octanol/water partition coefficients (Kow) > 3 (Huckins et al. 1993) and having molecular masses less than 600 (Petty et al. 2000). This solute size limitation ensures that only the dissolved and vapor phases of hydrophobic contaminants are sampled, thereby excluding large molecules as well as hydrophobic compounds adsorbed on colloids or humic acids (Vrana et al. 2005, Vrana and Schuurmann 2002, Petty et al. 2000). These properties of SPMDs thus mimic the transfer of biomolecules through biomembranes (Vrana and Schuurmann 2002).

Although SPMDs have proven to be extremely useful tools for monitoring hydrophobic contaminants in the field, interpretation of contaminants sequestered in field-deployed SPMDs for the estimation of time-weighted average water concentrations has been shown to be dependent on the variation of field uptake or sampling rates due to differences in water temperature, flow velocity, and the extent of biofouling in the field (Louch et al. 2003, Vrana et al. 2002, Huckins et al. 1999). Several studies have published SPMD uptake rates for a number of different contaminants under controlled temperature or flow conditions (Huckins et al. 2004, Booij et al. 2003, Luellen and Shea 2002, Rantalainen et al. 2000, Huckins et al. 1999, Meadows, 1998). These studies have provided critical information and an improved understanding of SPMD sampling rates for a number of contaminants.

SPMD sampling rates have been shown to increase with an increase in both the contaminant's Kow and temperature (Petty et al. 2000, Huckins et al. 1999). For example, sampling rates for chlorobenzenes, PCBs and PAHs at 30°C were shown to be higher than those at 2°C by a factor of 3 (Booij et al. 2003), and 1.5 times higher for PAHs sequestered at 26°C compared to 10°C (Huckins et al. 1999). However, unless large geographical or temporal scales are involved, temperature may not be as important as flow velocity or biofouling in controlling SPMD field sampling rates (Booij et al. 2003), especially in tropical areas where high year-round temperatures are much more consistent than in temperate zones.

Based on the theory of a decreased aqueous boundary layer, SPMD sampling rates are known to increase with increased flow velocities, with the effect increasing with increasing contaminant hydrophobicity (Huckins et al. 2006, Vrana and Schuurmann 2002). For example, SPMD sampling rates for penta- and hexachlorobenzene were shown to increase from 4 to 14 L/day with an increase in the linear flow velocity from 0.06 to 0.28 cm/s. Similarly, Booij et al. (2003) found increased SPMD sampling rates in the magnitude of 20-200 L/day for PAHs in water with flow velocities of 90 cm/s compared to PAH sampling rates of 2-8 L/day in water with flow velocities of 0.004 cm/s (Huckins et al. 1999). Flow hydrodynamics, however, may be the most difficult factor to measure for determining SPMD sampling rates as stream flow velocities have been shown to be very different for flow velocities inside SPMD-deployed canisters where sampling is actually taking place (Louch et al. 2003). In one study comparing SPMD sampling rates, Louch et al. (2003) measured stream flow rates between 0.23 to 1.02 m/s, while within SPMD canister flow rates ranged between 0.14 to 0.44 m/s.

Biofouling describes the physical impedance of contaminant uptake due to the adsorption or growth of sediment or a biofilm on the outside of the SPMD membrane surface. For little or no biofouling, generally no correction is made to laboratory-established or previously calibrated SPMD sampling rates. There are only three known studies on the effect of biofouling on SPMD sampling rates (Booij et al. 2006a, Richardson et al. 2002, Huckins et al. 1996 in Petty et al. 2000). In a laboratory experiment, Richardson et al. (2002) found a 50% reduction in the uptake of organochlorine pesticides and PAHs in biofouled SPMDs compared to non-fouled SPMDs in Hong Kong seawater. In contrast, results from a field experiment in the use of anti-fouling agents to control SPMD biofouling in the Western Waddell Sea suggested that heavy biofouling did not always result in reduced sampling rates (Booij et al. 2006a). However, no studies are known to have examined the effect of biofouling on field SPMD uptake rates under tropical conditions. As SPMD membranes can experience heavy biofouling especially during extended exposures in warm or tropical surface waters (Huckins et al. 2006), the objectives of this study were to determine the effect of biofouling and deployment time on pesticide uptake in field-deployed SPMDs under tropical conditions.

Background: SPMD Theory

SPMDs are described as kinetic, rather than equilibrium samplers. In equilibrium passive samplers, the exposure time is sufficient to establish a thermodynamic equilibrium between the water and reference phases (Vrana et al. 2005). Kinetic passive samplers assume that the rate of mass transfer to the reference or receiving phase, such as triolein in SPMDs, is linearly proportional to the difference between the contaminant activity in water and the sampler (Vrana et al. 2005). In which case, SPMDs can be deployed for time-periods where they will reach equilibrium with the water phase, but can also be deployed for shorter periods of time for kinetic or integrative sampling to sequester contaminants from episodic events not captured with spot sampling and where water concentrations are variable (Vrana et al. 2005). When constant water concentrations of a specific analyte are assumed (Booij et al. 2003), the exchange kinetics between SPMD and the water phase are described by a first-order, one-compartment mathematical model:

$$C_{SPMD} = Cw\ K_{SPMD}(1-e^{-KeT})$$

where the time-weighted average concentration of an analyte in the water (Cw) can be predicted from C_{SPMD}, the analyte concentration in the SPMD membrane (ng/g), based on the specific SPMD-water partition coefficient for the analyte (K_{SPMD}), the elimination or exchange rate coefficient (Ke), and time of deployment (T in days). The exchange rate coefficient Ke describes the loss of analyte from the SPMD with time and is defined by:

$$Ke = (Ak_o)/(K_{SPMD}V)$$

where A and V are the surface area and volume of the SPMD and k_o is the overall mass transfer coefficient. The mass transfer coefficient (k_o) describes the resistance to mass transfer:

$$1/k_o = 1/k_w+1/(k_m k_{mw})$$

where k_w is the aqueous boundary layer transfer coefficient and k_m and k_{mw} are the membrane and membrane-water partition coefficients. This model assumes negligible resistance in the triolein and is based on the theory of aqueous vs. membrane boundary layer control (Booij et al. 2003). In aqueous boundary layer control ($k_o \cong k_w$), the SPMD-water exchange kinetics for a given analyte are governed by the thickness of the aqueous boundary layer and the analyte's aqueous diffusion coefficient D_w and molecular size M.

$$K_w = D_w^{2/3}=M^{-0.53}$$

Conditions of aqueous boundary layer control generally dominate in high flow conditions, when the thickness of the aqueous boundary layer is reduced, and for compounds with Kow values in the range of about 4.4 to 8.0. Under low flow conditions and for compounds with lower Kow values, the uptake is controlled by the membrane boundary layer (Booij et al. 2003, Huckins et al. 2002). In membrane-controlled uptake ($ko \cong K_m K_{mw}$), the membrane partition coefficient (k_m) is related to the diffusion coefficient in the membrane (D_m) and membrane thickness (δ_m) by $k_m = D_m/\delta_m$. The membrane-water partition coefficient (k_{mw}) is related to the analyte's Kow value and a temperature constant (Tc) (Booij et al. 2003).

$$\log K_{mw} = 0.972 \log Kow + Tc$$

The K_{SPMD} value for a given analyte is determined in the laboratory, but can also be estimated based on the following equation: $\log K_{SPMD} = 0.715 \log Kow +1.29$ (Booij et al. 2003). The elimination rate coefficient (ke) is best estimated in the field with the use of permeability/performance reference compounds (PRC) (Huckins et al. 2002). PRCs are analytically non-interfering organic compounds with moderate to high Kows that are added to the SPMDs before deployment to determine rates of loss in the field, based on the assumption that similar isotropic exchange kinetics govern the accumulation of hydrophobic compounds by SPMDs (Huckins et al. 2002).

During the initial stages of uptake, well before equilibrium can be established and before the ratio of Cw to C_{SPMD} is 0.5 (Louch et al. 2003), desorption or loss from the receiving phase (Ke) is negligible and uptake can be described as linear:

$$C_{SPMD} = Cw\ RsT$$

where Rs is the SPMD sampling rate or volume of water cleared per unit time (L/day). Linear uptake is only expected up to the chemical-specific SPMD "half-life" or $t_{1/2}$, defined by $t_{1/2} = (0.693K_{SPMD}V)/Rs$, with full equilibrium or steady-state conditions at four times $t_{1/2}$ (Huckins et al. 2002). The Rs value is related to aqueous or membrane boundary layer control as $Rs = K_oA$ (Booij et al. 2003), and varies for each analyte as $Rs = ke\ K_{SPMD}\ V$ (Huckins et al. 1999). Ke is affected by changes in the boundary layer due to different flow velocity and biofouling, and K_{SPMD} is dependent on temperature (Booij et al. 2003, Huckins et al. 1999, Prest and Jacobson 1997). Thus, actual field sampling rates (Rsf) are likely to be different than laboratory-calibrated or calculated Rs values due to site differences in temperature, flow velocity or turbulence, and biofouling.

Study Site Description

In Sixaola River Watershed, located in the Talamanca region of southeastern Costa Rica, a variety of pesticides are applied in the year-round cultivation of export-quality banana and plantain (Polidoro et al., in prep). Fungicides to combat black sigatoka (*Mycosphaerella fijiensis*) include difenoconazole, propiconazole, mancozeb, tridemorph, and bitertanol, and are applied in rotation every 8 d throughout the year. Nematicides are generally applied three times a year, usually in February, June, and October, and include terbufos, oxamil, and ethoprofos. Herbicides such as glyphosate, diuron, and paraquat are applied two to six times a year. Insecticide-impregnated plastic bags containing 1% by weight chlorpyrifos are placed around maturing fruit throughout banana or plantain plantations. This agrochemical regime provides a year-round constant loading of pesticides, particularly of chlorpyrifos and difenoconazole.

Cana Creek and the Sixaola River are located in Talamanca region of southeastern Costa Rica (Figure 1). The Sixaola River is the principal river in Talamanca and drains a 2700-m^2 watershed (de la Cruz and Castillo 2003). In the upper Sixaola River Valley, four rivers descend from the Talamanca Mountains to converge on an extensive alluvial plain, forming the Sixaola River, which then runs another 100 km to the Atlantic Coast. Rainfall throughout the watershed increases with elevation from approximately 2600 mm of rain on the lower reaches of the Sixaola River to over 5000 mm of rain in the surrounding mountainous areas (4000 m elevation), with evapotranspiration rates throughout the region estimated to be between 1565-1719 mm/yr (Kapp 1989). Average daily air temperatures in Talamanca range from 18° to 28°C, also reflecting the large variation in altitude.

The Sixaola River study site is located just downstream from the town of Sixaola on the Costa Rican side of its border with Panama. The Sixaola River, from its origin on the upper alluvial plain to the coast, is lined with commercial banana plantations and national plantain cooperatives intermixed with small patches of remnant secondary forest and small towns. Average monthly discharge from 1972-1993 for the Sixaola River ranged from over 100 to approximately 300 m^3/s, while suspended solids ranged from 50 to over 350 Mtons/month with peak flows and suspended sediment concentrations primarily occurring in November and December (Corrales and Salas 1997, Borge and Castillo 1997). Year-round stream temperatures are quite constant at 25°C. Flow conditions also provide for consistently high dissolved oxygen levels, although flow velocity, stream turbidity, and discharge vary with upstream rainfall. The Cana Creek study site is located in a smaller stream that is the principal drainage canal of a large banana plantation. Cana Creek eventually meets the Sixaola River below the Sixaola River study site. Year-round stream water temperatures in Cana Creek are between 25-30 C°, with large fluctuations in stream turbidity, flow velocity and discharge, and dissolved oxygen. Regular fish kills have been observed at the site, usually during hot, sunny conditions after a large rain event, when dissolved oxygen is low and stream surface temperatures are above 30°C (Polidoro, unpublished observation, Castillo et al. 2007).

Methods

Research Design

Two one-month long experiments were conducted at the Cana Creek study site during February and June of 2006, and one month-long experiment was conducted in the Sixaola River during June of 2006. Although there is technically no dry season in Talamanca, Costa Rica, 180 mm of rain was recorded around the study sites during the February study period, and 80 mm of rain during the June study period. During each study period, stainless steel canisters containing a total of 9 standard 91.4-cm long SPMD membranes (Environmental Sampling Technologies, St. Joseph, MO, USA) were deployed along a cutbank in each stream, where flow and depth could be maximized to allow for optimum mixing and avoidance of SPMD exposure to air during potential low flow conditions. Three SPMD membranes were removed at 4, 15, and 28 d during each study period. A visual biofouling estimate was made on site during SPMD membrane retrieval using graphic percent cover charts (NRCS 2002).

In addition to SPMD deployment, 4 L of water, 2 L at 0-20 cm depth and 2 L at 20-40 cm depth were collected each week, immediately put on ice and the contained pesticides extracted within 48 hrs. Every 2 d, approximately 4 L of water was collected; 2 L from 0-20 cm and 2 L from 20-40 cm depth. Two 200-ml water subsamples were filtered using 0.7 μm glass fiber filters (Whatman GF/F) which were later oven-dried to quantify total suspended solids for that day. The remaining approximately 3.6 L of water was filtered for capture of suspended solids with the same 0.7 μm glass fiber filters (Whatman GF/F), which remained frozen until extraction for pesticides. Once a week, a composite of approximately 250 g of bottom sediment was taken from the 0-5 cm depth along a transect established across a part of (in the Sixaola River) or all of (in Cana Creek) the stream bottom and kept frozen until extraction. Sediment samples were composited by week for a total of 4 samples per site per study period. In summary, in each of the three experiments (Cana February 2006, Cana June 2006, and Sixaola June 2006), we deployed 9 SPMD membranes, collected 16 L of water grab samples, filtered approximately 50 L of water for suspended solids, and collected 4 composite bottom sediment samples. Two-way analyses of variance (ANOVA) were conducted to determine significant relationships among SPMD pesticide concentrations, biofouling, and deployment time.

Measurements of stream discharge, temperature, pH, dissolved oxygen, conductivity, and salinity were also made every one or two days at approximately 8:00 am. Stream discharge was calculated by multiplying average stream velocity by stream width and average depth. Stream flow was measured by averaging flow meter (Ben Meadows, Janesville, WI, USA) readings at equal depths at three different points in the stream, while stream width was measured with a measuring tape in the case of Cana Creek, or with a laser rangefinder (Optilogic XL, Tullahoma, TN, USA) in the case of the Sixaola River. Average stream depth measurements for Cana Creek were made by first creating an integrated depth profile of the stream bottom, then choosing a daily reference point to ascertain regular changes in average depth. For the Sixaola River, a pre-installed depth chart on the side of the Panama-Costa Rica Bridge was used for average depth. A laboratory calibrated multimeter (YSI 556 Multiprobe, Yellow Springs, OH, USA) was used to record dissolved oxygen, pH, conductivity, salinity, and temperature during the study periods. During the June study periods, a HOBO® temperature data logger (Pocasset, MA, USA) was attached to an SPMD canister in both the Cana Creek and Sixaola River. One sampling day in June also included a "snapshot" study of all streams in the Talamanca watershed, where water samples were collected from Cana Creek and the Sixaola River at approximately the same time on the same day to compare several water chemistry parameters between sites at the same point in time. During "snapshot" sampling, 2-L replicates were taken from each site and placed on ice for immediate laboratory analyses of pH, conductivity, alkalinity, hardness, dissolved calcium, magnesium, sodium, chlorine, ammonium, and nitrate; while field measurements of dissolved oxygen, pH, electrical conductivity, and temperature were made for comparison.

Laboratory Analyses

Passive Samplers (SPMDs)

Each SPMD was weighed before and after surface cleaning to calculate the weight of the biofilm for an additional estimate of biofouling. SPMDs were dialyzed and extracted based on methods developed by Environmental Sampling Technologies (EST 2007), where SPMDs are dialyzed in hexane for 24 h, then again for 8 h. The extracts were concentrated by rotary evaporation and then by nitrogen gas, with final extracts dissolved in 1mL acetone:cyclohexane (1:9). SPMD samples and blanks were spiked with the organophosphate Ethion as an internal standard. SPMD extracts and blanks were analyzed with GC-ECD and FPD, with detected compounds confirmation in a capillary column of other polarity.

Water Grab Samples

For each 2-L water sample, 1 L was extracted for HPLC analyses and the other for GC analyses. For GC analyses Ethion was used as an internal standard. One-liter water samples were extracted with SPE cartridges (Isolute ENV+ 200 mg/6 mL) conditioned with ethyl acetate, water, and methanol. For HPLC-PDA analysis, cartridges were eluted with methanol and concentrated to a final volume of 1 mL and dissolved in methanol:water (60:40). For GC-ECD, FPD, and GC-MS analysis, cartridges were eluted with ethyl acetate and concentrated to approximately 0.1 mL with nitrogen gas. Acetone: cyclohexane (1:9) was added to achieve a final extract volume of 1 mL.

Snapshot Water Samples

Two-liter replicate water samples collected from Cana Creek and Sixaola River on the same day were analyzed for pH, conductivity, alkalinity, hardness, calcium, magnesium, potassium, sodium, free chloride, phosphorus, ammonium, and nitrate at the soil and water research lab at CATIE in Turrialba, Costa Rica (Centro Agronómico de Investigación y Enseñanza). Methods of analysis were based on standard methods for the examination of water and wastewater (APHA, 1995), using the following listed alternatives: titration method 2320 for alkalinity, atomic adsorption method 3110 for Ca, Mg, K, Na, argentometric method 4500-Cl for chloride, method 4500-P for phosphorus, colorimetry from Berthelot reaction in water for ammonium, and colorimetry method 4500-NO_3 for nitrate.

Suspended Solids (TSS) Samples

Suspended solids samples on glass fiber filters were composited by site and month, for a total of three suspended solids composites, two 4-g (dry weight) samples from the two Cana Creek study periods, and one 8-g (dry weight) sample from the Sixaola River study period. Under little or low light conditions, glass fiber filter composites were placed into several glass jars, spiked with the internal standard p-terphenyl, filled with approximately 20 ml of 1:1 acetone: dichloromethane, and then placed in an ultrasonic bath for 20 min. Extracts were combined, and the process was repeated two more times, for a total of three washings per group of glass fiber filter composites. Composited extracts were dried with sodium sulfate and concentrated to approximately 0.1 mL with nitrogen gas. Acetone: cyclohexane (1:9) was added to achieve a final extract volume of 1 mL. Extracts were analyzed by GC-FPD and GC-ECD for pesticide residues, with confirmation of found compounds and quantification of p-terphenyl recovery with GC-MS (EPA method 8141A). Recovery of the internal standard p-terphenyl averaged 75%. The remaining unused extract was kept below 2°C under no light conditions and then analyzed for chlorophyll a and degraded chlorophyll a (phaeophytin) based on standard spectrophotometric methods (APHA 1995).

Suspended solids subsamples on pre-weighed paper filters were oven dried at 60°C for 48 h to quantify total suspended solids (TSS) concentrations for each sampling day throughout the study periods. After oven-drying, suspended sediment samples were grouped by SPMD deployment time with each composite containing approximately 1-2 g dry weight of suspended sediments. Composite samples were then carefully scraped into plastic centrifuge vials for total carbon and nitrogen analysis, using a ratioing mass spectrometer (Finnigan-MAT IRMS) at the University of Idaho Stable Isotopes Laboratory.

Sediment Samples

Stream bed sediment samples composited by week were thawed, homogenized, and passed through a coarse metal sieve of approximately 1.5-mm mesh size to remove gravel and coarse sand. For each sample, approximately 100 g of sediment was centrifuged for 5 min at 3200 rpm (g = 2400) and decanted to remove excess water. Sediment samples were then extracted based on a modified EPA method 3510C. Two replicates from each sample of approximately 35 g (wet weight) each were mixed with $NaSO_4$ until a sand-like texture was achieved. Samples were then spiked with p-terphenyl as the internal standard. Approximately 20 mL of 0.2 M $CaCl_2$ was added to each sample and left to sit for 15 min. Each sample was then extracted three times with 50 mL of 1:1 solution of acetone: dichloromethane. For each successive extraction, samples were placed on a shaker for 30 min and the organic phase decanted. The three organic phase decants were combined, dried with $NaSO_4$, and rotary evaporated to a volume of 2 mL. Final extracts were further concentrated to 0.1 mL using a stream of nitrogen gas, and then filled to a volume of 1 mL with 1:9 acetone:cyclohexane. Extracted samples were analyzed by GC-FPD and GC-ECD for pesticide residues, with confirmation of found compounds and quantification of p-terphenyl recovery with GC-MS (EPA method 8141A). Recovery of the internal standard p-terphenyl ranged between 40 and 70%.

The remaining sediment was combined by study site, subsampled, and analyzed for total carbon and nitrogen, using a ratioing mass spectrometer (Finnigan-MAT IRMS) at the University of Idaho Stable Isotopes Laboratory. Mineralogical analyses were also conducted on sediment subsamples by x-ray diffraction (Dixon and Schultz 2002) to identify the types of clay present in stream bottom sediments. Composite sediment subsamples from the Sixaola River and from Cana Creek were first treated for removal of any carbonates (none found), organic matter, and oxides. Clays were then isolated by dispersal and centrifugation, and then treated for x-ray diffraction.

Results

Water, Suspended Solids and Bottom Sediment Characteristics

A summary of the Cana Creek water quality parameters compared to those of the Sixaola River from a "snapshot" study of principal rivers in Talamanca is shown in Table 1. At sampling time, both streams showed a similar pH and temperature. During the June study period, however, Cana Creek temperature averaged 27.6°C, with minimum temperature of 24.6 and a maximum temperature of 31.2°C while Sixaola River temperature averaged 24.9, with a minimum temperature of 23.2, and a maximum temperature of 28.2°C. The larger variation and warmer temperatures observed in Cana Creek, as well as lower dissolved oxygen, are likely due to lower flow velocity conditions. Cana Creek is also observably higher in dissolved calcium, sodium, chloride, and nitrate, resulting in higher conductivity, hardness, and alkalinity.

Comparisons of related flow parameters including stream discharge, stream flow, total suspended solids, and dissolved oxygen during all of the study periods are shown in Figure 2. In general, stream discharge in the Sixaola River is several magnitudes higher than in Cana Creek. During the 28 d period, Sixaola River discharge averaged 338 m^3/s during June study period, with an average flow velocity of 1.2 m/s. In Cana Creek, June discharge averaged only 2.3 m^3/s, with an average flow velocity of 0.03 m/s; while February discharge averaged 7.5 m^3/s, with an average flow velocity of 0.13 m/s. Suspended sediment concentration was also higher in the Sixaola River, averaging 0.2 g/L during the June study period, while in Cana Creek suspended sediment concentration averaged 0.05 g/L in June and 0.08 g/L in February. Due to the higher flow velocities in the Sixaola River, dissolved oxygen concentrations are higher and more stable than in the Cana Creek, especially in June when high temperatures and low flow conditions in Cana Creek occasionally created episodes of eutrophication as evidenced by the very low dissolved oxygen conditions around sampling days 8 and 10.

A comparison of suspended sediment and bottom sediment characteristics is shown in Table 2. Suspended solids in the Cana Creek and Sixaola River have similar carbon content (3.5%) and carbon to nitrogen ratios. Bottom sediment mineralogy is also very similar with clay fractions primarily comprised of smectite, with some vermiculite, mica, kaolin, and quartz. Measures of chlorophyll a in suspended sediment extracts, however, showed 10 times more chlorophyll-a (including the degradation product phaeophytin) in suspended sediments in Cana Creek during the June study period compared to the February study period and in the Sixaola River. It was also observed that in June, Cana Creek was dominated by algal blooms and the suspended solids were green, while in February, substantially fewer algal blooms were observed in Cana Creek, and in the Sixaola River none were observed.

Pesticides Detected in SPMD, Water, Suspended Solids, and Sediment Samples

All SPMD, water, suspended solids, and bottom sediment samples were analyzed for 29 current-use pesticides (including 3 metabolites) in Costa Rica, with detection limits and log Kow values reported in Table 3. Three current-use pesticides: chlorpyrifos, terbufos, and difenoconazole were found above method detection limits in SPMD membranes (Fig. 3). In water samples, only difenoconazole and the less hydrophobic herbicide diuron were found above method detection limits, and only in the Cana study site (data not shown). Over the two study periods in the Cana site, difenoconazole was detected 50% of the time with an average concentration of 0.6 μg/L, and diuron was detected 40% of the time with an average concentration of 0.4 μg/L. No pesticides were found above method detection limits in suspended solids samples or in stream bottom sediment samples. In the case of suspended solids, small sample sizes of 4 or 8 g may have not provided enough sample material to meet detection limits for low concentration compounds. Similarly, low method recovery rates without a successful clean-up step for stream bottom sediment extracts may have inhibited detection of low concentration compounds.

SPMD Pesticide Uptake and Deployment Time

Chlorpyrifos was the pesticide found at every sampling period across both study sites and study periods (Figure 3). Precision among all replicate SPMD membranes was very good with an average of +/- 0.02 ng/SPMD variation among replicates. For chlorpyrifos, uptake clearly increased during both of the Cana Creek study periods. As previously mentioned, chlorpyrifos is assumed to have constant environmental loading in this area due to frequent, consistent year-round application. However, terbufos was only found in Cana Creek during the June study, and difenoconazole only found at the end of the Cana Creek February study, and in very similar concentrations during the Cana Creek June study (Figure 3). As nematicides are only applied approximately three times a year, terbufos was likely not applied during the February Cana Creek study period, with quantities detected in June just above method quantification limits. Difenoconazole is applied roughly every 8 to 15 d year-round, thus the uptake pattern seen in Cana Creek during the February study period indicates that it was likely applied near the end of the study period, while in June it was likely applied near the beginning of the study period.

Biofouling and SPMD Pesticide Uptake

There was no significant relationship between biofilm weight and SPMD uptake of pesticides. For example, during both the February and June Cana study periods (Figure 4) nearly equivalent replicate concentrations of chlorpyrifos in individual SPMDs were found with biofilm weight varying as much as 1 to 3 g on replicate membranes. In a two-way ANOVA, total biofilm weight on Cana Creek SPMDs was significantly ($p<0.05$) higher in February than in June. Also, SPMD-chlorpyrifos in Cana Creek was significantly different among deployment times and in the interaction between deployment time and sampling period (June vs. February).

Although somewhat subjective, estimates of visual biofouling on SPMD membranes do not show any clear relationships with SPMD biofilm weight, depicted as percent of membrane weight, or stream suspended solids concentration in the February and June Cana Creek study periods (Figure 5). In contrast to biofilm weight, which remains more or less constant during both Cana study periods, percent visual biofouling increased over the deployment time. In the Sixaola River, however, visual biofouling rates decreased at the end of the study period, indicating that some of the biofilm was likely washed off membranes by high flows. In summary, final SPMD-chlorpyrifos concentrations were higher during the February study in Cana Creek when there was higher visual biofouling, higher stream TSS, and significantly higher biofilm weight compared to the June Cana Creek study period. In the Sixaola River, SPMD-chlorpyrifos was not significantly different among deployment times and therefore no relationship can be seen among SPMD-chlorpyrifos, visual biofouling, biofilm weight, or stream TSS.

Discussion

Although the Cana Creek and Sixaola River show different degrees of similarity in water and sediment characteristics, the most important differences related to SPMD sequestration of pesticides between the two sites are related to the magnitude of difference in stream discharge and flow velocity. The Sixaola River had lower SPMD chlorpyrifos sequestration compared to either Cana Creek study period primarily likely due to lower chlorpyrifos concentration as a result of a much higher volume of water and stream discharge. However, the February Cana Creek study period showed higher discharge as well as higher biofouling (as determined by average biofilm weight and visual biofouling estimates) higher turbidity, higher suspended solids concentration, and higher SPMD chlorpyrifos sequestration compared to the June Cana Creek study. As chlorpyrifos was not detected in any water grab samples, it is not known if differences in SPMD sequestration of chlorpyrifos during the two Cana study periods are due to differences in chlorpyrifos water concentration or differences in SPMD uptake rates. Although constant environmental loading of chlorpyrifos is assumed in this region of Costa Rica, the concentration of SPMD-available chlorpyrifos in streams can be reduced under conditions of increased water volumes during temporary changes in stream discharge, or in the presence of increased dissolved organic carbon or suspended solids (Warren et al. 2003). The use of SPMDs cannot account for fluctuations in pesticide concentration during deployment time. Interpretation of SPMD data assumes constant chemical concentrations in the water column, and can only provide information on the presence or absence of contaminants and a time-weighted average of contaminant concentration (Vrana et al. 2005).

If chlorpyrifos concentrations were different between the two Cana Creek study periods, SPMD uptake rates are still assumed to be independent of chemical concentration (Huckins et al. 2006). SPMD uptake rates have also been also been shown to be independent of water salinity and pH (Petty et al. 2000, Huckins et al. 1999), but may be affected by the enhanced movement of contaminants across the membrane by organism ventilation in the biofilm (Huckins et al. 2006). Even though no pesticides were found in suspended solids above detection limits, SPMD uptake of chlorpyrifos with heavy biofouling may also be affected by the slow desorption of chlorpyrifos from biofouling sediments, especially those that include smectitic clays which are known to sorb organic matter, humic acids and pesticides (Li et al. 2003, Kaiser and Guggenberger 2003*)*. Although some studies have attempted to measure the slow desorption of contaminants from sediments with SPMDs, it has not been well documented (Leppanen and Kukkkonen 2000).

However, biofouling measured either as biofilm weight or from visual estimation did not appear to be an important influence on SPMD uptake of pesticides, especially as replicate membranes under the same study stream conditions had excellent precision in chlorpyrifos sequestration, but had different biofilm weights and no clear relationship with visual biofouling estimates. However, measurement of biofilm weight is likely not a reliable measure of the potential effects of biofouling on SPMD uptake rates. Biofilm weight is a function of its composition and the respective densities of the accumulating materials such as periphitic organisms, varying amounts of sand or clay, and mineral precipitates. Clay type is also important, as smectitic clays are known to hold more water and organic matter (Juo and Franzlubbers 2003). In a sense, biofilms can be viewed as a layer of immobilized water with dispersed sites of organic carbon (Huckins et al. 2006). Biofilms comprised of living material, such as algae and microorganisms, may actually aid in sequestration of contaminants in SPMDs as they serve as a water pump or internal ventilation to facilitate the transfer of materials across the SPMD membrane (Huckins et al. 2006). Additionally, as seen clearly in the case of the Sixaola River, the amount and composition of the biofilm on SPMDs may change frequently during deployment, especially during high flow events when the biofilm may be physically removed or accumulate in low flow events as in Cana Creek, when eutrophic conditions promote the growth of algae on SPMDs.

Visual estimation of the percent of biofouling on SPMDs is subjective and cannot account for the effect of different types of biofilms on membranes. However, visual estimation of percent cover or volume is an accepted method of quantification in many different disciplines with examples of scientific studies including estimating rock fragments in soil, percent crystals in rock, land-cover in landscape ecology, substrate type in stream ecology, and vegetation cover or organism occurrence (Latulippe et al. 2001, Zhou 1998, Brakenhielm and Qinghong 1995, Meese and Tomich 1992, Kidwell and Holland 1991), and should not be immediately dismissed as a valid field method. When viewed at a coarse-scale, estimates of visual biofouling were more reflective of overall changes in stream turbidity and suspended solids concentrations during the study periods compared to more specific measurements of biofilm weight. However, visual biofouling can also decrease along with biofilm weight, as seen in the case of the Sixaola River, within the deployment time. This was likely due to physical removal of debris from membranes during periods of high flow.

If similar chlorpyrifos water concentrations are assumed between the two Cana sampling periods, increased SPMD chlorpyrifos uptake rates observed in Cana Creek during February are likely due to higher flow velocities compared to the June study period, as heavy biofouling does not necessarily preclude the effect of flow velocities on SPMD uptake rates

(Booij et al. 2006a). Average flow velocities in Cana Creek were four times higher during the February study period (0.13 m/s) compared to the June study period (0.03m/s). This is consistent with the aqueous boundary theory, where field uptake rates have been shown to be higher with increased flow velocities due to a decreased aqueous boundary layer. The aqueous boundary layer thickness can vary from 1000 μm in calm waters such as those in deep seas, to 10 μm in very turbulent waters (Vrana and Schuurmann 2002). Under lower laminar flow conditions (0.003 to 0.01 m/s), Vrana and Schuurmann (2002) did not show any significant changes in mass transfer of penta- and hexachlorobenzenes, and suggested that under these conditions aqueous boundary control may switch back to membrane boundary control. However, Vrana and Schuurmann (2002) also predicted that the transition from laminar to turbulent flow would cause sampling rates to rise again at rates similar to those observed by Booij et al. (2003), where uptake rates increased by a factor of 14 with 80 times faster flow velocities.

Given these observations and interpretations, time-weighted average water concentrations can be estimated as an exercise. The laboratory SPMD sampling rate for chlorpyrifos at 26°C is 10.6 L/d (EST 2007), with a corresponding half-life to equilibrium ($t_{1/2}$) of approximately 12 d. As a guide, Petty et al. (2000) suggested that for mild biofouling a 10% reduction of the sampling rate can be assumed, for medium biofouling a 30% reduction, and for heavy biofouling a 50% reduction. Using the guide established by Petty et al. (2000) for heavy biofouling, the uptake rate becomes 5.3 L/day, with a corresponding half-life to equilibrium ($t_{1/2}$) of 26 d, which roughly correlates with the 28 d study periods in both the Cana and Sixaola sites. Figure 6 shows the time-weighted average water concentrations for chlorpyrifos estimated with available and adjusted SPMD uptake rates. In all cases, estimation of time-weighted water concentration using a linear uptake rate of 5.3 L/d throughout the study period obviously yields an approximately two times higher estimate of time-weighted water concentrations compared to the uptake rates of 10.6 L/d. However, final estimated water concentration values are dependent on the deployment time used. In a comparison of Cana Creek study periods, if 4 d deployment times are used, then average water concentrations are higher in June than in February. If 28 d deployments times are used, estimates of average water concentrations are higher in February than in June, while 15 d deployments yield roughly equivalent concentrations. This may be due to the fact that there were lower suspended solids and lower stream flow conditions during the first 4 d sampling period in June compared to February, which may have contributed to an increase in stream chlorpyrifos concentration and initial SPMD chlorpyrifos sequestration. Ultimately, however, one has to determine if the range of chlorpyrifos water concentration values in Cana Creek (from 0.86 to 7.31 pg/L) or in the Sixaola River (from 0.06 to 0.94 pg/L), all of which are well below current 1 L water grab sample detection limits, differ significantly such that distinct management options are necessary.

Difenoconazole was the only pesticide found in both water grab samples and SPMDs. However a direct comparison of grab sample and SPMD-derived stream concentration is problematic, as SPMD-difenoconazole can only provide a time-weighted average concentration, and it is unknown if water grab samples represent peak, low, or average difenoconazole concentrations. For example, 0.6 μg/L of difenoconazole was measured in water grab samples during the 4th week of the February Cana study period, with 0.4 ng/SPMD sequestered in the 28 d SPMD replicates. As no difenoconazole was sequestered in the previous 4 d or 15 d SPMD samples, sequestration of SPMD-difenoconazole occurred anytime over a period of 1 to 13 days. Given that the log Kow of difenoconazole is similar to that chlorpyrifos (log Kow 4.2 and 4.9, respectively), and both compounds were found in the same replicate SPMDs, the same field uptake rates can be used a surrogate to approximate time-weighted water concentration from SPMD-difenoconazole. Using an uptake rate of 5.3 L/d, time-weighted average difenoconazole concentrations will still only range between 75 pg/L for a 1 d average and 5 pg/L for a 13 d average, well below the 0.6 μg/L measured in replicate water grab samples.

For more accurate measures of field SPMD sampling rates, the use of performance reference compounds (PRCs) has recently been strongly recommended (Huckins et al. 2006, Booij et al. 2006a, Huckins et al. 2002). PRCs are compounds added to the SPMD triolein prior to exposure. PRCs must be compounds that do not occur in the environment, such as deuterated PCBs, but still have physiochemical properties representative of the target compounds (Huckins et al. 2006). It has been shown that the dissipation of PRCs from SPMDs with time can be used to calibrate SPMD sampling rates for the effects of biofouling, temperature, and flow-turbulence under controlled conditions (Huckins et al. 2002). However, these compounds are generally unavailable in many countries, and in the case of biofouling, very little experimental evidence is available (Huckins et al. 2006). Optionally, contaminants sequestered in SPMDs measured as membrane-lipid can be directly compared to lipid-normalized contaminants sequestered in organisms such as mussels (Booij et al. 2006b, Richardson et al. 2001) or worms (Leppanen and Kukkkonen 2000) to estimated bioavailable fractions and time-weighted water concentrations with partitioning models.

Interpretation of time-weighted average water concentrations and SPMD contaminant concentrations must be understood within the context of stream morphology and hydrologic regime. During periods of high flow, stream morphology and flow regime can change, as cut banks are scoured and eroded. Additionally, the deposition of debris and sedimentation during high flow events can actually block stream channels, resulting in a damming effect where stream velocities diminish, but actual standing water, measured as the width and depth of the stream, increases. This was seen during the June Cana Creek study period. In which case, not only would SPMD uptake rates decrease during this period of low flow velocity, but contaminants would be diluted due to the increased volume of standing water, complicating the interpretation of time-weighted average concentration data and the assumption of constant contaminant concentration. In addition to flow regime, both salinity and the amount of suspended solids or dissolved organic matter can affect contaminant solubility and subsequent contaminant water concentration and availability for SPMD uptake (Huckins et al. 1999, Rogers 1997). For example, Rogers (1997) found that recovery of ^{14}C methylnaphthalene in SPMDs decreased from 85% to 70% in stream water with 0.01 mg/L vs. 1 mg/L suspended solids. Similarly, pH can affect the proportion of charged vs. SPMD-available neutral form of the contaminant (Granmo et al. 2000).

These different sources of variation affecting contaminant concentration, such as stream discharge, flow velocity, standing water, and turbidity, are important factors in the assumption of constant contaminant concentrations. Plume effects can distort SPMD uptake rates and subsequent time-weighted average stream concentrations. In pulsed-flow tests, Rogers (1997) found that final SPMD concentrations of methylnaphthalene were higher when equivalent contaminant pulses were added late in the experiment compared to earlier. This might explain the higher SPMD-difenoconazole observed late in the February Cana study compared to the June Cana Creek study, where SPMD difenoconazole was present earlier but in lower concentrations. Other sources of variation of contaminant concentration during low flow events include increased volatilization of contaminants and the potential stratification of contaminants. In the case of Talamanca, fungicides are applied with an agricultural oil to prevent pesticides from washing off leaves during rain events. This oil can often be seen floating on the top of streams after an application event. Similarly, with its longer half life and higher log Kow, chlorpyrifos is generally associated with soil and sediments. Thus, during low flow events, the water column is likely to be less well-mixed, with difenoconazole floating at the top, chlorpyrifos associated more strongly with settled bottom sediments, and terbufos somewhere in between (Figure 7). This may explain why difenoconazole measured in surface water grab samples was much higher than the time-weighted average concentration calculated from difenoconazole sequestered in SPMDs, which were deployed lower in the water column. Similarly, a study of SPMDs deployed in a stream transect by Louch et al. (2003) also suggested heterogeneous concentrations in the water column due to different temperature, TSS, and flow variation in water column.

Conclusion

The use of SPMDs allowed for detection of compounds previously undetected in routine water samples, such as chlorpyrifos and terbufos. In order to estimate time-weighted average water concentrations of contaminants in tropical areas, available SPMD sampling rates must be adjusted for the effects of biofouling and flow. Due to the complexity of different types of biofilm, biofilm weight is not a good measure of SPMD biofouling. Similarly, as sequestration of SPMD-chlorpyrifos increased in replicate stream sites with higher flow velocities, even with heavy membrane biofouling and higher stream suspended solids, flow velocity is likely more important for estimating field SPMD uptake rates than biofouling. However, factors that influence spatial and temporal changes in contaminant concentration such as stream morphology and flow regime may be important in estimating final water concentrations due to complex relationships in stream discharge (standing water vs. flow velocity), turbidity, and stratification of compounds during extended periods of low flow velocity. Additional field experiments using appropriate performance reference compounds (PRCs) for tropical climates and target compounds, as well as more detailed measurements of flow velocity and hydrologic regime, are necessary to determine the effect of environmental variables on field SPMD uptake rates and for the interpretation of SPMD-derived time-weighted water concentrations.

References

APHA (American Public Health Association). 1995. Standard Methods for the Examination of Water and Wastewater. Eaton, A.D., Clesceri, L.S., Greenberg, A.E. (Eds), American Public Health Association, Washington D.C.

Booij, K., van Bommel, R., Mets, A., Dekker, R. 2006a. Little effect of excessive biofouling on the uptake of organic contaminants by semipermeable membrane devices. Chemosphere 65: 2485-2492.

Booij, K., Smedes, F., Van Weerlee, E.M., Honkoop, P.J.C. 2006b. Environmental monitoring of hydrophobic organic contaminants: the case of mussels vs. semipermeable membrane devices. Environmental Science and Technology 40: 3893-3900.

Booij, K., Hofmans, H.E., Fischer, C.V., Van Weerlee, E.M. 2003. Temperature-dependent uptake rates of nonpolar organic compounds by semipermeable membrane devices and low-density polyethylene membranes. Environmental Science and Technology 37: 361-366.

Borge, C., Castillo, R. 1997. Cultura y Conservación en la Talamanca Indígena. EUNED, San Jose, Costa Rica.

Brakenhielm, S., Qinghong, L. 1995. Comparison of field methods in vegetation monitoring. Water, Air and Soil Pollution 79: 75-87.

Castillo, L.E., Ruepert, C., Polidoro, B., de la Cruz, E. 2007. Mortality of aquatic organisms in agricultural areas of Costa Rica, risk factors and actions needed. Presentation at the Society for Toxicology and Environmental Chemistry European Annual Meeting, 20- 24 May 2007, Porto, Portugal.

Castillo, L.E., Ruepert, C., Solis, E. 2000. Pesticide residues in the aquatic environment of banana areas in the North Atlantic zone of Costa Rica. Environmental Chemistry and Toxicology 19: 1942-1950.

Castillo, L.E., de la Cruz, E., Ruepert, C. 1997. Ecotoxicology and pesticides in tropical aquatic ecosystems of Central America. Environmental Toxicology and Chemistry 16: 41-51.

CERC (Columbia Environmental Research Center). 2007. http://www.aux.cerc.cr.usgs.gov, accessed May 10 2007.

Corrales, L., Salas, A. 1997. Diagnostico ambiental de la actividad bananera en Sarapiqui, Tortuguero y Talamanca, Costa Rica, 1990-1992 (con actualizaciones parciales a 1996). Informe de UICN/ORMA and MINAE, San Jose, Costa Rica.

De la Cruz, E., Castillo, L.E., 2003. The use of pesticides in Costa Rica and their impact on coastal ecosystems. In: Taylor, M.D., Klaine, S.J., Carvalho, F.P., Barcelo, D., Everaats, J. (Eds.), Pesticide Residues in Coastal Tropical Ecosystems: Distribution, Fate and Effects. Taylor and Francis, London.

Dixon, J.B., Schulze, D.G. 2002. Soil Mineralogy with Environmental Applications. SSSA Book Series 7. Soil Science Society of America, Inc. Madison, Wisconsin.

EPA (United States Environmental Protection Agency). 2002. Test Methods for Evaluating Solid Waste, Physical and Chemical Methods (SW-846), 3rd Ed. USEPA, Washington D.C

EPA (United States Environmental Protection Agency). 1999. Methods and Guidance for the Analysis of Water (500 Series), USEPA. Washington, D.C.

EST (Environmental Sampling Technologies). 2007. http://www.est-lab.com, accessed July 7, 2007.

Episuite. 2007. United States Environmental Protection Agency Episuite Program Version 3.2. http://www.epa.gov/opptintr/exposure/pubs/episuite.htm, accessed May 2007.

Granmo, A, Ekelund, R., Berggren, M., Brorstrom-Lunden, E, Bergqvist, P.A. 2000. Temporal trend of organochlorine marine pollution indicated by concentrations in mussels, semipermeable membrane devices, and sediment. Environmental Science and Technology 34: 3323-3329.

Huckins, J.N., Petty, J.D., Booij, K. 2006. Monitors of Organic Chemicals in the Environment: Semipermeable Membrane Devices. Springer Science, New York.

Huckins, J.N., Prest, H.F., Petty, J.D., Lebo, J.A., Hodgins, M.M., Clark, R.C., Alvarez, D.A., Gala, W.R., Steen, A., Gale, G.W., Ingersoll, C.G. 2004. Overview and comparison of lipid-containing semipermeable membrane devices (SPMDs) and oysters (Crassostrea gigas) for assessing chemical exposure. Environmental Toxicology and Chemistry 23: 1617-1628.

Huckins, J.N., Petty, J.D., Lebo, J.A., Almeida, F.V., Booij, K., Alvarez, D.A., Cranor, W.L., Clark, R.C., Mogensen, B.B. 2002. Development of the permeability/ performance reference compound approach for in situ calibration of semipermeable membrane devices. Environmental Science and Technology 36: 85-91.

Huckins, J.N., Petty, J.D., Orazio, C.E., Lebo, J.A., Clark, R.C., Gibson, V.L., Gala, W.R., Echols, K.R. 1999. Determination of uptake kinetics (sampling rates) by lipid-containing semipermeable membrane devices (SPMDs) for polycyclic aromatic hydrocarbons (PAHs) in water. Environmental Science and Technology 33: 3918-3923.

Huckins, J.N., Manuweera, G.K., Petty, J.D., Mackay, D., Lebo, J.A. 1993. Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. Environmental Science and Technology 27: 2489-2496.

Huckins, J.N, Tubergen, M.W., Manuweera, G.K. 1990. Semipermeable membrane devices containing model lipid: A new approach to monitoring the availability of lipophilic contaminants and estimating their bioconcentration potential. Chemosphere 20: 533-552.

Juo, A.S.R, Franzluebbers, K. 2003. Tropical Soils: Properties and Management for Sustainable Agriculture. Oxford University Press, New York.

Kaiser, K., Guggenberger, G. 2003. Mineral surfaces and soil organic matter. European Journal of Soil Science 54: 219-236.

Kapp, GB. 1989. Perfil ambiental de la zona Baja de Talamanca, Costa Rica. Turrialba, Costa Rica. Informe Técnico No.155,CATIE, Turrialba, Costa Rica.

Kidwell, S.M., Holland, S.M. 1991. Field description of coarse bioclastic fabrics. Palaios 6: 426-434.

Latulippe, C., Lapointe, M.F., Talbot, T. 2001. Visual characterization technique for gravel-cobble river bed surface sediments; validation and environmental applications contribution to the programme of CIRSA (Centre Interuniversitaire de Recherche sur le Saumon Atlantique). Earth Surface Processes and Landforms 26: 301-318.

Leppanen, M.T., Kukkonen, J.V.K. 2000. Effect of sediment-contact time on availability of sediment associated pyrene and benzo[a]pyrene to oligochaete worms and semi-permeable membrane devices. Aquatic Toxicology 49: 227-241.

Li, H., Sheng, G., Teppen, B.J., Johnston, C.T., Boyd, S.A. 2003. Sorption and desorption of pesticides by clay minerals and humic acid-clay complexes. Soil Science Society of America Journal 67: 122-131.

Louch, J., Allen, G., Erickson, C, Wilson, G, Schmedding, D. 2003. Interpreting results from field deployments of semipermeable membrane devices. Environmental Science and Technology 37: 1202-1207.

Luellen, D.A., Shea, D. 2002. Calibration and field verification of semipermeable membrane devices for measuring polycyclic aromatic hydrocarbons in water. Environmental Science and Technology 36: 1791-1797.

Meadows, J.C., Ecols, K.R., Huckins, J.N., Borsuk, F.A., Carline, R.F, Tillitt, D.E. 1998. Estimation of uptake rate constants for PCB congeners accumulated by semipermeable membrane devices and brown trout (Salmo trutta). Environmental Science and Technology 32: 1847-1852.

Meese, R.J., Tomich, P.A. 1992. Dots on the rocks: a comparison of percent cover estimation methods. Journal of Experimental Marine Biology and Ecology 165: 59-73.

NRCS (Natural Resources Conservation Service). 2002. Field Book for Describing and Sampling Soils, Version 2.0. NRCS, USDA, Lincoln, Nebraska.

Petty, J.D., Orazio, C.E., Huckins, J.N., Gale, R.W., Lebo, J.A., Meadows, J.C., Echols, K.R, Cranor, W.L. 2000. Considerations involved with the use of semipermeable membrane devices for monitoring environmental contaminants. Journal of Chromatography A 879: 83-95.

Prest, H.F., Jacobson, L.A. 1997. Passive water sampling for polynuclear aromatic hydrocarbons using lipid-containing semipermeable membrane devices (SPMDs): application to contaminant residence times. Chemosphere 35: 3047-3063.

Racke, K.D. 1993. Environmental fate of chlorpyrifos. Reviews of Environmental Contamination and Toxicology 131: 1-154.

Rantalainen, A.-L., Cretney, W., Ikonomou, M.G., 2000. Uptake rates of semipermeable membrane devices (SPMDs) for PCDDs, PCDFs, and PCBs in water and sediment. Chemosphere 40: 147-158.

Richardson, B.J., Lam, P.K.S., Zheng, G.J., McClellan, K.E., de Luca-Abbott, S.B. 2002. Biofouling confounds the uptake of trace organic contaminants by semi-permeable membrane devices (SPMDs). Marine Pollution Bulletin 44: 1372-1379.

Richardson, B.J., Zheng, G.J., Tse, E.S.C., Lam, P.K.S. 2001. A comparison of mussels (Perna viridis) and semi-permeable membrane devices (SPMDs) for monitoring chlorinated trace organic contaminants in Hong Kong coastal waters. Chemosphere 45: 1201-1208.

Rogers, H.R. 1997. Influence of suspended solids and back diffusion on organic contaminant uptake by semi-permeable membranes (SPMDs). Chemosphere 35: 1651-1657.

Scott, G.I., Fulton, M.H., Wirth, E.F., Chandler, G.T., Key, P.B., Daugomah, J.W., Bearden, D., Chung, K.W., Strozier, E.D., DeLorenzo, M., Sivertsen, S., Dias, A., Sanders, M., Macauley, J.M., Goodman, L.R., LaCroix, M.W., Thayer, G.W., Kucklick, J. 2002. Toxicological studies in tropical ecosystems: an ecotoxicological risk assessment of pesticide runoff in South Florida estuarine ecosystems. Journal of Agricultural and Food Chemistry 50: 4400-4408.

Verweij, F., Booij, K., Satumalay, K., van der Molen, N., van der Oost, R. 2004. Assessment of bioavailable PAH, PCB and OCP concentrations in water using semipermeable membrane devices (SPMDs), sediments and caged carp. Chemosphere 54: 1675-1689.

Vrana, B., Mills, G.A., Allan, I.J., Dominiak, E., Svensson, K., Knutsson, J., Morrison, G., Greenwood, R. 2005. Passive sampling techniques for monitoring pollutants in water. Trends in Analytical Chemistry 24: 845-868.

Vrana, B., Schuurmann, G. 2002. Calibrating the uptake kinetics of semipermeable membrane devices in water: impact of hydrodynamics. Environmental Science and Technology 36: 290-295.

Warren, N., Allan, I.J., Carter, J.E., House, W.A., Parker, A. 2003. Pesticides and other micro-organic contaminants in freshwater sedimentary environments - a review. Applied Geochemistry 18: 159-194.

Zhou, Q. 1998. On the ground estimation of vegetation cover in Australian rangelands. International Journal of Remote Sensing 19: 1815-1820.

Table 1. A comparison of Sixaola River and Cana Creek water chemistry characteristics from a one-day "snapshot" sample of streams in June 2006

	Sixaola	**Cana**
Characteristic		
Field Temperature (°C)	28.1	28.8
Field Dissolved Oxygen (mg/L)	7.5	4.7
Field pH	7.8	7.7
Field Conductivity (μS/cm)	140	259
Alkalinity (mg$CaCO_3$/ L at pH 4.6)	60.0	98.2
Hardness (mg $CaCO_3$/ L)	53.6	97.2
Micronutrient Analyses (mg/L)		
Ca	16.4	26.8
Mg	3.1	7.3
K	1.0	2.7
Na	5.4	12.0
Cl^-	0.8	12.3
PO_4^{-3}	0.2	0.3
NH_4^+-N	0.1	0.2
NO_3^--N	0.0	2.1

Table 2. Comparison of suspended solids and bottom sediment characteristics in the Sixaola River and the Cana Creek study sites

Suspended Solids	**Sixaola**	**Cana**
Average Carbon (%)	3.5	3.6
Average Nitrogen (%)	0.20	0.34
Average C:N Ratio	17.5	11.5
Average Chlorophyll-a (μg/g)		
February	N/A	8.99
June	1.74	93.4
Bottom Sediments		
Clay minerals present	Smectite Vermiculite Mica Kaolin Quartz	Smectite Vermiculite Mica Kaolin Quartz
Average Carbon (%)	1.1	0.6
Average Nitrogen (%)	0.09	0.06
Average C:N Ratio	9.7	9.3

Table 3. Current pesticides used in Costa Rica and their respective analytical parameters

Pesticide	Log Kow	Method	Method Detection Limit µg/mL extract**
Ametryne	2.8	LC-PDA	<0.05
Atrazine	2.6[2]	LC-PDA	<0.05
Atrazine Deethyl	1.5[2]	LC-PDA	<0.05
Biphenthrin	8.1[2]	GC-ECD	<0.05
Bromacil	2.1[2]	LC-PDA	<0.02
Carbaryl	2.4[2]	LC-PDA	<0.1
Chlorothalonil	2.4 - 3.0	GC-ECD	<0.04
Chlorpyrifos	4.7 - 5.3[1]	GC-ECD/FPD	<0.02
Cis-permethrin	6.5[2]	GC-ECD	<0.1
Cyhalothrin	6.8-7.0[2]	GC-ECD	<0.05
Deltamethrin	6.2[2]	GC-ECD	<0.1
Diazinon	3.3	GC-FPD	<0.1
Difenoconazole	4.2	GC-ECD	<0.2
Dimethoate	0.7	GC-FPD	<0.1
Diuron	2.7[2]	LC-PDA	<0.1
Edifenphos	3.8	GC-FPD	<0.2
Endosulfan-a	3.8[2]	GC-ECD	<0.01
Endosulfan-b	3.8[2]	GC-ECD	<0.01
Ethoprofos	3.6	GC-FPD	<0.1
Fenamiphos	3.3	GC-FPD	<0.2
Hexazinone	1.85[2]	LC-PDA	<0.1
Lindane	3.7 - 4.1[2]	GC-ECD	<0.02
Malathion	2.8	GC-FPD	<0.2
Parathion-diethyl	3.8[2]	GC-FPD	<0.1
Parathion-methyl	3.0	GC-FPD	<0.1
Permethrin	6.5[2]	GC-ECD	<0.2
Propiconazole	2.8 - 3.7	GC-ECD	<0.05
Terbufos	3.7-4.5	GC-FPD	<0.1
Terbuthylazine	3.2[2]	LC-PDA	<0.05

** 1 mL extract represents 1 standard 91.4 cm SPMD membrane, 1 L of water, 4 or 8 g of suspended sediments, or 35 g wet weight stream bottom sediment sample.

Sources: IRET (Instituto Nacional de Estudios de Sustancias Toxicas, Universidad Nacional, Heredia, Costa Rica), except [1]Racke 1993, [2]EPA EpiSuite Database

Figure 1. Location of SPMD experimental sites in the Sixaola Watershed

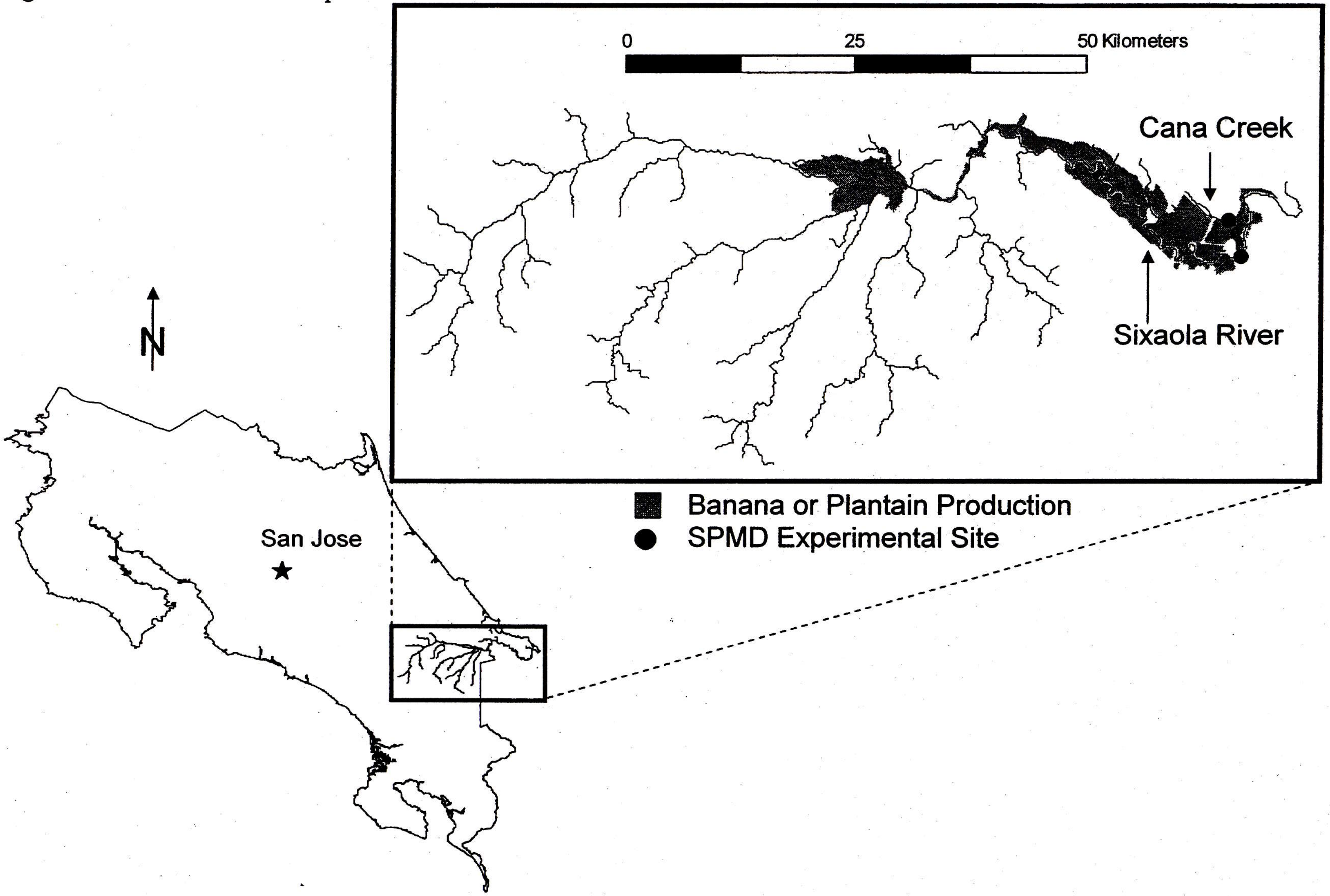
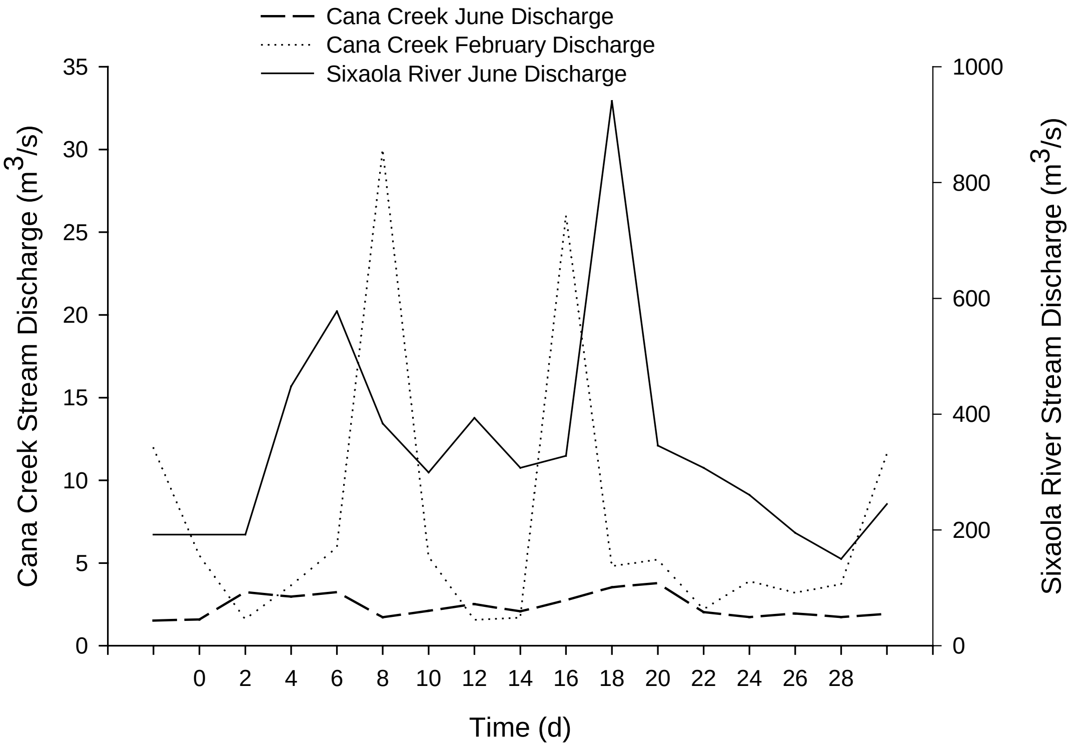
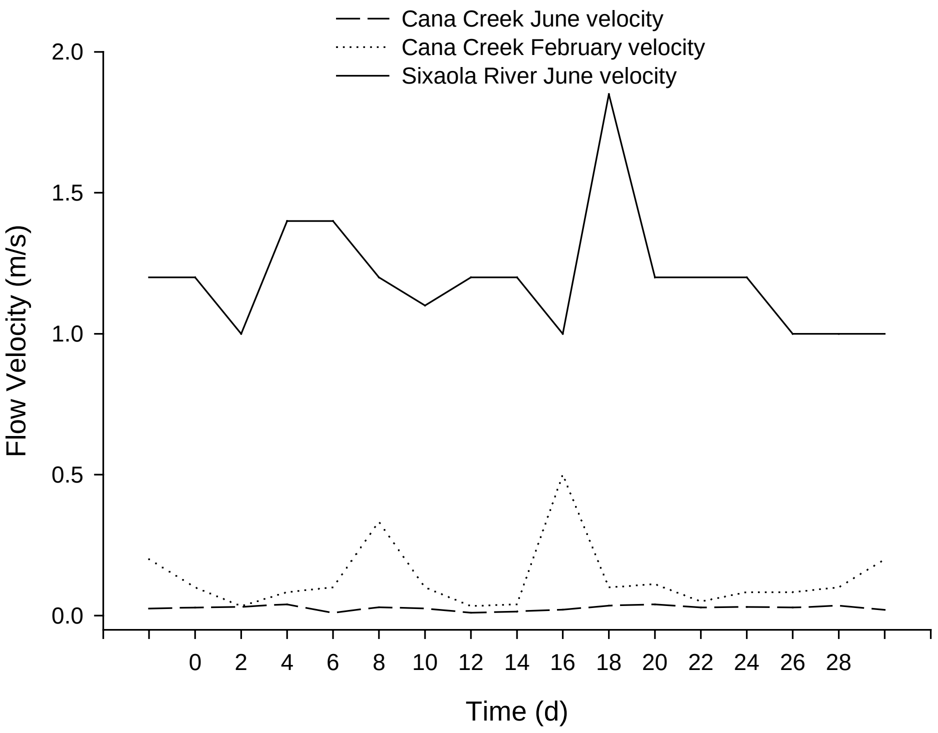


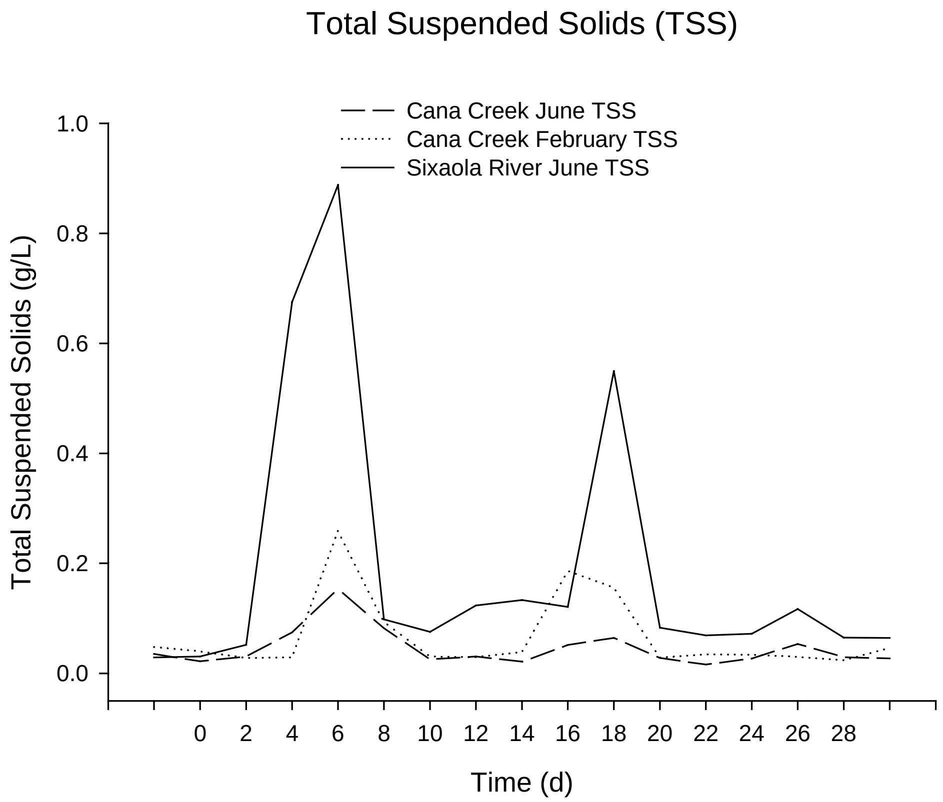
Figure 2. Comparison of stream characteristics (stream discharge, flow velocity, total suspended solids, and dissolved oxygen) among study sites and study periods

Stream Discharge



Flow Velocity




Total Suspended Solids (TSS)
Cana Creek June TSS
Cana Creek February TSS
Sixaola River June TSS
Total Suspended Solids (g/L)
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
Time (d)

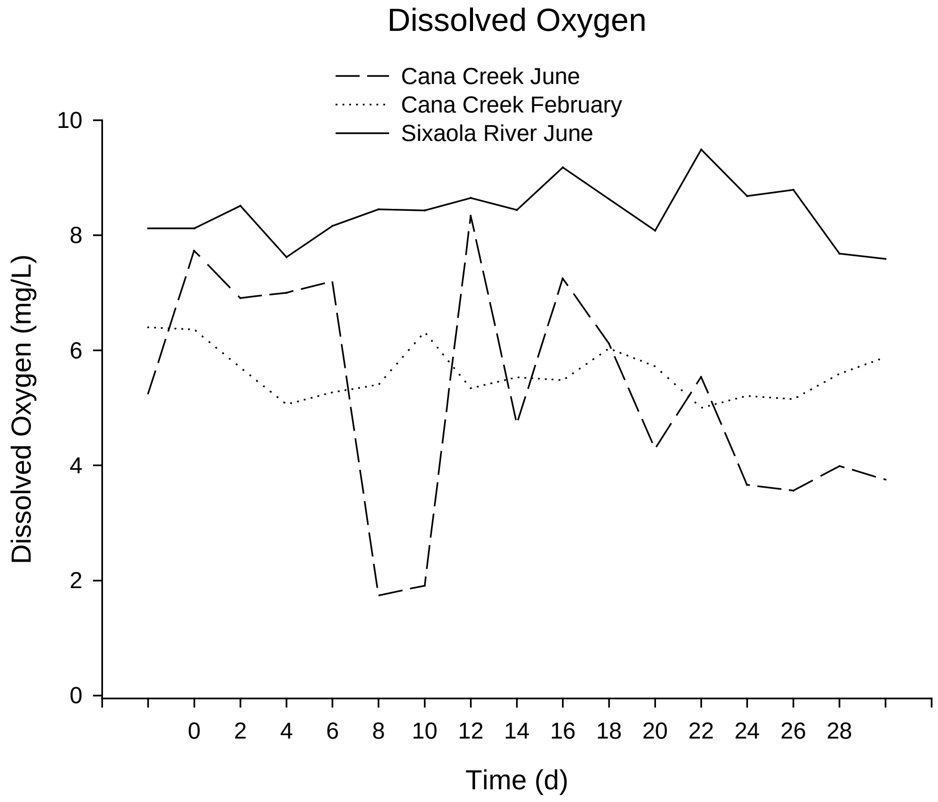

Dissolved Oxygen
Cana Creek June
Cana Creek February
Sixaola River June
Dissolved Oxygen (mg/L)
10
8
6
4
2
0
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
Time (d)

Figure 3. SPMD sequestration of current-use pesticides, chlorpyrifos, terbufos, and difenoconazole

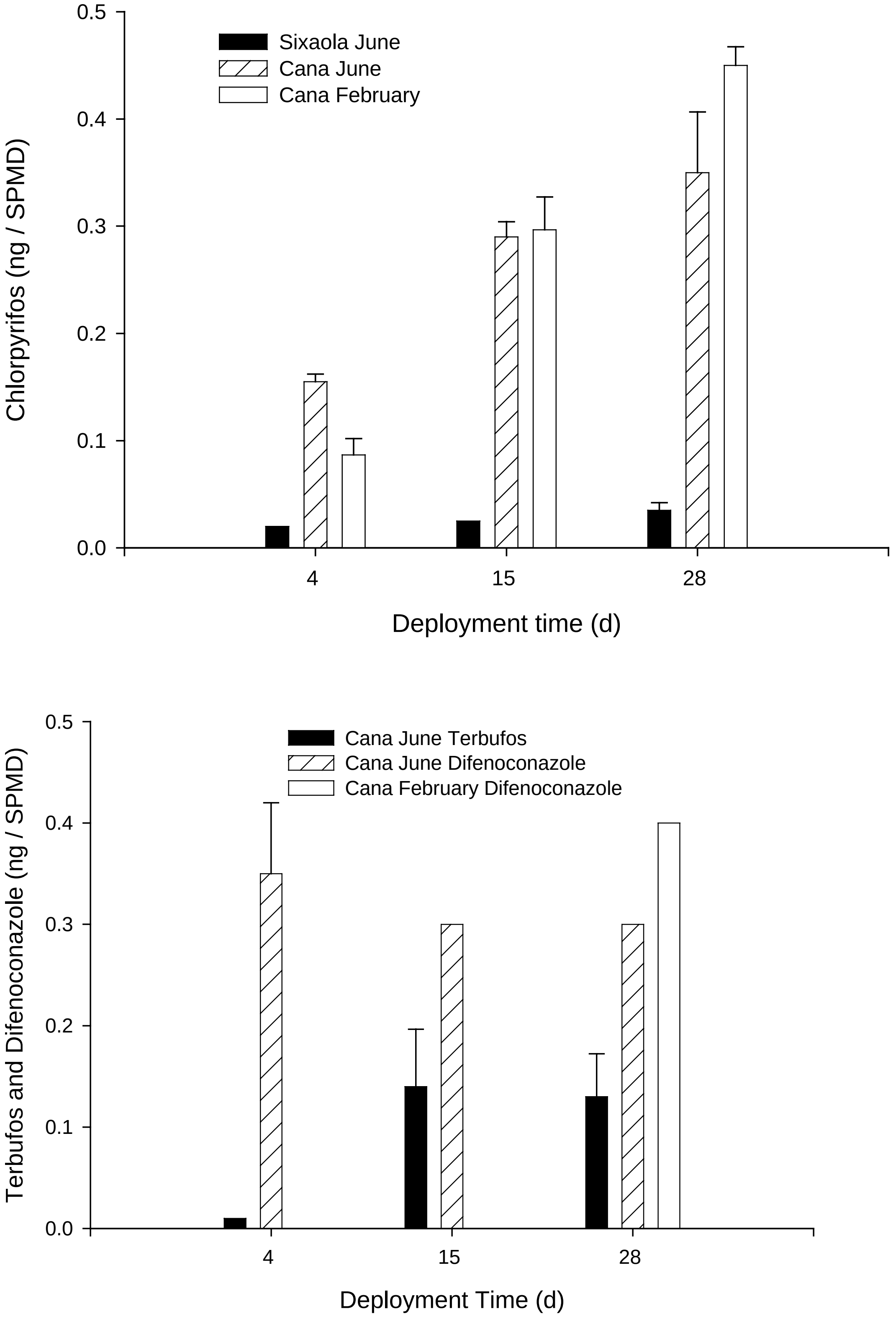


Figure 4. Biofilm weight vs. SPMD-chlorpyrifos in Cana Creek

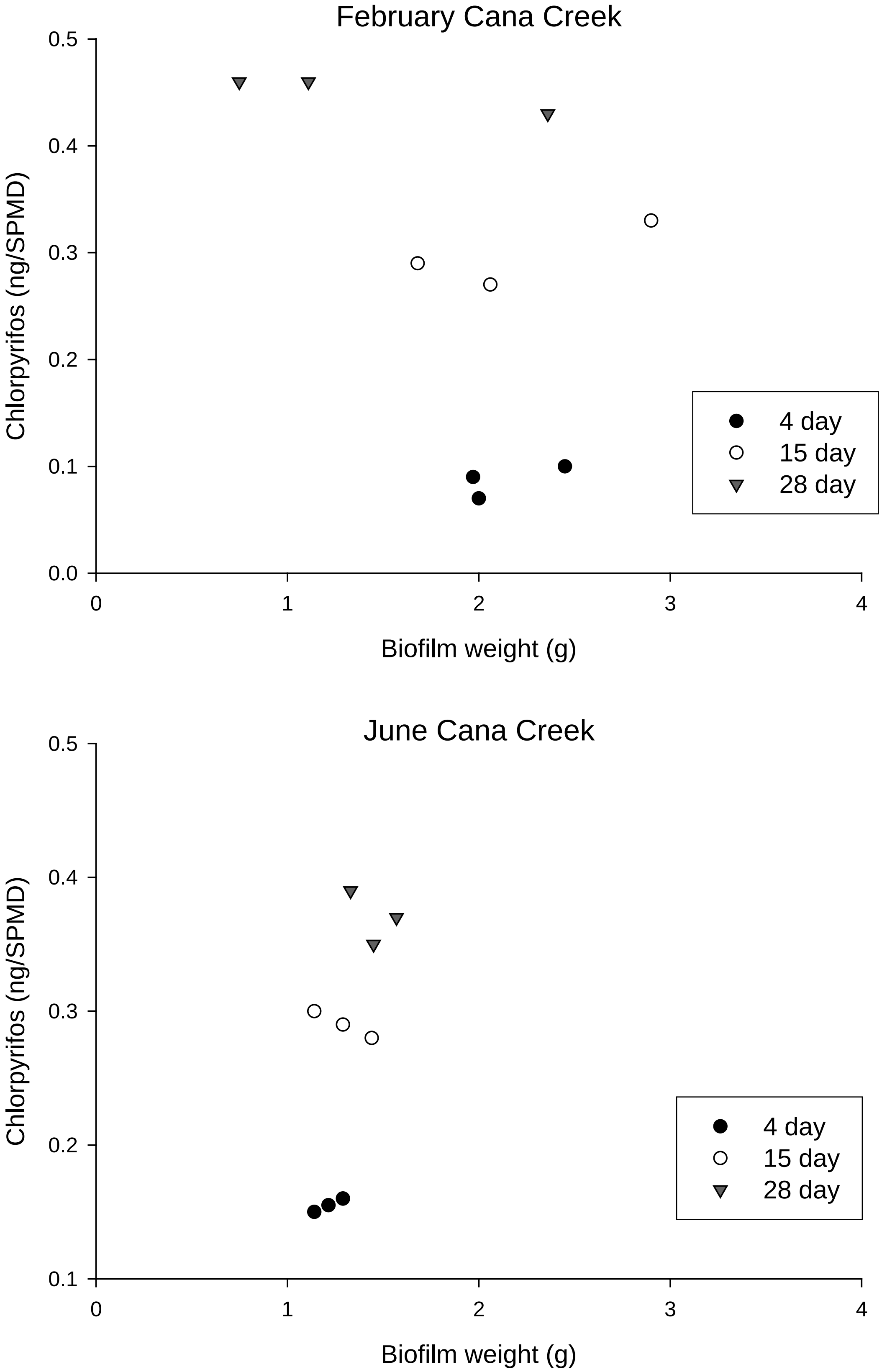
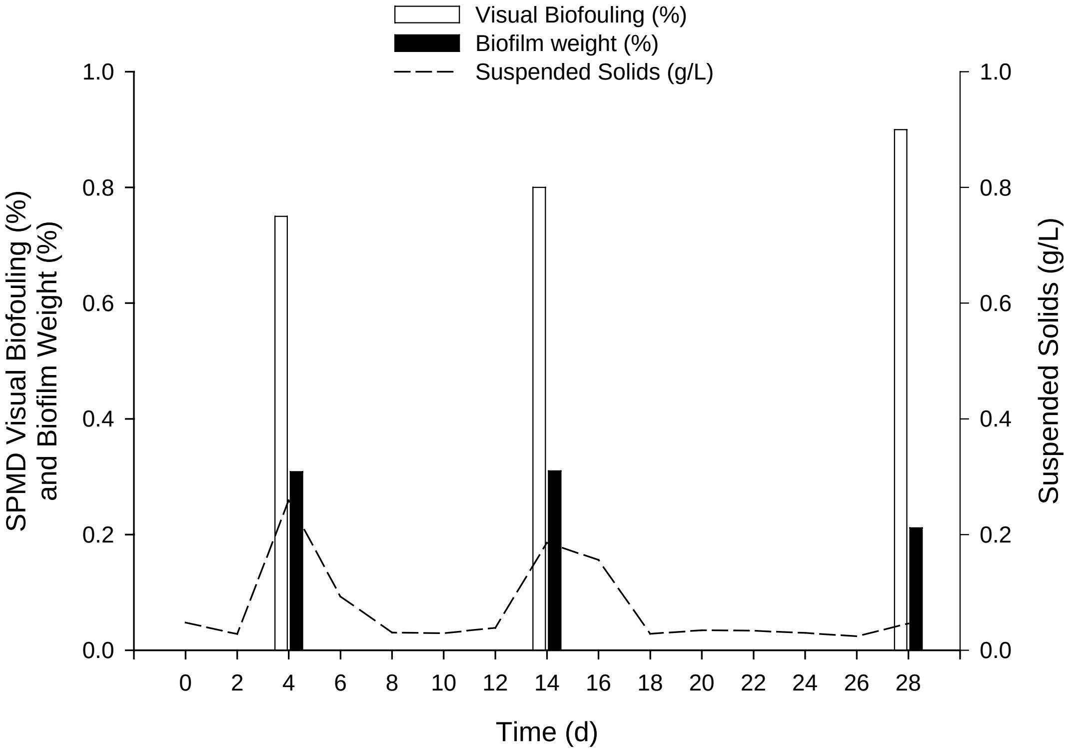
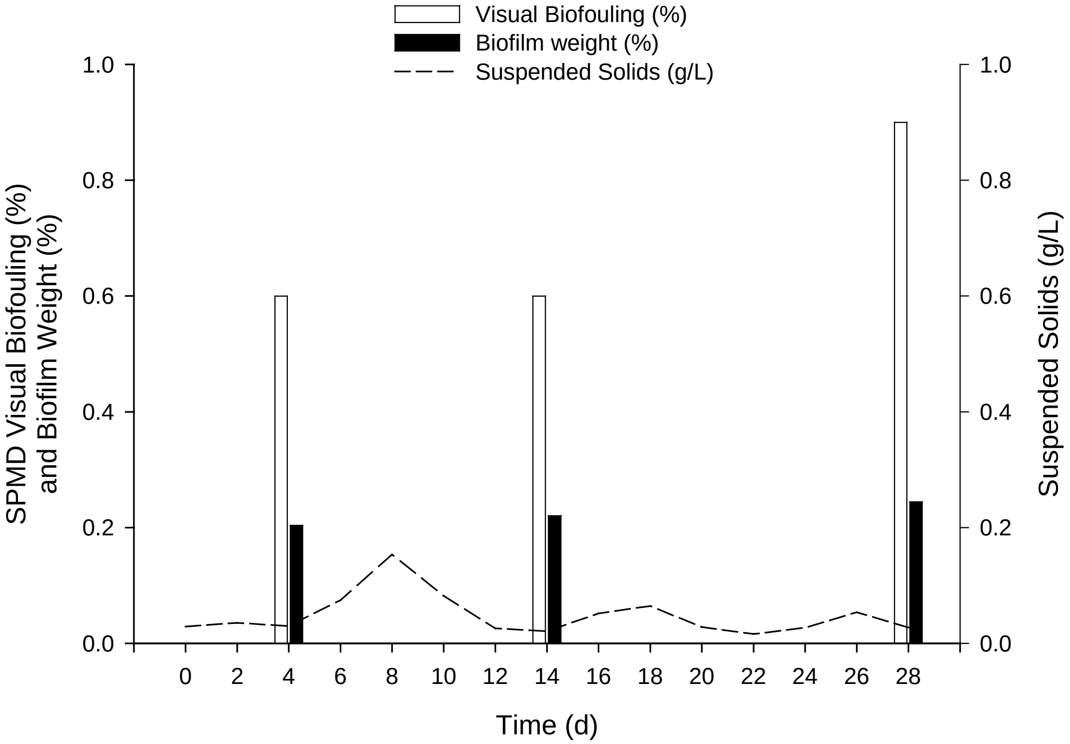


Figure 5. Comparison of visual biofouling, total suspended solids, average biofilm weight as percent of SPMD weight in Cana Creek and Sixaola River

February Cana Creek



June Cana Creek



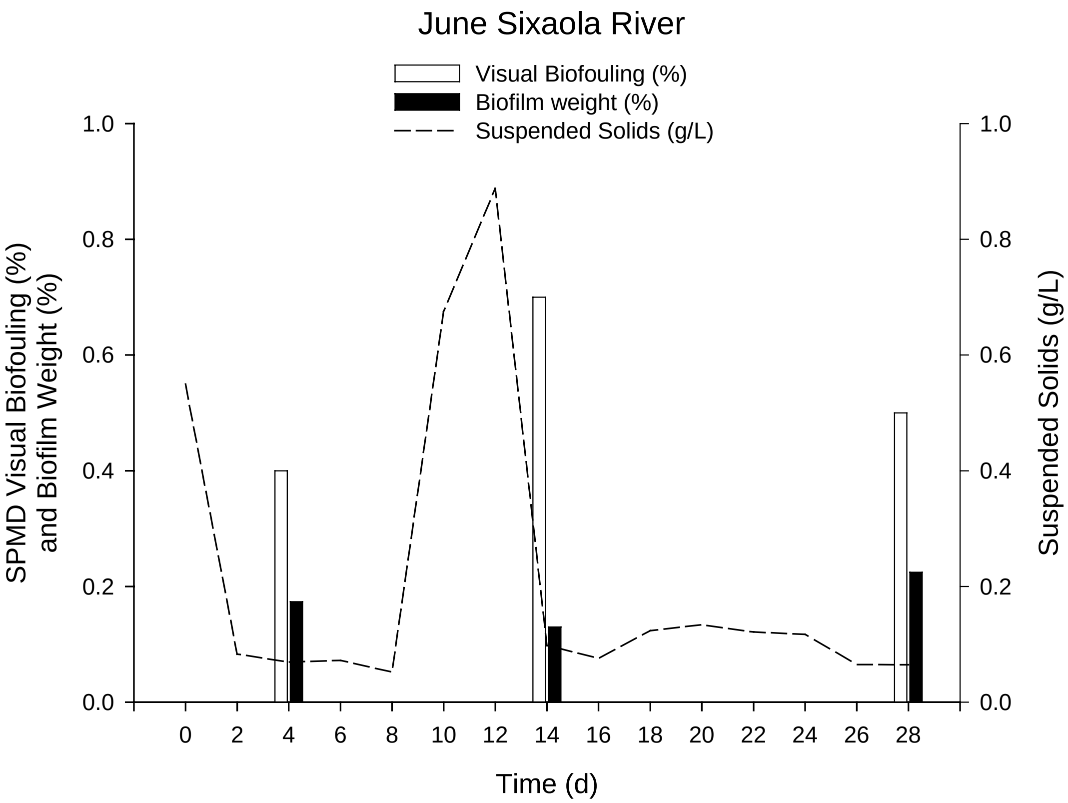
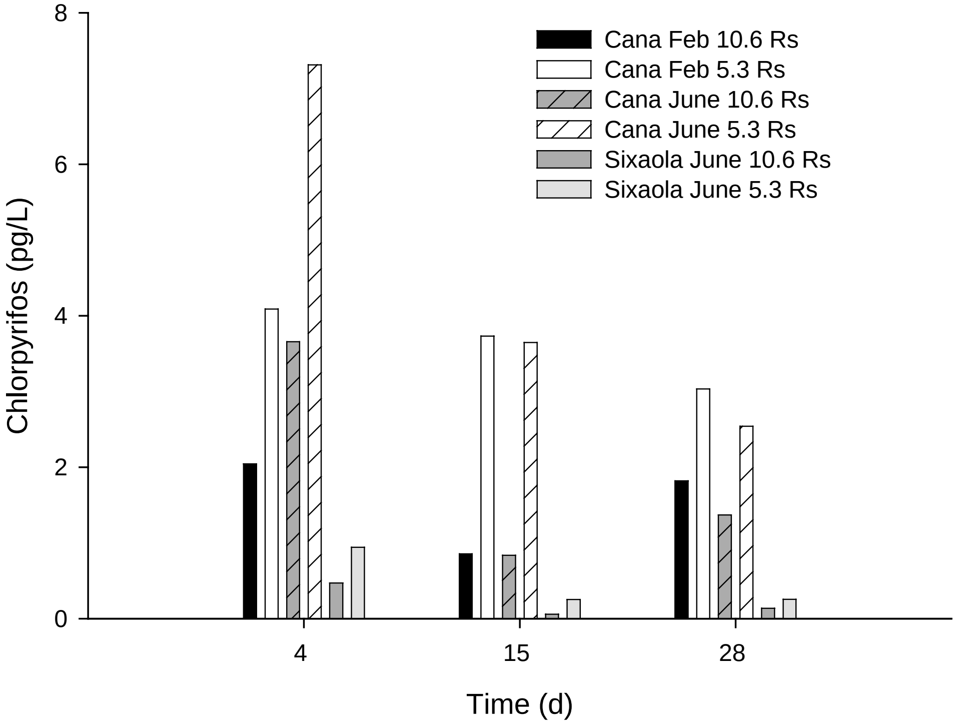

June Sixaola River
Visual Biofouling (%)
Biofilm weight (%)
Suspended Solids (g/L)
SPMD Visual Biofouling (%) and Biofilm Weight (%)
Suspended Solids (g/L)
0.0
0.2
0.4
0.6
0.8
1.0
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
Time (d)

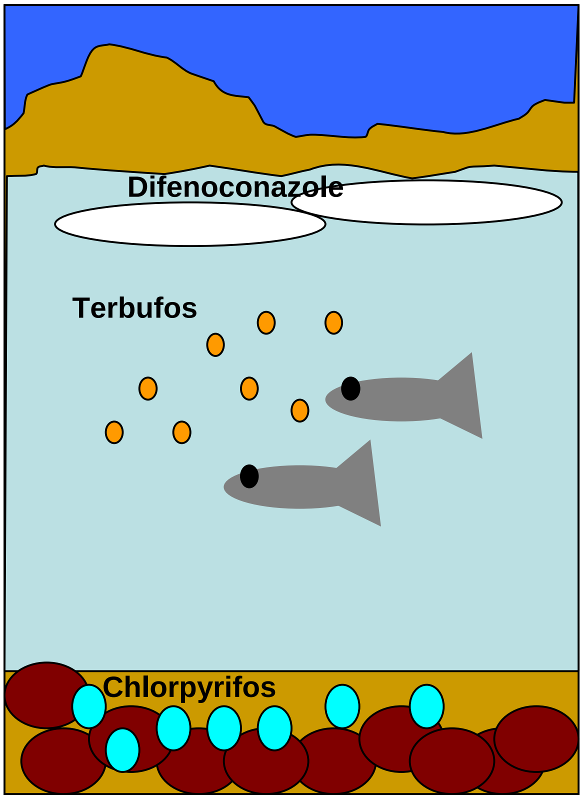
Figure 6. Prediction of time-weighted chlorpyrifos water concentrations using different Rs values for SPMD uptake rates (Rs = 10.6, with linear uptake* until $t_{1/2}$ = 12 d**, and Rs=5.3 with only linear uptake*)



*Linear Uptake: Cw = ((Cspmd/Mspmd)/(Rs/Mspmd))*1000/t

**At $t_{1/2}$: Cw = ((Cspmd/Mspmd)*0.96/Kspmd)*(1-EXP((Rs/Kspmd/Vs)*t))*1000000

Figure 7. Potential stratification of compounds during low flow conditions



Chapter Four

Aquatic Ecological Risk Assessment of Current-Use Pesticides: A Comparison of Field Measurements vs. Traditional Risk Assessment Models

Abstract

In the southeastern coast of Costa Rica, pesticides are intensively applied to produce export-quality plantains and bananas. Based on an ecological risk assessment framework, principal exposure pathways, environmental concentration, and toxicity of chlorpyrifos, terbufos, and difenoconazole are presented in a risk assessment using a hazard quotient. Comparison of modeled and observed pesticide concentration and biological effect highlight major discrepancies in estimating pesticide environmental concentration and toxicity in tropical environments from temperate-based fugacity models and toxicity data. Observations of fish kills and measured pesticide concentrations in the field indicate that current species toxicity datasets may not be applicable for estimating toxicological effects, especially in tropical areas with high biodiversity and complex species interactions. Similarly, environmental fate models developed for use in temperate zones must be modified to account for different application technologies as well as tropical climatic effects on pesticide dissipation and degradation. Alternatives to traditional hazard quotient methods and single-species toxicity datasets are discussed for their suitability and potential adaptability in tropical regions for site-specific or landscape-level risk assessment.

Introduction

One of the most important research priorities identified in tropical ecotoxicology is the need for risk assessment models specific to pesticide fate and toxicity in tropical watersheds (Lacher and Goldstein 1997, Elinder et al. 1998). The US Environmental Protection Agency's (1992) ecological risk assessment model has been recommended as an appropriate paradigm that could be adapted for use in tropical regions (Henriques et al. 1997, Lacher and Goldstein 1997, Peters et al. 1997). The US EPA's ecological risk assessment model is based on the integration of four components: 1) problem definition, 2) analysis of environmental exposure, 3) analysis of biological effect, and 4) risk characterization (USEPA 1998). In problem definition, the impetus for the assessment is defined based on the determination of the potential pathways and sources of potential exposure. Analysis and characterization of exposure is based on the measurement or modeling of contaminant concentration in selected environmental compartments, such as soil, water, or air. Analysis of effect is a measurement of the biologic response of different components of the ecosystem to the exposure such as contaminant bioavailability and bioaccumulation based on the use of biomarkers, indicator species, bioassays, and community and species level characterizations (Vermeire et al. 2003). In the final step, data from analysis of exposure and analysis of effect are combined to provide a risk characterization based on selected endpoints or pre-determined thresholds of contaminant effects.

Pesticide fate and transport in the Sixaola watershed of southeastern Costa Rica is a concern, as many area residents directly work with pesticides to maintain agricultural production on household or commercial banana and plantain farms, as well as rely on river and groundwater resources for consumption, fishing activities, and household use. Several environmental and human poisonings have been documented in banana plantations in Central America (Castillo et al. 1997, Castillo et al. 2000, Wesseling et al. 2001, Wesseling et al. 2005). However, few studies regarding environmental distribution, toxic effects on aquatic organisms, or general impact on ecosystems have been undertaken in tropical areas (Elinder et al. 1998, Castillo et al. 2000). For these reasons, evaluation of the presence and biological effect of current-use pesticides in water resources has been the focus of a three-year study of ecological risk from current pesticide application practices and for the development of better management practices and integration into regional conservation planning. Our objective was to compare field measurements and observations of pesticide concentration and biological effect in the Sixaola watershed, Costa Rica to modeled pesticide concentration and biological effect for the assessment of risk. In light of observed fish kills and measured pesticide concentrations, the benefits and limitations of the traditional risk assessment approach are discussed and alternative measures for assessing risk are proposed for similar tropical floodplain and coastal landscapes where few relevant ecological or biophysical data are available.

Study Site and Problem Definition

The 2700 km^2 Sixaola watershed is a tropical floodplain-coastal landscape characterized by a network of highland and floodplain rivers that flow from the 3800 m Talamanca mountains through a mosaic of forests, pasture, and agricultural lands to the sea, where the last living near and offshore reefs in Costa Rica are found. Due to rapid changes in elevation, the region is characterized by a wide diversity of ecological systems, including lowland tropical rainforest, premontane forest, oak-dominated montane forests, elfin woodlands, and the northernmost occurrence of páramo grasslands in Latin America at the highest elevations in the Talamanca Cordillera. The flora and fauna of this region are extremely diverse due to the correspondingly wide variety of life zones, and to the fact that is it a convergence zone for tropical and temperate genera from southern North America and northern South America (Graham 1995). However, relatively few biological, geophysical, social, or economic data exist to guide conservation planning decisions, sustainable agricultural activities, or to develop best management practices.

The floodplain soils of the Sixaola River and its tributaries are important areas for the production of export-quality plantain and banana (Chapter 2). Farms located on the Sixaola River floodplains produce 52% of the plantain, 90% of the organic banana, and 6% percent of the commercial banana in Costa Rica (Municipality of Talamanca 2003). It is estimated that 150 km^2 or approximately 30% of the entire Sixaola floodplain is cultivated with banana or plantain. Between 15 and 45 kg a.i./ha of pesticides (IRET 2000) and an average of 375 kg a.i./ha of fertilizers (Chapter 1) are estimated to be applied to non-organic plantain and commercial banana farms in the Sixaola River Valley. Average rainfall in the Sixaola watershed is approximately 3000 mm/yr (Grant et al. 2004). Annual temperatures average 25-27°C with evapotranspiration reported to be 1565-1710 mm/yr (Kapp 1989). In this region of Costa Rica, the toxicity and application methods of pesticides being applied combined with the clearing of riparian vegetation in a region characterized by high rainfall, runoff, and regular flooding events, create a high risk for pesticide contamination of aquatic resources.

Primary routes of exposure and pesticide application rates in the Sixaola watershed have been previously identified (Chapter 1). In summary, a variety of fungicides, nematicides, insecticides, and herbicides are applied year-round in plantain and banana production. Although pesticide products are primarily the same in plantain and banana production, the frequency and quantity of agrochemicals applied in the Sixaola watershed range from less than 2 kg a.i./ha/yr in low intensity plantain production, from 3 to 9 kg a.i./ha/yr in moderate plantain, from 10-15 kg a.i./ha yr in intensive plantain, and to up to 45 kg a.i./ha/yr in intensive banana production (Chapter 1). Primary routes of exposure that pose a threat to both human and ecological health stem from a lack of regulatory infrastructure as well as the absence of appropriate application knowledge and safe-handling practices. Principal human exposure routes include the lack of protective clothing during application, hazardous application and formulation techniques, and the use of poorly maintained equipment. Principal aquatic exposure routes include spray drift and direct spray from aerial application of fungicides, runoff from packing plants, runoff and leaching during storm events, and direct entry of pesticides or waste products due to accidents during transport or storage or the unavailability of waste disposal facilities (Chapter 1). Many of these routes of exposure are similar to those reported in other parts of the world where farmers in poor agricultural areas are applying pesticides without sufficient knowledge or infrastructure (Aragon et al. 2001, Mekonnen and Agonafir 2002, Dinham et al. 2003, Matthews et al. 2003).

Methods

Field and Laboratory Methods

Water Grab Samples

Seven sampling sites (Figure 1) were chosen in the Sixaola watershed, 6 surface water sites (Sixaola, Gandoca, Cana, Margarita, Shirolita, Sandbox), and another site representing drinking water sources in the town of Sixaola (consisting of 3 wells and 2 rainwater catchment systems). For comparison, data were also collected in an intensive banana production site in the adjacent Estrella watershed. The Estrella site is an oxbow lake (Aviarios Rescate) with little or no flow that is connected to the large Estrella River. The Sixaola and Margarita sites represent upstream and downstream sections of the large Sixaola River (average annual flow 232 m^3/s). The Cana site is in a medium-size river that drains into the Sixaola River and has been highly altered to serve as a principal drainage canal for a large banana plantation. The Shirolita and Sandbox sites are smaller streams located in upstream plantain growing areas. The Gandoca site is in the middle of the Gandoca estuary, a coastal lagoon in the Gandoca-Manzanillo National Wildlife Refuge.

Each site was sampled at least 5 times during an 18-month period (approximately every 3-4 months) from November 2004 through June 2006. Sampling consisted of collecting 2 L of surface water from a 10-30 cm depth, which were immediately put on ice and extracted within 24 h at the Institute for Studies of Toxic Substances (IRET) at the National University of Costa Rica in Heredia. At least one water grab sampling event occurred during an actual "fish kill" event, where several species of fish and invertebrates were already dead or in the process of dying during sampling. Measurements of stream discharge, temperature, pH, dissolved oxygen, conductivity, and salinity were made during every sampling event. Stream discharge was calculated by multiplying average stream velocity by stream width and average depth. Stream velocity was measured by averaging flow meter (Ben Meadows, Janesville, WI, USA) readings at equal depths at three different points in the stream, while stream width was measured with a measuring tape when possible in smaller rivers or with a laser view finder in the case of the Sixaola River. Average stream depth measurements were made by first creating an integrated depth profile of the stream bottom, then choosing a daily reference point to ascertain regular changes in average depth. For larger rivers, such as the Sixaola River, a pre-installed depth chart on the side of the Panama-Costa Rica Bridge was used for average depth. A laboratory calibrated multimeter (YSI 556 Multiprobe, Yellow Springs, OH, USA) was used to record dissolved oxygen, pH, conductivity, salinity, and temperature during sampling.

For each 2 L water sample, 1 L was extracted for HPLC analyses and the other liter for GC analyses. One liter water samples were extracted with SPE cartridges (Isolute ENV+ 200 mg - 6 mL) conditioned with ethyl acetate, water, and methanol. For HPLC-PDA analysis, cartridges were eluted with methanol and concentrated to a final volume of 1 mL. For GC-ECD, FPD, and GC-MS analysis, cartridges were eluted with methylene chloride and acetone, the extract dried with sodium sulfate, and concentrated to approximately 0.1 mL with nitrogen gas. Acetone: cyclohexane (1:9) was added to achieve a final extract volume of 1 ml. All samples were analyzed for 29 current-use pesticides (including 3 metabolites) in Costa Rica, with detection limits and log Kow values reported in Chapter 3.

Snapshot Water Sampling

A "snapshot" study of 14 rivers and streams in the Estrella and Sixaola watersheds, including the 6 primary surface water sampling sites (one of which was undergoing a second observed "fish kill" event) was conducted in a single day over a 10-h period in May 2006. During "snapshot" sampling, 2-L replicates were taken from each site and placed on ice for immediate laboratory analyses of pH, conductivity, alkalinity, hardness, dissolved calcium, magnesium, sodium, chlorine, ammonium, and nitrate. Field measurements of dissolved oxygen, pH, electrical conductivity, and temperature were made for comparison. Two-liter replicate water snapshot samples collected from 14 sites within the Estrella and Sixaola watersheds on the same day were analyzed for pH, conductivity, alkalinity, hardness, calcium, magnesium, potassium, sodium, free chloride, phosphorus, ammonium, and nitrate at the soil and water research lab at CATIE (Centro Agronómico de Investigación y Enseñanza) in Turrialba, Costa Rica. Methods of analysis were based on standard methods for the examination of water and wastewater (APHA 1995). At the one site undergoing an observed fish kill, the maximum body length of all species observed to be dead or dying was also recorded.

Deployment of Passive Samplers (SPMDs)

Passive samplers or semi-permeable membrane devices (SPMDs) have been used effectively to screen for the presence or absence of environmental contaminants, to monitor the spatial distribution and source of pollutants, as well as to provide a time-weighted average of aqueous concentrations and estimation of organism exposure (Vrana et al. 2005). Based on their construction, SPMDs effectively sequester compounds with octanol/water partition coefficients (Kow) > 3 (Huckins et al. 1993) and with molecular masses less than 600 (Petty et al. 2000). This solute size limitation samples only the dissolved and vapor phase of hydrophobic contaminants, and excludes large molecules as well as those that are adsorbed on colloids or humic acids (Petty et al. 2000, Vrana and Schuurmann 2002, Vrana et al.

2005) while mimicking the transfer of biomolecules through biomembranes (Vrana and Schuurmann 2002). In addition to providing an estimate of the potentially bioavailable contaminants in the region, the longer exposure time in SPMD field deployments allowed for the detection of lower concentrations of contaminants compared to routine grab samples the Sixaola watershed (Chapter 3).

Replicate SPMDs (two or three standard 91.4-cm SPMD membranes from Environmental Sampling Technologies) were placed in all six of the surface water sites in the Sixaola watershed for a period of 28 d. Two of the six sites, the Sixaola site and the Quebrada Cana site were sampled more intensively (11 additional water samples and 3 additional months of SPMD deployments), as they became sites for SPMD experiments to estimate the effect of biofouling and time on SPMD uptake of pesticides (Chapter 3). Upon removal from the water, SPMDs were kept frozen until analysis at the Institute for Studies of Toxic Substances (IRET) at the National University of Costa Rica in Heredia. For analysis, each SPMD was weighed before and after surface cleaning to calculate the weight of the biofilm for the estimation of biofouling and the calibration of uptake rates (Chapter 3). SPMDs were dialyzed and extracted based on methods developed by Environmental Sampling Technologies (EST 2007), where the membranes are dialyzed in hexane for 24 h, then again for 8 h. Dialyzed extracts were cleaned up with gel permeation chromatography (GPC). SPMD extracts and blanks were analyzed with GC-ECD and FPD, with compound confirmation by GC-MS. All samples were analyzed for 29 current-use pesticides (including 3 metabolites) in Costa Rica, with detection limits and log Kow values reported in Chapter 3. Pesticide concentrations sequestered in SPMD membranes were used to calculate time-weighted average concentrations in streams where they were deployed based on the methods described in Chapter 3. Due to excellent precision among replicate membranes (+/- 0.02 μg/ml extract), similar biofouling rates on membranes throughout the study period, and similar Kow values among the three pesticides (chlorpyrifos, difenoconazole and terbufos) primarily sequestered in the SPMDs (Kow of 4.9, 4.3 and 4.4), a generic uptake value of 5.0 L/day was chosen to estimate time-weighted average pesticide concentrations during the 28-d deployments (Chapter 3).

Modeling of Environmental Concentration

Three pesticides applied under four different banana and plantain production regimes were chosen to model environmental concentration, biological effect, and risk assessment in the Sixaola watershed based on annual application rates (kg a.i./ha) shown in Table 1. The four production regimes: intensive banana, intensive plantain, moderate plantain, and low-intensity plantain (Figure 1), have been previously described (Chapter 1) based on differences in pesticide application rate (i.e., frequency and amount applied during application) with a combined total pesticide loading in the Sixaola watershed of approximately 280 metric tons a.i. per year (Figure 2). The three pesticides chosen - the fungicide difenoconazole, the nematicide terbufos, and the insecticide chlorpyrifos - represent the most widely used products in their pesticide class and combined represent approximately 75% of pesticide loading in the Sixaola watershed (Figure 3), each with a different application rate and application method.

Chlorpyrifos is the most widely used agrochemical in banana and plantain cultivation as it is impregnated into plastic bags that cover all maturing fruit to prevent cosmetic damage caused by the thrips insect *Chaetanaphothrips signipennis*. Every banana or plantain plant is covered by the 40-g plastic bag impregnated with approximately 0.4 g a.i. chlorpyrifos once during the crop cycle (approximately 11- to 12-month crop cycle in moderate to low-intensity plantain and 9-month crop cycle in intensive banana and plantain) (IRET 2000, Hernandez et al. 2000). Thus, yearly application rates are based on the approximate number of plants per hectare in each production regime. Difenoconazole is a systemic fungicide that is applied aerially by airplane in intensive banana or motorized hand sprayer in plantain. In intensive banana and intensive plantain, it is often applied in combination with other fungicides, such as mancozeb, chlorothalonil, bitertanol, or tridemorph, to combat against black sigatoka disease (*Mycosphaerella fijiensis*) (Marin et al. 2003). Difenoconazole application rates are based on the listed active ingredients in available formulated products in the study region (0.25 kg a.i./L) and the average amount of formulated product applied annually in each application regime (Chapter 1). It is important to note that plantain farmers were found to apply 1.5 L/ha of difenoconazole (Chapter 1), which is slightly more than the 1 L/ha reported to be applied in commercial banana farms (Matlock and de la Cruz 2003). This is likely due to the fact that difenoconazole is often mixed with other fungicides in commercial banana farms, while in contrast it is often the only fungicide available to household plantain farmers (Chapter 1). Terbufos is a granular nematicide with insecticidal activity that is applied to the soil around each banana or plantain plant both during and after seeding to protect against nematodes and the banana weevil (*Cosmopolites sordidus* Germar). Application rates are based on the average amount or "galons" of formulated product (2.5 kg a.i.) applied per hectare both during and after seeding as reported by plantain farmers (Chapter 1), and average terbufos application rates reported in intensive banana production (Matlock and de la Cruz 2002).

As little biophysical data are available for the Sixaola watershed, concentration of chlorpyrifos, difenoconazole, and terbufos in aquatic resources in the Sixaola watershed was modeled based on the principle that environmental persistence is a function of the mode of entry and partitioning properties (Webster et al. 1998). A simple tier-one prediction of environmental concentration (PEC) (Van den Brink et al. 2003) was conducted using a fugacity approach modified for three different levels of possible pesticide entry scenarios in the Sixaola watershed:

$$\text{PEC} = (\text{Dose} * \text{Entry Fraction}) / 10 * 1\ \text{m}^3\ \text{water}$$

where PEC (mg/m3 or µg/L) is the predicted concentration of chlorpyrifos, difenoconazole, or terbufos in a generic volume of 1 m^3 of water adjacent to each of the four production regimes. The PEC concentration is then diluted by the known volume of water along a given stream reach in the Sixaola watershed to predict the concentration for the study site of interest.

The dose (g a.i./ha) is the maximum application rate of chlorpyrifos, difenoconazole, or terbufos in each of the four production regimes in a 1-month period. Maximum application rate was chosen as it represents the most conservative or protective approach generally associated with tier-one assessments as well as presents a worst case scenario. A time frame of 1 month was used in order to minimize the effects of pesticide degradation and multiple applications during the approximately 1-yr crop cycle.

The entry fraction (0 to 1) is the percent of pesticide that is estimated to enter water resources. To estimate entry fraction, three different pesticide scenarios were developed based on pesticide application methods and a fugacity approach. The first entry method (EF1) provides the worst case scenario where 100% of the applied pesticide enters the aquatic resource. Relevant examples in the Sixaola watershed include direct spray of difenoconazole into streams during aerial application, direct disposal or movement of chlorpyrifos-impregnated bags into streams during transportation accidents or flooding events, and direct spillage of terbufos into streams during transportation accidents or inappropriate fishing activities. The second and third entry methods (EF2 and EF3) are based on the output from an equilibrium criterion or EQC fugacity model developed by MacKay et al. (1996a). Using fixed environmental parameters (Mackay et al. 1996a, Mackay et al. 1996b), the model partitions a given pesticide into different environmental compartments (atmosphere, soil, water, and sediment) based on its physiochemical properties. The second entry fraction (EF2) is based on the percent of applied pesticide modeled to be in the water compartment based on level 2 fugacity calculations, which assume steady state equilibrium among environmental compartments and a fixed emissions rate of 1000 kg/h balanced by reaction and advection losses. The third entry fraction (EF3) is based on the percent of applied pesticide modeled to be in the water compartment based on level 3 fugacity calculations. Level 3 fugacity calculations allow the user to set the environmental compartments to which the pesticide is first being applied and assume steady state non-equilibrium to account for transport among environmental compartments.

Physiochemical properties for chlorpyrifos, difenoconazole, and terbufos used for fugacity models as well as all model inputs, outputs, and calculated generic PECs for 1 m^3 of water are listed in Appendix A. For level 3 fugacity calculations, chlorpyrifos emission was initiated in air to represent application in plastic bags, terbufos in soil as it is applied directly to the soil, and difenoconazole equally to air, water, and soil to account for the effects of direct aerial spraying on all three environmental compartments. To estimate the pesticide concentration for a study stream site based on each of the three pesticide entry scenarios, the generic PEC for a scenario under the dominant production regime adjacent to the selected stream site was diluted by the average volume of water (depth x width) observed in the study stream. This method therefore cannot account for any differences in application rates or water pesticide concentrations along the stream reach (length).

Estimation of Biological Effect and Risk Assessment

The majority of ecological risk assessments estimate biological effect of selected pesticides using single species acute or chronic toxicity tests as toxicity endpoints to estimate the lowest no effect concentrations (Versteeg et al. 1999, Burns 2001, van den Brink 2003). To estimate the biological effect based on no effect concentrations (NECs) of chlorpyrifos, difenoconazole, and terbufos, all available databases and literature were searched for the lowest acute and chronic toxicity values for daphnia, crustaceans, and fish. For acute toxicity, only 96-hr LC50 values were considered. For chronic toxicity, only maximum allowable toxic concentration (MATC) values were selected in order to standardize the various measures of chronic toxicity (i.e. growth, reproduction, enzyme activity, etc.), test length, and organism life-stage. As no toxicity data were found for relevant tropical species, toxicity values were multiplied by an assessment factor of 0.01 for acute toxicity and of 0.1 for chronic toxicity to account for uncertainties in extrapolation of data from one species to another and as a safety factor protective of potentially more sensitive tropical species (Van den Brink et al. 2003, Kwok et al. 2007). After application of the assessment factors, the lowest acute and chronic values for each pesticide were used as the toxicity endpoint for biological effect and the acute and chronic no effect concentration (NEC). To assess risk, a simple tier I hazard quotient (EPA 1998) was calculated by dividing the observed or predicted environmental concentration (PEC) by the NEC. Risk quotients greater than 100 were then classified as very high risk, between 1-100 as high risk, between 0.1-1.0 as moderate risk, and less than 0.1 as low risk.

Results and Discussion

Environmental Exposure: Measured Aquatic Concentrations vs. Modeled Concentrations

Measured pesticides in stream study sites are shown in Figures 4 and 5, and study stream measured physiochemical characteristics during the study period are listed in Appendix B.

As replicate water samples and SPMD membranes gave excellent precision, pesticides that were observed just above detection limits in replicate samples, but were unable to be quantified, are reported with a "T" for trace concentration. Most commonly found pesticides across all samples were difenoconazole and diuron in water grab samples, and chlorpyrifos, difenoconazole, and terbufos in SPMD samples. In general, water grab samples are unable to capture the low concentrations of chlorpyrifos and terbufos sequestered by SPMDs, but SPMDs are unable to capture "peak" concentrations as they can only provide an average concentration over time. All sites where SPMDs were deployed showed at least a trace of chlorpyrifos, which was calculated to represent less than 0.2 pg/L. The majority of pesticide detections were at the Cana study site, a stream that primarily drains a large banana plantation. At this site, the highest concentration pesticide observed was difenoconazole at 6 μg/L. The highest chlorpyrifos and terbufos concentrations calculated from SPMDs were 3.3 pg/L and 1.3 pg/L, respectively. Based on the study stream characteristics reported in Appendix B, study sites that had the most frequent detections and highest pesticide concentrations were smaller streams or canals adjacent to intensive banana plantations with little or no discharge or flow velocity (i.e., Cana site in Sixaola watershed and Aviarios Rescate in Estrella watershed).

Although chlorpyrifos and terbufos were not found above detection limits in water grab samples, they have been detected in streams, lagoons, and packing plant effluents adjacent to banana plantations in other areas of Central America in maximum concentrations of approximately 0.1 μg/L (Castillo et al. 2000, Carvalho et al. 2002). In other studies of current use pesticides in Central America, chlorpyrifos and terbufos have primarily been quantified in stream or marine sediments at concentrations as high as 320 μg/kg and 154 μg/kg, respectively (Albarca and Ruepert 1993, Readman et al. 1992, Castillo et al. 2000). As difenoconazole is a relatively new fungicide that has primarily replaced propiconazole in banana production, no studies to date have reported detection of difenoconazole in surface waters or sediments.

Modeled pesticide concentrations for five of the stream study sites in the Sixaola watershed are shown in Table 2. The Gandoca study site was not included as it is located outside of any significant production regime and the volume of water has not been accurately measured. Only difenoconazole measured in water grab samples can be directly compared to the different predicted environmental concentrations (PECs) in study stream sites. Terbufos and chlorpyrifos were not detected above method quantification limits in water grab samples and over one-third of the model PECs were below water grab sample method detection limits, most of which are represented by the Sixaola and Margarita sites due to the large volume of the Sixaola River. The first predicted environmental concentration (PEC1) calculated for each site is based on 100% entry fraction (EF1) and thus represents the worst case scenario or highest possible concentration based on known application rates. With approximately 9 μg/L of difenoconazole predicted under this scenario, the Cana site is the only study stream where maximum difenoconazole concentrations measured in water grab samples were within range of PEC1 values. This indicates that direct spraying of the stream is likely occurring during aerial fungicide applications.

Difenoconazole was detected in 75% of water samples from the Cana site with an average concentration of 0.5 μg/L and 20 percent of water samples in the Shirolita site with an average concentration of 0.3 μg/L. Both of these concentrations fit well into the second and third predicted environmental concentrations (PEC2 or PEC3) derived from second and third level fugacity models and are best representative of other modes of entry. Both the level two and level three fugacity models show that large-scale atmospheric transport is unlikely as 92% of difenoconazole partitions to soil, even when emissions or application is assumed to be equal among soil, water, and air compartments. Thus, if difenoconazole is not directly sprayed into streams, spray drift is likely to be localized and spray falling onto soil may be an important route of difenoconazole entry to aquatic resources during flooding or high runoff events. In Costa Rican banana production regions, it has been estimated that in addition to direct spray, 15% of aerially applied fungicides are lost to wind drift, 40% to falling on soil, and 35% washed off by rain, resulting in a 90% loss of formulated fungicides annually (Hernandez and Witter 1996). With its relatively high solubility and very low vapor pressure, difenoconazole is not persistent in air, and is expected to be very stable in both the soil and water compartments (IRET 1999).

Pesticide concentrations derived from field deployed SPMDs are at least 300 times lower than those predicted by the fugacity or mass balance models. There are several reasons why fugacity models do not come within the range of field measurements. Pesticide concentrations calculated from field-deployed SPMDs represent 28 d averages and therefore, cannot capture peak concentration events or short-lived contaminant "pulses" in streams. Unlike difenoconazole where 100% entry based on direct spray is feasible due to frequent aerial spraying in the Sixaola watershed, it is less likely that all chlorpyrifos-impregnated bags or a "galon" of terbufos will accidentally fall into a stream. However, fugacity-model assumptions may not be representative of the environmental conditions and pesticide application methods in tropical areas. Both level 2 and 3 fugacity models for chlorpyrifos indicate that the majority of chlorpyrifos will partition into soil and sediment compartments. This has been well documented in many studies of chlorpyrifos (Racke 1993), as partitioning is strongly correlated with organic carbon content (Baskaran et al. 2003). However in the vast majority of these studies, chlorpyrifos is applied directly to the soil. Although a small portion of chlorpyrifos is likely reaching the soil during high rain events or when bags are left or buried underground, no studies are known to have examined the environmental behavior of chlorpyrifos when applied in a plastic bag hanging 5 m above the ground.

In banana and plantain production, volatilization is likely a primary pathway of chlorpyrifos dissipation and degradation due to its unique application method and exposure to high temperatures in tropical regions. Volatility of chlorpyrifos from surfaces other than soil such as plant foliage and other surfaces such as paper, enamel, and latex has been shown to be an important process and a significant route of exposure for select target pests (Racke 1993). Similarly, when chlorpyrifos emissions are set to originate in air in the level 3 fugacity model, 6% of chlorpyrifos remains in the air compartment, indicating a weak propensity for atmospheric transport and potential for redistribution during rain events, which may explain the trace amounts of chlorpyrifos found in one Sixaola rainwater sample and in all sites where SPMDs were deployed. Chlorpyrifos has been found in snow and rain samples at both high and low elevations in California (McConnell et al. 1998). Under tropical conditions however, volatile chlorpyrifos is likely to undergo rapid photolysis. A half-life of 2.6 d was reported in laboratory studies of chlorpyrifos photodegredation in moist air with 60% relative humidity and a temperature of 25°C (Fontaine and Teeter 1987 in Racke 1993). Although volatilization is likely the most important pathway of chlorpyrifos dissipation and degradation in the Sixaola watershed, primary pathways to aquatic resources may include the redistribution of chlorpyrifos from the air during rain events, or from the soil as chlorpyrifos sorbed to soils and sediments is mobilized during erosional events. Although the dissipation or degradation of chlorpyrifos under tropical field conditions is not well known, a half-life between 30 and 43 d was observed for chlorpyrifos applied to greenhouse soils in Costa Rica (Roque Roque 2004). In a model tropical seawater environment, chlorpyrifos has been shown to partition rapidly ($t_{1/2}$ =7.8 d) into sediments and biota (Lalah et al. 2003). In freshwater systems at 25°C and a pH 7.0, chlorpyrifos that is not partitioned into sediments or biota is primarily degraded through hydrolysis with reported half-lives ranging from 35 to 78 d (Howard 1991).

When terbufos is directly applied to soil, fugacity models predict that between 92 and 99% of terbufos will remain in the soil compartment. Thus, the primary route of entry into aquatic resources is likely to be soil runoff during high rain and flooding events. Degradation half-lives for terbufos are reported to be less than 40 d (EPA 1988a), however degradation rates have been found to decrease with increased soil organic matter (Felsot 1982). Floodplain soils where banana and plantain are grown in the Sixaola watershed are relatively high in organic matter, with concentrations of organic matter as high as 10% in topsoils and 4% in lower horizons (Chapter 2). Due to its low solubility and relatively high Kow value, terbufos is unlikely to leach into groundwater resources (Felsot et al. 1982, EPA 1988a), although it has been found in a few groundwater sites in the US (EPA 1988b). In tropical areas, accelerated biodegradation of terbufos due to enhanced microbial activity has been documented (Racke 2003, Felsot 1998), but not in similar experiments in Costa Rica (Moens et al. 2004). In water resources, terbufos rapidly degrades through photolysis with half-lives reported as low as 1.2 d and through hydrolysis with half-lives reported of 2.2 weeks (EPA 1988a). The relatively short half lives reported in temperate studies, combined with the fact that terbufos is only applied to the soil three times a year, may account for the very small amount of terbufos sequestered in SPMD stream samples.

Biological Effect

Acute and chronic no effect concentrations calculated for chlorpyrifos, difenoconazole, and terbufos from lowest found toxicity values (Appendix C) are shown in Table 3. Based on available data, chlorpyrifos is calculated to be the most toxic pesticide followed by terbufos and then difenoconazole. However, toxicity data for chlorpyrifos far outnumber those available for most current-use pesticides. Compared to chlorpyrifos, which has been used in agriculture in the United States since the late 1960s, very few data exist for terbufos and difenoconazole toxicities. In the comprehensive online Pesticide Action Network Database (PAN 2007), over 1844 aquatic acute and chronic toxicity records are listed for chlorpyrifos compared to 177 acute toxicity studies listed for terbufos and only 4 acute toxicity studies for difenoconazole. The only available report of terbufos chronic toxicity was that reported for daphnia (EPA 1999). This explains why the chronic toxicity value is higher than the acute toxicity value, as one is for shrimp and the other for apparently more tolerant daphnia. The majority of acute and chronic toxicity data for difenoconazole was obtained from a manufacturer's material safety data sheet (MSDS), which specifically states that "difenoconazole may cause adverse long-term effects in the aquatic environment" (Agriliance 2007).

Although difenoconazole is a relatively new triazole fungicide, the first triazole fungicides were introduced in the 1980s. As a group, the primary mode of action of triazoles is to inhibit the biosynthesis of sterol in fungal cell membranes. This site-specific action can lead to resistance, which is why difenoconazole is applied in rotation with other classes of fungicides (Fischel 2005) in commercial banana plantations. In general, triazole fungicides are not considered toxic to bees or birds, but are considered toxic to fish and other aquatic organisms, with difenoconazole being the most highly toxic of the triazole group to fish (Fischel 2005). Compared to difenoconazole or older organochlorine pesticides, organophosphate pesticides such as chlorpyrifos and terbufos degrade more rapidly in the aquatic environment, but are considered to be far more toxic (Readman et al. 1992). The principal mode of action for organophosphate pesticides is acetylocholinesterase (AChE) inhibition, which occurs through phosphorylation of the chlorpyrifos oxon during metabolic activation. The extent of AChE inactivation is entirely species, dose, and duration dependent, and can result in over stimulation of the organism's peripheral nervous system with subsequent lethal or sublethal toxicity (Giesy et al. 1999). As a result, differences among species in behavior, feeding ecology, receptor sensitivity, and pharmacokinetics result in a greater than 1 million-fold variation in sensitivity to chlorpyrifos among species (Barron and Woodburn 1995).

Risk Assessment

Calculations of all acute and chronic risk factors for both predicted and observed environmental concentrations of chlorpyrifos, difenoconazole, and terbufos in stream study sites are shown in Appendix D. Based on these data, the unlikely scenarios of 100% entry of chlorpyrifos and terbufos were eliminated and a summary of acute risk categories for study streams is shown in Figure 6 for predicted environmental concentrations based on direct spraying of difenoconazole (100% entry) and level 3 fugacity models for chlorpyrifos and terbufos. Modeled results show that small streams adjacent to intensive banana, intensive plantain, and moderate plantain production regimes (such as the Cana, Shirolita, and Sandbox) are at very high risk of acute toxicity and corresponding aquatic organism mortality primarily from chlorpyrifos. Direct spraying of difenoconazole and entry of terbufos during erosional events also presents a high risk to these streams compared to larger streams represented by the Sixaola and Margarita sites.

The hazard quotient method is often used a screening tool as it cannot express indirect effects, incremental dose impacts, or effects on higher levels of organism organization (Burns 2001). With additional environmental and toxicity data, more refined risk assessments can be made using the Monte Carlo Method (Firestone et al. 1997), which incorporates uncertainty and point estimates into tier II risk assessments; the Probable Risk Assessment (Solomon et al. 2000), which depicts the percent of species likely to be affected and the percent of observations likely to cause a level of effect; or the Cumulative Exposure Concentration Model (Morton et al. 2000) which incorporates LC50 values to estimate cumulative episodic exposure and to predict the percent of species potentially at risk. However, even if these types of data were available for species and environments representative of tropical areas, these more sensitive methods may not provide better results than the hazard quotient method, as it is often considered the most conservative or overprotective.

Compared to modeled results, risk quotients calculated based on field measurements of average pesticide concentrations found in water and SPMD samples can all be categorized as low risk, with the exception of 100% entry (direct spray) of difenoconazole measured in the Cana stream site and categorized as moderate risk. However, two fish kill events were observed during stream sampling in the Cana stream site during the study period. Field environmental conditions, observed species mortality, and pesticide measurements during the two fish kills are reported in Appendix E, with the acute and chronic risk quotients for detected pesticides in SPMDs and water samples shown in Figure 7. In general, fish kills were observed during periods of sun and high temperatures, 2 or 3 d after large rain events in drier months. It is theorized that pesticide residues "built up" on soils and plants during weeks of applications in dry periods and moved in to aquatic resources during a large rain event, which if followed by 1 or 2 d of high temperatures and no rain, would concentrate in water resources as stream flow rapidly decreased. However, even though chlorpyrifos, terbufos, and difenoconazole were detected in SPMDs and water samples during the observed fish kill event, none of the measured concentrations provided a chronic or acute risk quotient above 1 (i.e., where measured water concentrations were equal to or exceed no effect toxicity concentrations). Only difenoconazole measured in water grab samples (0.3 μg/L) is even within the range of published toxicity values, although only after the safety factor of 0.1 for acute or 0.01 for chronic toxicity is applied. As these current-use pesticides do not bioaccumulate and measured pesticide concentrations were below toxicity thresholds, it is difficult to provide concrete evidence that fish mortality was directly caused by the pesticides found. However, as several fill kills a year are observed at this site, which is adjacent to intensive banana and plantain plantations, and many environmental and health organizations have recorded both human and environmental poisonings from pesticide applications in adjacent banana plantations (Chapter 1), a combination of stressful environmental conditions and pesticide mixtures is suspected. In either case, the applicability of temperate-based fugacity models and single-species toxicity data as well as the use of hazard risk quotients to estimate risk in these tropical systems should be questioned.

There are several reasons why the hazard risk quotient method may not be able to accurately predict risk. In tropical climates, pesticide degradation is faster, but pesticide solubility, rate of oxygen depletion, biological uptake, and impact of nutrients may be higher which can result in lower toxicity thresholds or no effect concentrations (Henriques et al. 1997). For example, Mayer et al. (1994) showed that organophosphate toxicity thresholds are particularly lowered by increases in temperature, and suggested that the 96-hr log LC50 value for organophosphate pesticides be lowered by a factor of 0.7 and all other chemicals by a factor of 0.5 for every 10°C increase in temperature. During the observed fish kills, stream temperatures were relatively high, dissolved oxygen concentrations were low, and stream flow velocity was negligible. These conditions alone or in combination with excess nutrient loading from agricultural fertilizers can contribute to stressful or eutrophic conditions that if not directly fatal, can lower toxicity thresholds for aquatic organisms (Gunnarson et al. 1995, Traas et al. 2004). Although high concentrations of dissolved organic matter, humic acids, or suspended sediments can be linked to a decrease in pesticide bioavailability (Warren et al. 2003), increased pesticide bioavailability in the presence of increased organic matter or humic acids has also been reported under different environmental conditions such as increased salinity or for different life stages of aquatic organisms (Phillips et al. 2003, Mezin and Hale 2004).

In addition to environmental conditions that may have contributed to lowered pesticide bioavailability or lower toxicity thresholds, the possibility that other pesticides were present and were undetected, or that the toxicological effects observed were the result of a combination of pesticides present, or pesticides and fertilizers, cannot be ruled out. Very little is known about the combined effects of pesticide mixtures on toxicological thresholds or the synergistic effects between pesticides and other natural ecological stressors such as changes in predator-prey relationships or limited food resources (Preston 2002, Raylea and Hoverman 2006).

Alternative Approaches to Risk Assessment

Given the amount of uncertainty and potentially aquatic-life threatening inaccuracies in predicting environmental concentrations and transferring temperate species toxicity data to tropical environments for site-specific risk assessment, alternative methods for assessing risk should be pursued. In fact, single-species toxicity tests may be of little use in the tropics due to high species diversity with complex interactions and lower vertebrate density, making it difficult to choose an indicator species (Larcher and Goldstein 1997). Instead, assemblages, ensemble, community, or ecosystem-level indices should be pursued. For example, several studies have found that macro invertebrate community composition and biotic indices are useful bioassessment tools for examining the toxicity effects in water resources draining banana plantations in Costa Rica (Ramirez and Pringle 1998, Castillo et al. 2006), and may provide a better indication of site-specific contaminant effects for management policy rather than risk assessment.

However, site-specific indicators of the potentially harmful effects of pesticides, such as macro-invertebrates, cannot provide information on larger landscape-level ecological effects (Cairns and Niederlehner 1996) or on the effects for organisms that move among and between different habitats, such as amphibians, birds, or migratory fish. In ecological terms, risk is a function of temporal and spatial scale for components of habitat, pollutant, and organisms, and these need to be considered before risk can be quantified (Jepson 1997). In the Sixaola watershed for example, terrestrial, freshwater, and marine systems are highly integrated, with a number of different very sensitive ecotones or interfaces (floodplain lakes, wetlands, riparian forests, estuaries, mangroves, lagoons, and beaches) among systems. These interfaces link terrestrial systems, where pesticide application primarily occurs, with freshwater or marine systems, where pesticides and other contaminants are deposited. Interfaces, however, often support higher biodiversity (Nakano and Murakami 2001), provide important ecosystem services (Cairns and Niederlehner 1994), as well as are critical habitat and breeding grounds for many of the region's endemic or threatened species, such as estuarine nurseries for the Atlantic tarpon or beach nesting sites for leatherback, green, hawksbill, and loggerhead sea turtles (Cortez 1998, Wilkinson 2004).

Biodiversity and habitat data, including the identification of important interfaces, can be used to help assess ecological risk for agricultural practices on a landscape scale. In regional conservation planning activities, agricultural intensity is considered as a primary threat in the identification of priority areas for freshwater, marine, and terrestrial biodiversity and habitat conservation (Huggins et al. 2007). In the Sixaola watershed, for example, there are several studies available on multitaxa biodiversity across a number of freshwater, marine, and terrestrial ecosystems (Palminteri et al. 2006, ANAI 2007) that could be assessed against the agricultural intensity of banana and plantain, measured as pesticide application or predicted environmental concentration, in the Sixaola watershed. In this way, incorporation of principles of landscape ecology, ecological processes, and biodiversity surrogates may provide a more feasible and protective approach to risk assessment than single-species toxicity data, especially in tropical regions like the Sixaola watershed where data and resources are relatively few.

Summary and Conclusions

The fate and toxicity of pesticides in tropical ecosystems is not as well understood as in temperate regions, as the bulk of pesticide fate and toxicology research has been conducted in temperate zones and the applicability of this research to tropical ecosystems is questionable. In some instances, pesticides appear to dissipate and degrade more quickly in tropical environments due to higher rainfall, increased temperatures, and accelerated photodegradation and volatilization. In a comparison of observed vs. modeled environmental concentrations in the Sixaola watershed, fugacity models primarily predicted pesticide concentrations well below current method detection limits for water grab samples. Similarly, time-weighted water concentrations derived from field deployed SPMDs cannot capture peak concentrations, and are therefore difficult to compare with both water grab samples and fugacity models.

Fugacity models to predict environmental concentrations of pesticides may work well for certain pesticides or not at all for others, due to inherent assumptions of application method and the applicability of available physiochemical data for pesticides applied in tropical climates. However, fugacity models have been shown to be very useful in identifying the primary route of entry for specific pesticides into aquatic resources. Difenoconazole is expected to be persistent in water resources and likely to enter small streams adjacent to banana plantations primarily through direct spray and by erosion after rain events.

Volatilization is likely the primary pathway for dispersion and degradation of chlorpyrifos, with aquatic exposure occurring during rain events and from soil during erosion and runoff events. Similarly, terbufos, although relatively quick to degrade and only applied three times a year, is likely to enter aquatic resources from the soil during high rainfall and erosion events after application. Although chlorpyrifos, terbufos, and difenoconazole all presented cases of high risk, especially in smaller streams with little or no flow, the timing and intensity of risk is expected to vary based on application frequency and pesticide persistence in water resources.

Single-species toxicity data derived from temperate species and risk assessment based on the hazard quotient method do not appear protective of tropical species. Although observed fish kills could not be directly linked to measured stream pesticide concentrations, the possibility that pesticides played a role, likely in combination with a number of other factors, can not be ruled out. Toxicity thresholds can be lowered under "stressful" environmental conditions such as low dissolved oxygen or high temperatures or in the presence of pesticide mixtures, excess nutrients, and synergistic effects related to intricate tropical food webs and complex species interactions. In tropical areas, where relatively few resources and data exist, alternate risk assessment methods that incorporate biodiversity indices or identification of critical habitat at the site or landscape level may provide a more feasible and protective approach.

References

Abarca, L., Ruepert, C. 1992. Plaguicidas encontrados en el valle de la estrella: estudio preliminar. Tecnología en Marcha 12:31-38.

Agriliance. 2007. Difenoconazole MSDS, http://www.cdms.net/LDat/mp67C013.pdf, accessed June 20, 2007.

ANAI (Asociación ANAI). 2007. http://www.anaicr.org, accessed June 2007.

APHA (American Public Health Association). 1995. Standard Methods for the Examination of Water and Wastewater. Eaton, A.D., Clesceri, L.S., Greenberg, A.E (Eds). American Public Health Association, Washington D.C.

Aragon, A., Aragon, C., Thorn, A. 2001. Pests, peasants, and pesticides on the Northern Nicaraguan Pacific Plain. International Journal of Occupational and Environmental Health 7: 295-302.

Baskaran, S., Kookana, R.S., Naidu, R. 2003. Contrasting behavior of chlorpyrifos and its primary metabolite, TCP (3,5,6-trichloro-2-pyridinol), with depth in soil profiles. Australian Journal of Soil Research 41: 749-760.

Barron, G.M., Woodburn, K.B. 1995. Ecotoxicology of chlorpyrifos. Reviews of Environmental Contamination and Toxicology 144:1-93.

Borthwick, P.W., Patrick, J.M., Middaugh, D.P. 1985. Comparative acute sensitivities of early life stages of atherinid fishes to chlorpyrifos and thiobencarb. Archives of Environmental Contamination and Toxicology 14: 465-473.

Burns, L.A. 2001. Probabilistic Aquatic Exposure Assessment for Pesticides 1. Foundations. National Exposure Research Laboratory USEPA.

Cairns, J., Niederlehner, B.R. 1996. Developing a field of landscape ecotoxicology. Ecological Applications 6: 790-796.

Cairns, J., Niederlehner, B.R. 1994. Estimating the effects of toxicants on ecosystem services. Environmental Health Perspectives 102: 936-939.

Carvalho, F.P., Villeneuve, J.P., Cattini, C., Tolosa, I., Montenegro-Guillen, S., Lacayo, M., Cruz, A. 2002. Ecological risk assessment of pesticide residues in coastal lagoons of Nicaragua. Journal of Environmental Monitoring 4: 778-787.

Castillo, L.E., Martinez, E., Ruepert, C., Savage, C., Gilek, M., Pinnock, M., Solis, E. 2006. Water quality and macroinvertebrate community response following pesticide applications in banana plantation. Science of the Total Environment 367: 418-432.

Castillo, L.E., Ruepert, C., Solis, E. 2000. Pesticide residues in the aquatic environment of banana plantation areas in the north Atlantic zone of Costa Rica. Environmental Toxicology and Chemistry 19: 1942-1950.

Castillo, L.E., de la Cruz, E., Ruepert, C. 1997. Ecotoxicology and pesticides in tropical aquatic ecosystems of Central America. Environmental Toxicology and Chemistry 16: 41-51.

Cortez, J. 1998. Cahuita and Laguna Gandoca, Costa Rica. In Kjerfve, B. (Ed), CARICOMP Caribbean Coral Reef, Seagrass and Mangrove Sites. UNESCO, France.

de la Cruz, E.M., Castillo, L.E. 2003. The use of pesticides in Costa Rica and their impact on coastal ecosystems. In Taylor, M.D., Klaine, S.J., Carvalho, F.P., Barcelo, D., Everaarts, J. (Eds), Pesticide Residues in Coastal Tropical Ecosystems. Taylor and Francis, London.

Dinham, B., Malik, S. 2003. Pesticides and human rights. International Journal of Occupational and Environmental Health 9: 40-52.

EcotoxNET. 2007. Terbufos fact sheet. http://extoxnet.orst.edu/pips/terbufos.htm, accessed June 2, 2007.

Elinder, C.G., Wesseling, C., Castillo, L. 1998. International conference on pesticide use in developing countries: Impact on environment and health, San Jose, Costa Rica 23-27 February 1998. Ambio 27: 494-495.

EPA (U.S. Environmental Protection Agency). 1999. Revised environmental fate and effects assessment (terbufos) Section 4, Ecological Toxicity Data: USEPA Sept, 14, 1999.

EPA (U.S. Environmental Protection Agency). 1998. Guidelines for ecological risk assessment. USEPA, Washington, D.C.

EPA (U.S. Environmental Protection Agency). 1992. Framework for ecological risk assessment EPA/630/R-92/001. Washington, D.C.

EPA (U.S. Environmental Protection Agency). 1988a. Pesticide Fact Sheet Number 5.2: Terbufos. Office of Pesticide and Toxic Substances, Washington, DC.

EPA (U.S. Environmental Protection Agency). 1988b. Pesticides in Ground Water Data Base. 1988 Interim Report. Washington, DC.

EST (Environmental Sampling Technologies). 2007. http://www.est-lab.com, accessed July 7, 2007.

Felsot, A.S. 1998. Enhanced biodegradation of nematicides in soils from Central American banana plantation: In: Astorga, Y. (Ed) International Conference on Pesticide Use in Developing Countries: Impact on Health in Environment, San Jose, Costa Rica, 23-28 February 1998. Universidad Nacional, Heredia, Costa Rica.

Felsot, A., Wei, L., Wilson, J. 1982. Environmental chemodynamic studies with terbufos ("Counter") insecticide in soil under laboratory and field conditions. Journal of Environmental Science and Health B 17: 649-673.

Fischel, F.M. 2005. Pesticides Toxicity Profile: Triazole Fungicides. Pesticide Information Office, Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, University of Florida.

Firestone, M., Fenner-Crisp, P., Barry, T., Bennet, D., Chang, S., Callahan, M., Burke, A., Michaud, J., Olsen, M., Cirone, P., Barnes, D., Wood, W.P., Knott, S.M. 1997. Guiding Principles for Monte Carlo Analysis EPA/630/R-97/001 US EPA, Washington, D.C.

Giesy, J.P., Solomon, KR., Coats, J.R., Dixon, K.R., Giddings, J M., Kenaga, E.E. 1999. Chlorpyrifos: Ecological risk assessment in North American aquatic environments. Reviews of Environmental Contamination and Toxicology 160: 1-129.

Graham, A. 1995. Development of affinities between Mexico/Central America and northern South American lowlands and lower montane vegetation during the Tertiary. In Churchill, S.P., Balslev, H., Forero, E., Luteyn, J.L. (Eds), Biodiversity and Conservation of Neotropical Montane Forests. The New York Botanical Gardens, New York.

Grant, A., Oreamuno, R., Serrano, A., Vargas, O. 2004. Inundaciones en la Vertiente Atlántica. Informe de Colegio Federado de Ingenieros y de Arquitectos de Costa Rica, San Jose, Costa Rica, May 2004.

Gunnarson, J., Broman, D., Jonsson, P., Olsson, M., Rosenberg, R. 1995. Interactions between eutrophication and contaminants: Towards a new research concept for the European aquatic environment. Ambio 24: 383-385.

Henriques, W., Jeffers, R.D., Lacher, T.E., Kendall, R.J. 1997. Agrochemical use on banana plantations in Latin America: Perspectives on ecological risk. Environmental Toxicology and Chemistry 16: 91-99.

Hernandez, C., Witter, S.G., Hall, C.A.S., Fridgen, C. 2000. The Costa Rican banana industry: Can it be sustainable? pp. 563-593 In Hall, C.A.S. (Ed), Quantifying Sustainable Development, Academic Press, Chicago.

Hernandez, C.E., Witter, S.G. 1996. Evaluating and managing the environmental impact of banana production in Costa Rica: A systems approach. Ambio 25:171-178.

Howard, P.H. 1991. Ed. Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Vol 3: Pesticides. Lewis Publishers, Chelsea, MI.

Howe, G.E., Marking, L.L., Bills, T.D., Rach, J.J., Mayer, F.L. 1994. Effects of water temperature and pH on toxicity of terbufos, trichlorfon, 4-nitrophenol and 2,4-dinitrophenol to the amphipod Gammarus pseudolimnaeus and rainbow trout (Oncorhynchus mykiss). Environmental Toxicology and Chemistry 13: 51-66.

Huckins, J.N., Manuweera, G.K., Petty, J.D., Mackay, D., Lebo, J.A. 1993. Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. Environmental Science and Technology 27: 2489-2496.

Huggins, A.E., Keel, S., Kramer, P., Nunez, F., Schill, S., Jeo, R., Chatwin, A., Thurlow, K., McPearson, M., Libby, M., Tingey, R., Palmer, M., Seybert, R. 2007. A Conservation Assessment of the Insular Caribbean Using the Caribbean Decision Support System. Summary Report, The Nature Conservancy.

IRET (Regional Institute for Studies of Toxic Substances). 2000. Reducción del escurrimiento de plaguicidas al mar caribe: Informe Nacional: Costa Rica GEF/11000-99-04/PNUMA. Dec. 2000.

IRET (Regional Institute for Studies of Toxic Substances). 1999. Manual de Plaguicidas: Guia para America Central, 2nd Ed. EUNA, Heredia, Costa Rica.

Jepson, P.C. 1997. Scale dependency in the ecological risks posed by pollutants: is there a role for ecological theory in risk assessment? In van Straalen, N.M., Lokke, H. (Eds.), Ecological Risk Assessment of Contaminants in Soil. Chapman and Hall, London.

Kapp, G.B. 1989. Perfil ambiental de la zona Baja de Talamanca, Costa Rica. Informe Técnico No.155, CATIE, Turrialba, Costa Rica, 97 pp.

Kwok, K.W.H., Lueng, K.M.Y., Lui, G.S.G., Chu, V.K.H., Lam, P.K.S., Morritt, D., Maltby, L., Brock, T.C.M., Van den Brink, P.J., Wame, M.S.J., Crane, M. 2007. Comparison of tropical and temperate freshwater animal species' acute sensitivities to chemicals: implications for deriving safe extrapolation factors. Integrated Environmental Assessment and Management 3: 49-67.

Lacher, T.E., Goldstein, M.I. 1997. Tropical ecotoxicology: status and needs. Environmental Toxicology and Chemistry 16: 100-111.

Lalah, J.O., Ondieki, D., Wandiga, S.O., Jumba, I.O. 2003. Dissipation, distribution and uptake of 14C-Chlorphyrifos in a model tropical seawater/sediment/fish ecosystem. Bulletin of Environmental Contamination and Toxicology 70: 883-890.

Leight, A.K., Van Dolah, R.F. 1999. Acute toxicity of the insecticides endosulfan, chlorpyrifos and malathion to the epibenthic estuarine amphipod Gammarus palustris (Bousfield). Environmental Toxicology and Chemistry 18: 958-964.

Mackay, D., DiGuardo, A., Paterson, S., Cowan, C.E. 1996a. Evaluating the environmental fate of a variety of types of chemicals using the EQC model. Environmental Toxicology and Chemistry 15: 1627-1637.

Mackay, D., DiGuardo, A., Paterson, S., Kicsi, G. 1996b. Assessment of chemical fate in the environment using evaluative regional and local-scale models: illustrative application to chlorobenzene and linear alkylbenzene sulfonates. Environemental Toxicology and Chemistry 15: 1638-1648.

Marin, D.H., Romero, R.A., Guzman, M., Sutton, T. 2003. Black Sigatoka: an increasing threat to banana cultivation. Plant Disease 87: 208-222.

Matlock, R.B, de la Cruz, R. 2002. An inventory of parasitic Hymenoptera in banana plantations under two pesticide regimes. Agriculture Ecosystems and Environment 93: 147-164.

Matthews, G., Wiles, T., Baleguel, P. 2003. A survey of pesticide application in Cameroon. Crop Protection 22: 707-714.

Mayer, F.L., Marking, L.L., Bills, T.D., Howe, G.E. 1994. Physiochemical factors affecting toxicity in freshwater: hardness, pH and temperature. In Hamelink, J.L., Landrum, P.F., Bergman, H.L., Benson, W.H. (Eds), Bioavailability: Physical, chemical and biological interactions, CRC Press, Boca Raton, Florida.

McConnell, L.L., LeNoir, J.S., Datta, S, Sieber, J.N. 1998. Wet deposition of current-use pesticides in the Sierra Nevada mountain range, California, USA. Environmental Toxicology and Chemistry 17: 1908-1916.

Mekonnen, Y., Agonafir, T. 2002. Pesticide sprayers' knowledge, attitude and practice of pesticide use on agricultural farms of Ethiopia. Occupational Medicine 52: 311-315.

Mezin, L.C., Hale, R.C. 2004. The effect of humic acids on toxicity of DDT and chlorpyrifos to freshwater and estuarine invertebrates. Environmental Toxicology and Chemistry 23: 583-590.

Moens, T., Araya, M, Swennen, R., DeWaele, D. 2004. Enhanced biodegradation of nematicides after repetitive applications and its effect on root and yield parameters in commercial banana plantations. Biology and Fertility of Soils 39: 407-414.

Morton, M.G., Dickson, K.L., Waller, W.T., Acevedo, M.F., Mayer, F.L. Jr., Ablan, M. 2000. Methodology for the evaluation of cumulative episodic exposure to chemical stressors in aquatic risk assessment. Environmental Toxicology and Chemistry 19: 1213-1221.

Municipality of Talamanca. 2003. Plan local de desarrollo: 2003:2013. Municipality of Talamanca, Bribri, Costa Rica.

Nakano, S., Murakami, M. 2001. Reciprocal subsidies: Dynamic interdependence between terrestrial and aquatic food webs. Proceedings of the National Academy of Science (PNAS) 98: 166-170.

Olima, C., Pablo, F. 1997. Comparative tolerance of three populations of the freshwater shrimp (Paratya australiensis) to the organophosphate pesticide, chlorpyrifos. Bulletin of Environmental Contamination and Toxicology 59: 321-328.

Palminteri, S., Powell, G., Fernandez, A., Tovar, D. 2006. Fase preliminar de reconocimiento de la ecoregion de los bosques montanos de Talamanca e istmicos del pacifico. WWF Centroamerica.

PAN (Pesticide Action Network Database). 2007. http://www.pesticideinfo.org, accessed June 20, 2007.

Peters, E.C., Gassman, N.J., Firman, J.C., Richmond, R.H, Power, E.A. 1997. Ecotoxicology of Tropical Marine Ecosystems. Environmental Toxicology and Chemistry 16:12-40.

Petty, J.D., Orazio, C.E. Huckins, J.N., Gale, R.W., Lebo, J.A., Meadows, J.C., Echols, K.R., Cranor, W.L. 2000. Considerations involved with the use of semipermeable membrane devices for monitoring of environmental contaminants. Journal of Chromatography A 879: 83-95.

Phillips, T.A., Summerfelt, R.C., Wu, J., Laird, D.A. 2003. Toxicity of chlorpyrifos adsorbed on humic colloids to larval walley (Stizostedion vitreum). Archives of Environmental Contamination and Toxicology 45: 258-263.

Preston, B.L. 2002. Indirect effects in aquatic ecotoxicology: Implications for ecological risk assessment. Environmental Management 29: 311-323.

Pringle, C.M., Ramirez, A. 1998. Use of both benthic and drift sampling techniques to assess tropical stream invertebrate communities along an altitudinal gradient, Costa Rica. Fresh Water Biology 39: 359-373.

Racke, K.D. 2003. What do we know about the fate of pesticides in tropical ecosystems? In Coats, J. R.,Yamamoto, H. (Eds), Environmental Fate and Effects of Pesticides, ACS Symposium Series 85, American Chemical Society, Washington, D.C.

Racke, K.D. 1993. Environmental fate of chlorpyrifos. Reviews of Environmental Contamination and Toxicology 131: 1-154.

Raylea, R., Hoverman, J. 2006. Assessing the ecology in ecotoxicology: a review and synthesis in freshwater systems. Ecology Letters 9: 1157-1171.

Readman, J.W., Kwong, L.L.W., Mee, L.D., Bartocci, J., Nilve, G., Rodriquez-Solano, J. A., Gonzales-Farias, F. 1992. Persistent organophosphorus pesticides in tropical marine environments. Marine Pollution Bulletin 21: 398-402.

Roque Roque, E. 2004. Degradacion de clorpirifos en dos tipos de suelos tropicales bajo condiciones de invernadero. University of Costa Rica Masters Thesis, San Jose, Costa Rica.

Siepmann, S., Finlayson, B. 2002. Water Quality Criteria for Diazinon and Chlorpyrifos. California Department of Fish and Game, Pesticide Investigations Unit, Rancho Cordova, CA. pp. 80.

Solomon, K., Giesy, J., Jones, P. 2000. Probabilistic risk assessment of agrochemicals in the environment. Crop Protection 19: 649-655.

Traas, T.P., Janse, J.H., van den Brink, P.J., Brock, T.C.M., Aldenberg, T. 2004. A freshwater food web model for the combined effects of nutrients and insecticide stress and subsequent recovery. Environmental Toxicology and Chemistry 23: 521-529.

Van den Brink, P.J., Sureshkumar, S.N., Daam, M.A., Domingues, I, Milwain, G.K., Beltman, W.H.J., Warnajith, M., Perera, P., Satapornvanit, K. 2003. Environmental and human risks of pesticide use in Thailand and Sri Lanka. Alterra-rapport 789, MAMAS Report Series No. 3/2003. Alterra, Green World Research, Wageningen, Netherlands.

Van Wijngaarden, R.P.A., Leeuwangh, P., Lucassen, W.G.H., Romijn, K., Ronday, R., van der Velde, R., Willigenburg, W. 1993. Acute toxicity of chlorpyrifos to fish, a newt and aquatic invertebrates. Bulletin of Environmental Contamination and Toxicology 51: 716-

723.

Vermeire, T., MacPhail, R., Waters, M. 2003. Integrated human and ecological risk assessment: a case study of organophosphorous pesticides in the environment. Human and Ecological Risk Assessment 9: 343-357.

Versteeg, D., Belanger, S., Carr, G. 1999. Understanding single-species and model ecosystem sensitivity: data-based comparison. Environmental Toxicology and Chemistry 18: 1329-1346.

Vrana, B., Mills, G.A., Allan, I.J., Dominiak, E., Svensson, K., Knutsson, J., Morrison, G., Greenwood, R. 2005. Passive sampling techniques for monitoring pollutants in water. Trends in Analytical Chemistry 24: 845-868.

Vrana, B., Schuurmann, G. 2002. Calibrating the uptake kinetics of semipermeable membrane devices in water: impact of hydrodynamics. Environmental Science and Technology 36: 290-295.

Warren, N., Allan, I.J., Carter, J.E., House, W.A., Parker, A. 2003. Pesticides and other micro-organic contaminants in freshwater sedimentary environments - a review. Applied Geochemistry 18: 159-194.

Webster, E., Mackay, D., Wania, F. 1998. Evaluating environmental persistence. Environmental Toxicology and Chemistry 17: 2148-2158.

Wesseling, C., Corriols, M., Bravo, V. 2005. Acute pesticide poisoning and pesticide registration in Central America. Toxicology and Applied Pharmacology 207: S697-S705.

Wesseling, C., van Wendel de Joode, B., Monge, P. 2001. Pesticide related illness among banana workers in Costa Rica: a comparison between 1993 and 1996. International Journal of Occupational and Environmental Health 7: 90-97.

Wilkinson, C. 2004. Status of Coral Reefs of the World: 2004 Vol. 2. Australian Institute of Marine Science, Townsville.

Table 1. Chlorpyrifos, difenoconazole, and terbufos application in four different banana and plantain production regimes in the Sixaola watershed

	Intensive Banana	**Intensive Plantain**	**Moderate Intensity Plantain**	**Low-Intensity Plantain**
Total Active Ingredients (a.i.) Applied*	35-45 kg/ha/yr	10-15 kg/ha/yr	3-9 kg/ha/yr	<2 kg/ha/yr
Hectares in Sixaola Watershed	4000	6700	2700	1800
Average plants / ha	1800	1800	1200	1000
Chlorpyrifos Application	Once per year	Once per year	Once per year	Once per year
Chlorpyrifos kg a.i./ha/yr	0.72	0.72	0.5	0.4
Difenoconazole Application	12 to 24 times per year	3 to 6 times per year	1 to 3 times per year	None
Difenoconazole kg a.i./ha/yr	3 - 6	1.1 - 2.3	0.38 - 1.1	None
Terbufos Application	3 times a year	3 times a year and during seeding	1 to 2 times a year and during seeding	Only during seeding
Terbufos kg a.i./ha/yr	18	10	5.0 -7.5	2.5

* Includes all pesticide products used (Chapter 1)

Table 2. Predicted Environmental Concentrations (PECs) based on three different pesticide entry fractions (EF) in five study sites based on average water volume and the dominant production regime along the stream reach

Study Site	Cana	Sixaola	Margarita	Sandbox	Shirolita
Production Regime	Intensive Banana	Intensive Banana	Intensive Plantain	Intensive Plantain	Moderate Plantain
PEC Chlorpyrifos (μg/L)					
EF1=100%	2.667	0.180	0.320	102.9	13.71
EF2 = 1.3%	0.037	0.002	0.004	1.409	0.188
EF3 = 2.6%	0.069	0.005	0.008	2.670	0.534
PEC Difenoconazole (μg/L)					
EF1=100%	9.523	0.125	0.111	35.71	7.143
EF2 = 5.2%	0.499	0.007	0.006	1.871	0.374
EF3 = 4.0%	0.386	0.005	0.005	1.446	0.289
PEC Terbufos (μg/L)					
EF1=100%	9.259	0.625	1.111	357.1	71.43
EF2= 4.1%	0.381	0.026	0.046	14.71	2.943
EF3 = 0.05%	0.005	0.0003	0.0006	0.193	0.038

Table 3: Lowest calculated acute and chronic no effect concentrations (NECs) for chlorpyrifos, difenoconazole, and terbufos

	Acute NEC μg/L	Species	Chronic NEC μg/L	Species
Chlorpyrifos	0.0008	Shrimp	0.0004	Shrimp
Difenoconazole	1.5	Shrimp	0.56	Fish
Terbufos	0.0017	Shrimp	0.003	Daphnia

Figure 1. Water and SPMD sampling sites in the Sixaola Watershed. Costa Rica

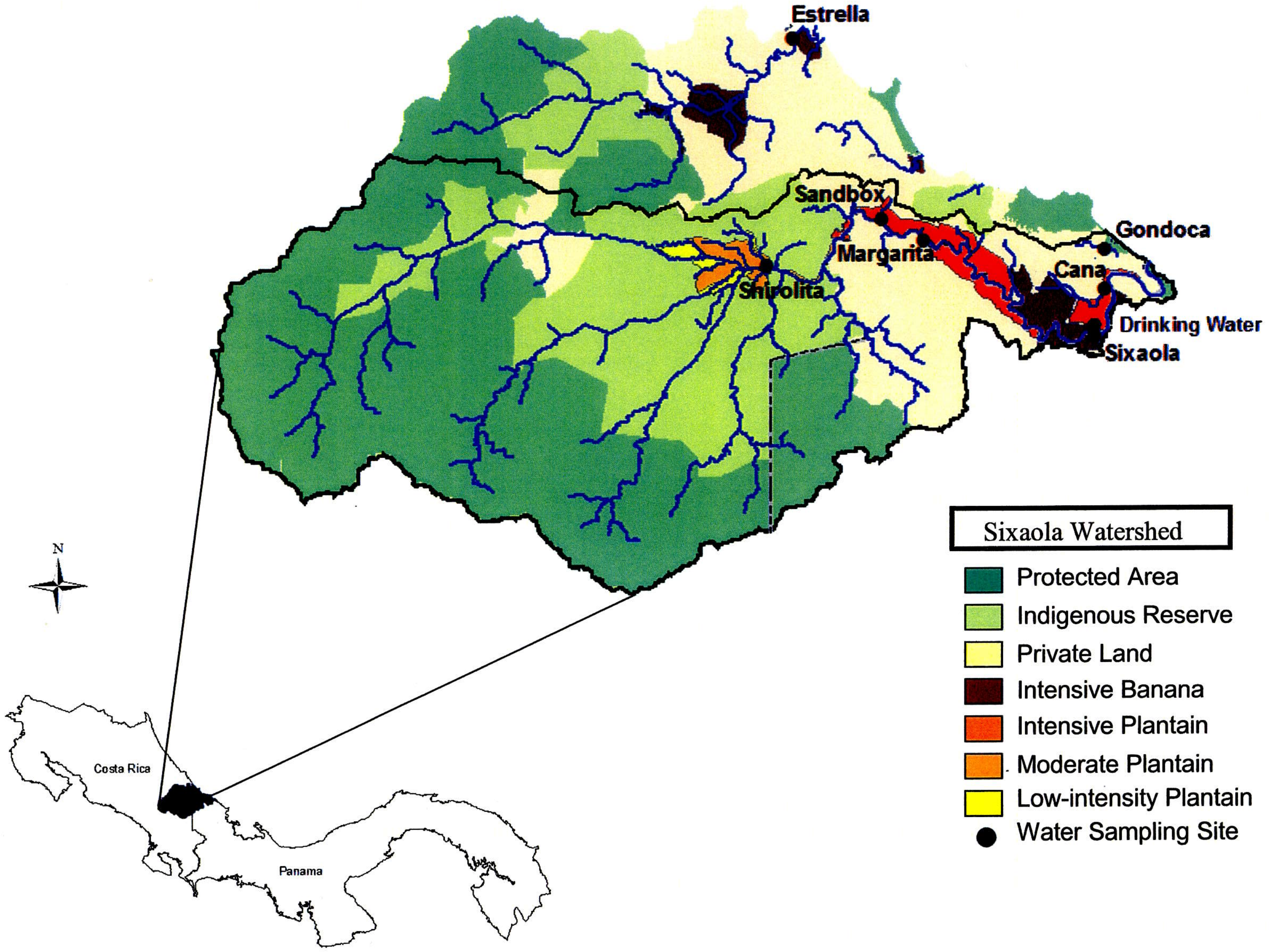


Figure 2. Contribution of production regime to total pesticide loading in Sixaola watershed (282 metric tons a.i./yr)

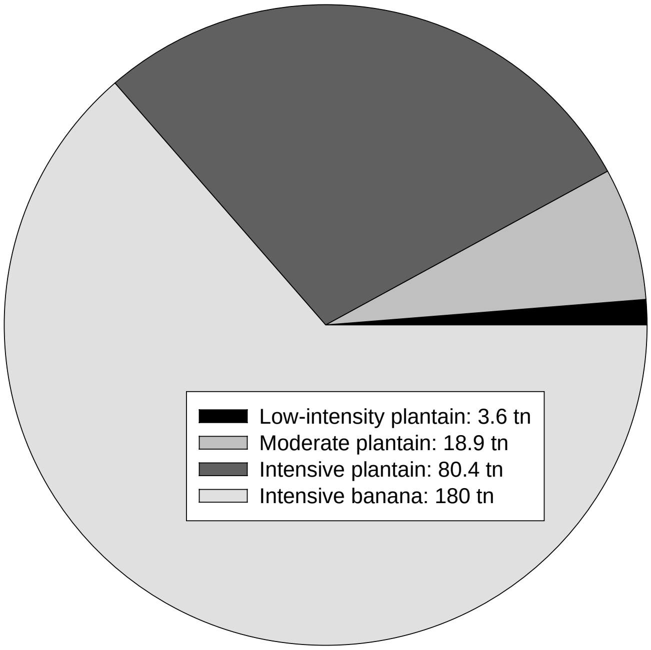


Figure 3. Contribution of chlorpyrifos, difenoconazole, and terbufos to total annual pesticide loading (282 metric tons a.i.) in Sixaola watershed

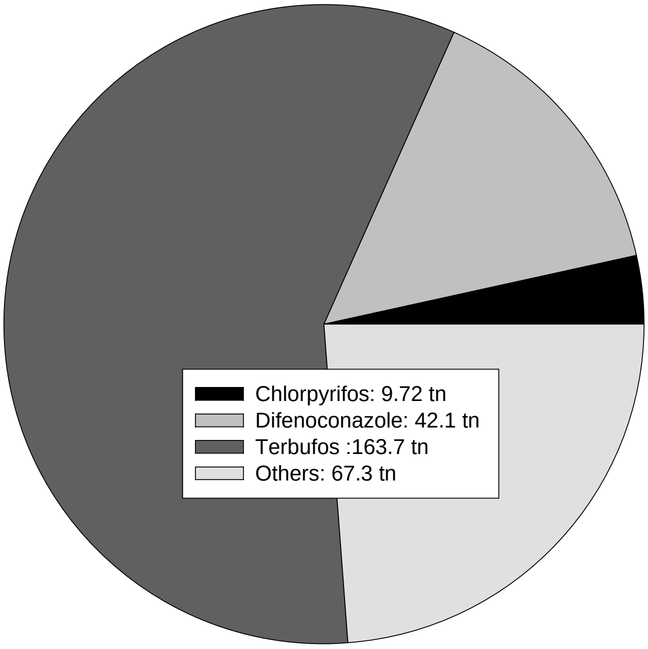


Figure 4. Maximum 28 d average pesticide concentrations (pg/L) in streams calculated from SPMD deployment in six surface water sites in the Sixaola watershed

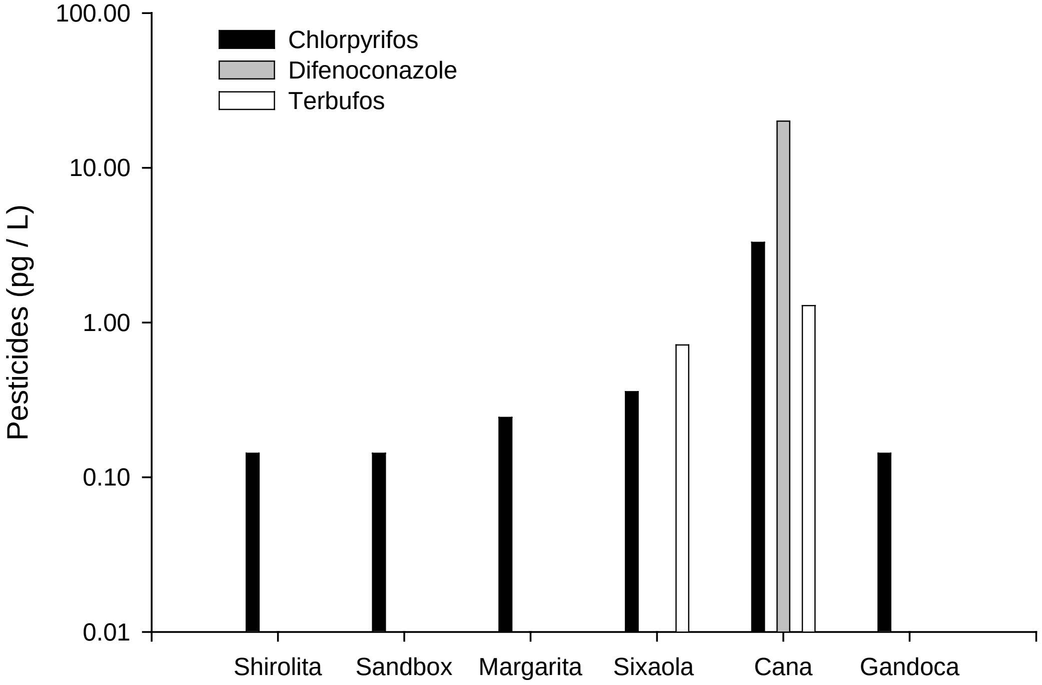


Figure 5. Maximum pesticide concentrations detected in streams from water grab samples with method detection limits (MDL) in seven Sixaola watershed sites and one Estrella watershed site

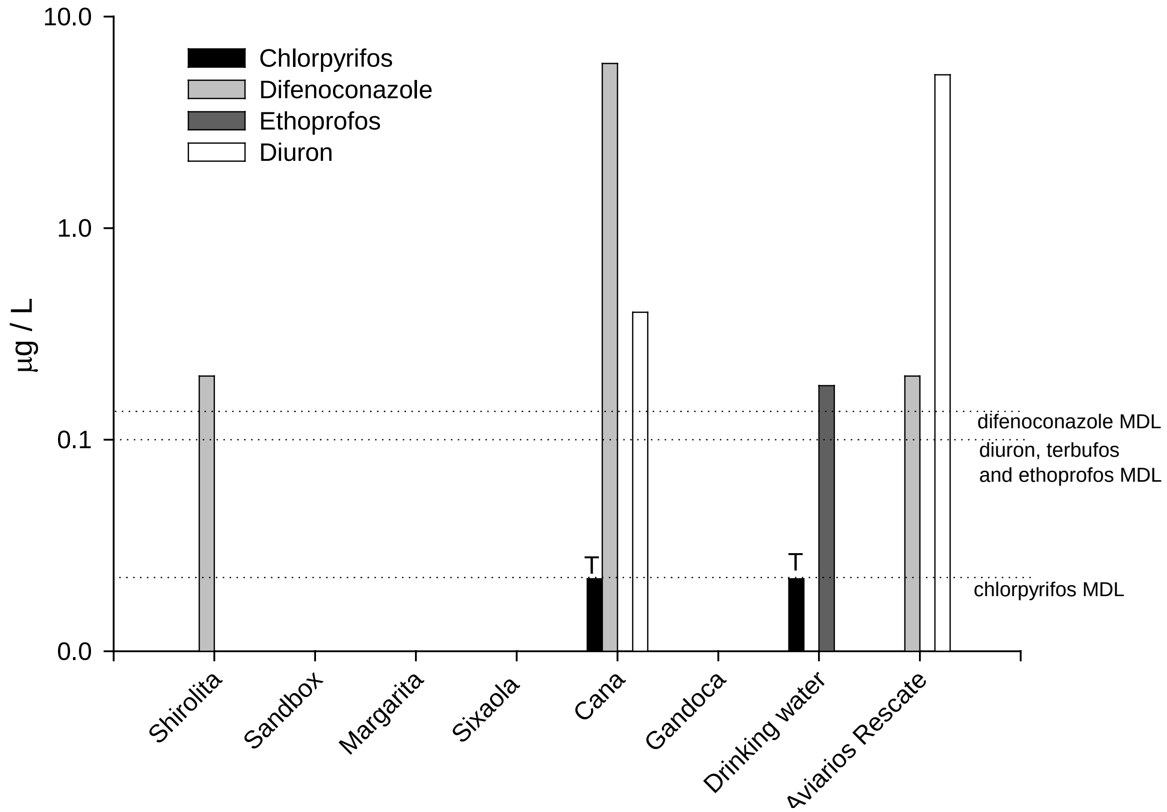


Figure 6. Modeled acute risk based using predicted environmental concentrations (PECs) based on 100% entry difenoconazole and level 3 fugacity models for chlorpyrifos and terbufos

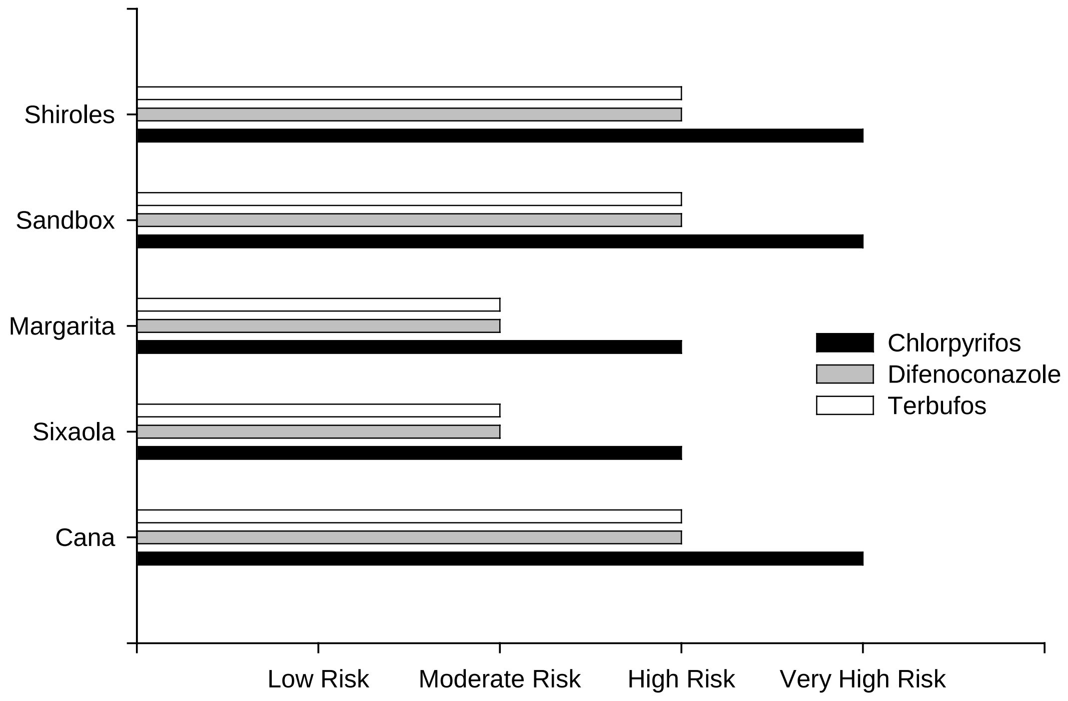
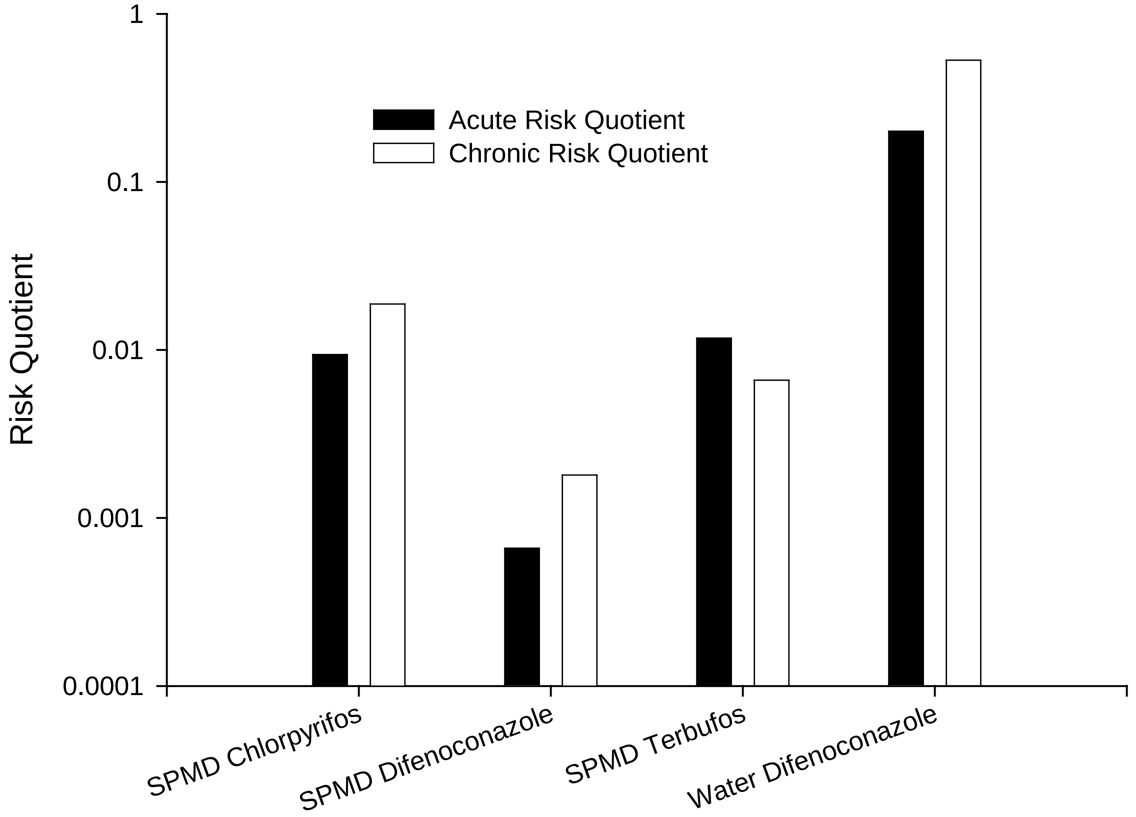


Figure 7. Acute and chronic risk quotients calculated from 96-hr SPMD time-weighted pesticide concentrations and water grab samples collected during an observed fish kill in the Cana study site



Chapter Four Appendices

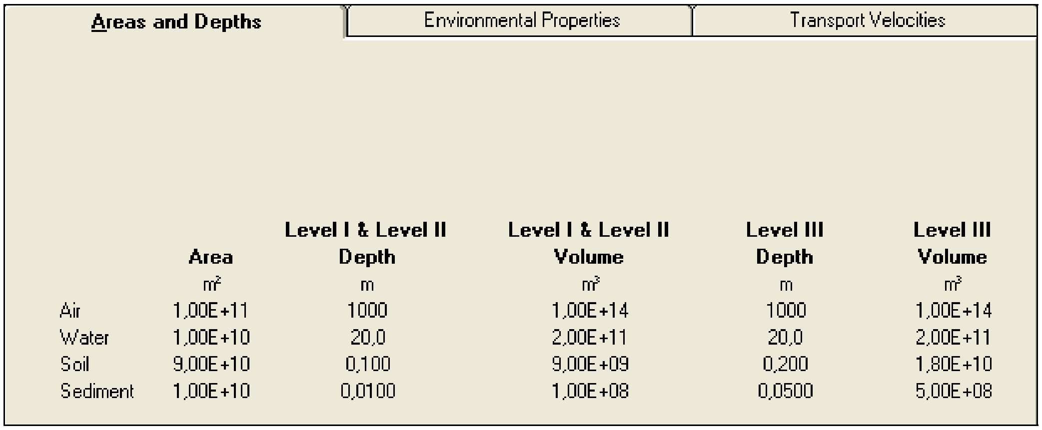
Appendix A: Fugacity Model (EQC) Inputs and Outputs

Pesticide physiochemical properties for EQC fugacity model

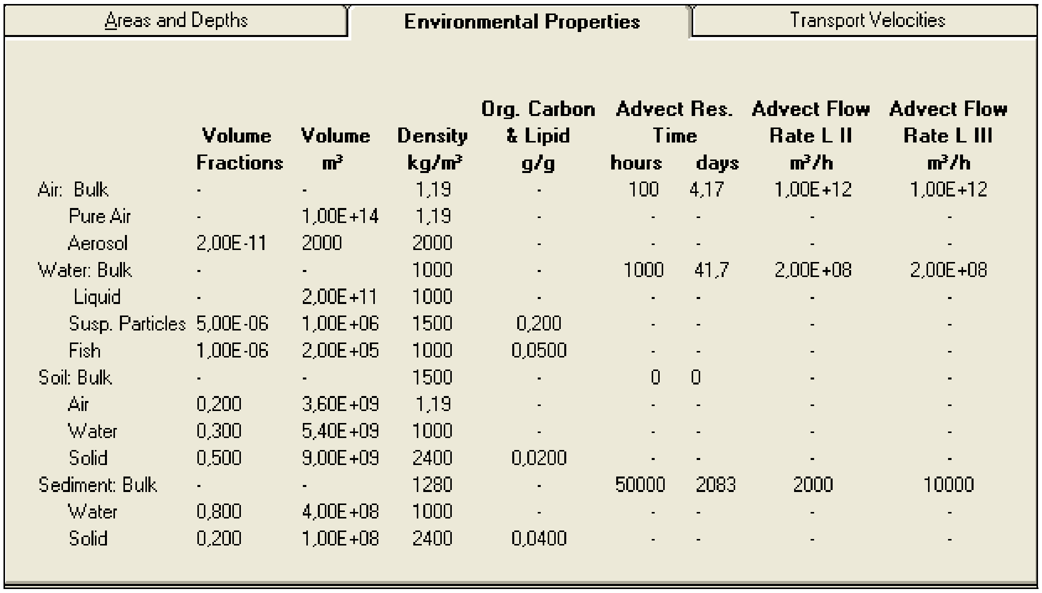
	chlorpyrifos	**difenoconazole**	**terbufos**
Compound class	organophosphate	triazole	organophosphate
molecular weight (g/mol)	350	406	288
log Kow	4.9	4.3	3.7 - 4.5 (4.4)
water solubility (mg/L) @ 25C	1.1	15.0	5.0
vapor pressure (Pa) @25C	0.0027	0.000000033	0.042
Henry's Law Constant (Pa/m^3/mol) @ 25C*	0.42	0.0000009	2.43
Henry's Law Constant (Pa/m^3/mol) from EQC Model	0.84	0.00000089	2.42
Kow EQC model	79433	19953	25119
Koc (L/kg) EQC model	32567	8181	10299
Kair-water EQC model	0.00034	0.00000000036	0.000976
Ksoil-water EQC model	1563	393	494
Ksediment-water EQC model	3126	785	989
Ksusp. solids-water EQC model	9770	2454	3090
Kfish-water EQC model	3972	998	2356
Kaerosol-Air EQC model	1510000000	56000000000000	143000000
Air Half Life (hours) **	2.8	12	1
Water Half Life (hours) **	4320	4340	9
Soil Half Life (hours) **	8640	8640	1800
Sediment Half Life (hours) **	38880	38880	8100

* From EPA HenryWin Ver. 3.12
** From EPA EpiWin Ver. 3.12

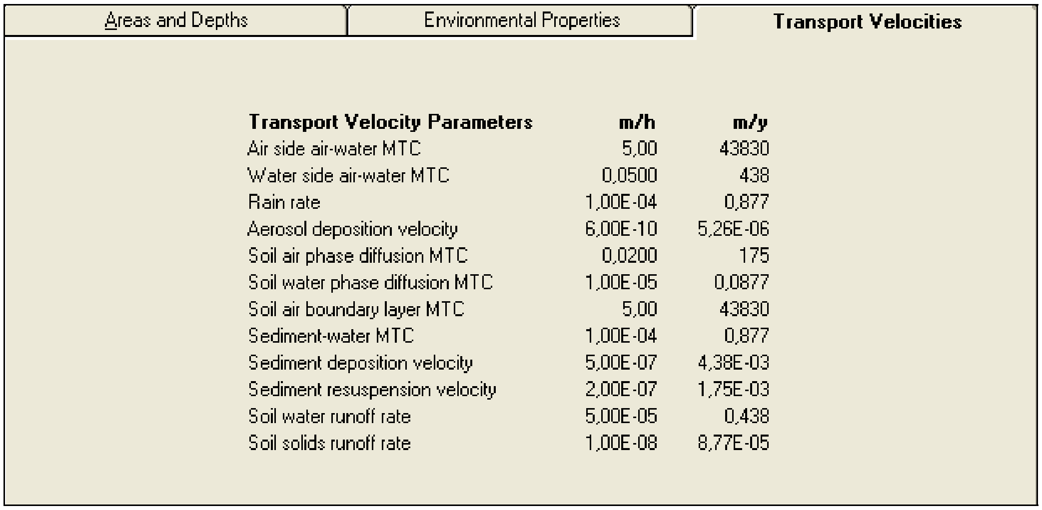
EQC Fugacity Model Version 2.02: Fixed environmental parameters



	Area	Level I & Level II Depth	Level I & Level II Volume	Level III Depth	Level III Volume
	m²	m	m³	m	m³
Air	1,00E+11	1000	1,00E+14	1000	1,00E+14
Water	1,00E+10	20,0	2,00E+11	20,0	2,00E+11
Soil	9,00E+10	0,100	9,00E+09	0,200	1,80E+10
Sediment	1,00E+10	0,0100	1,00E+08	0,0500	5,00E+08

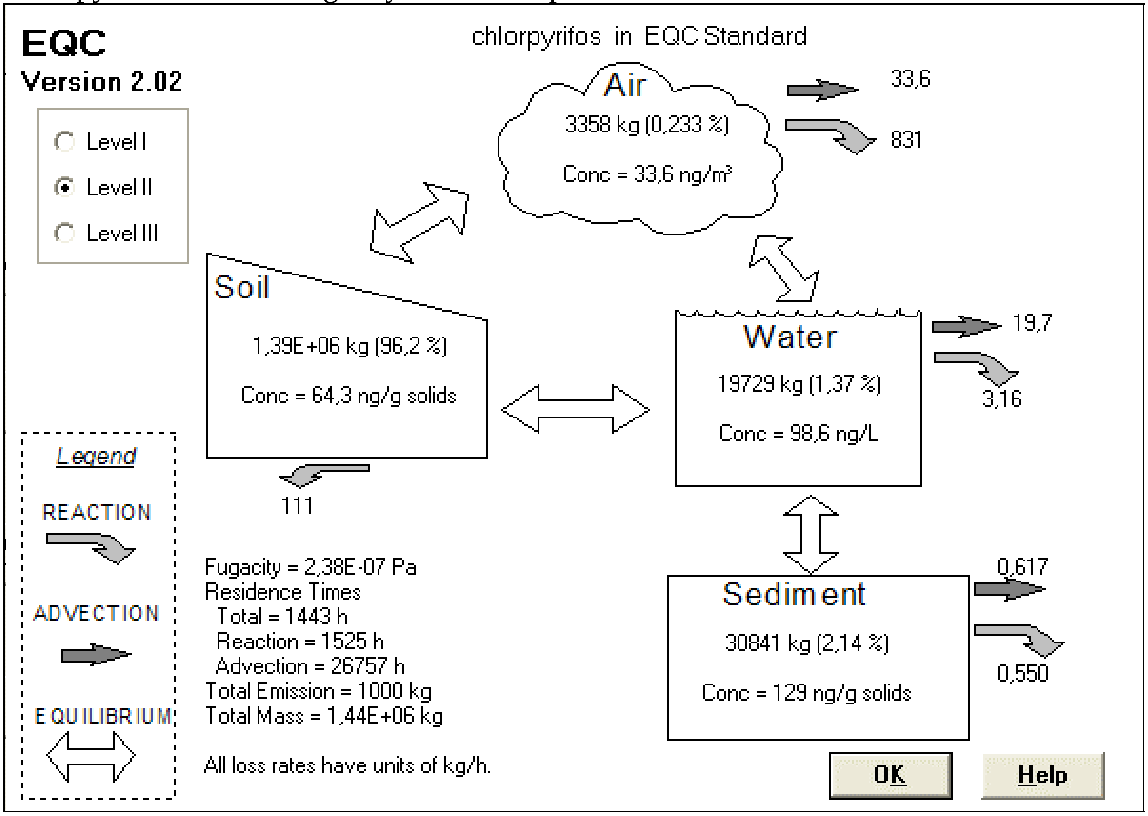


	Volume Fractions	Volume m³	Density kg/m³	Org. Carbon & Lipid g/g	Advect Res. Time hours	days	Advect Flow Rate L II m³/h	Advect Flow Rate L III m³/h
Air: Bulk	-	-	1,19	-	100	4,17	1,00E+12	1,00E+12
Pure Air	-	1,00E+14	1,19	-	-	-	-	-
Aerosol	2,00E-11	2000	2000	-	-	-	-	-
Water: Bulk	-	-	1000	-	1000	41,7	2,00E+08	2,00E+08
Liquid	-	2,00E+11	1000	-	-	-	-	-
Susp. Particles	5,00E-06	1,00E+06	1500	0,200	-	-	-	-
Fish	1,00E-06	2,00E+05	1000	0,0500	-	-	-	-
Soil: Bulk	-	-	1500	-	0	0	-	-
Air	0,200	3,60E+09	1,19	-	-	-	-	-
Water	0,300	5,40E+09	1000	-	-	-	-	-
Solid	0,500	9,00E+09	2400	0,0200	-	-	-	-
Sediment: Bulk	-	-	1280	-	50000	2083	2000	10000
Water	0,800	4,00E+08	1000	-	-	-	-	-
Solid	0,200	1,00E+08	2400	0,0400	-	-	-	-



Transport Velocity Parameters	m/h	m/y
Air side air-water MTC	5,00	43830
Water side air-water MTC	0,0500	438
Rain rate	1,00E-04	0,877
Aerosol deposition velocity	6,00E-10	5,26E-06
Soil air phase diffusion MTC	0,0200	175
Soil water phase diffusion MTC	1,00E-05	0,0877
Soil air boundary layer MTC	5,00	43830
Sediment-water MTC	1,00E-04	0,877
Sediment deposition velocity	5,00E-07	4,38E-03
Sediment resuspension velocity	2,00E-07	1,75E-03
Soil water runoff rate	5,00E-05	0,438
Soil solids runoff rate	1,00E-08	8,77E-05

Chlorpyrifos: Level 2 Fugacity Model Output



EQC
Version 2.02

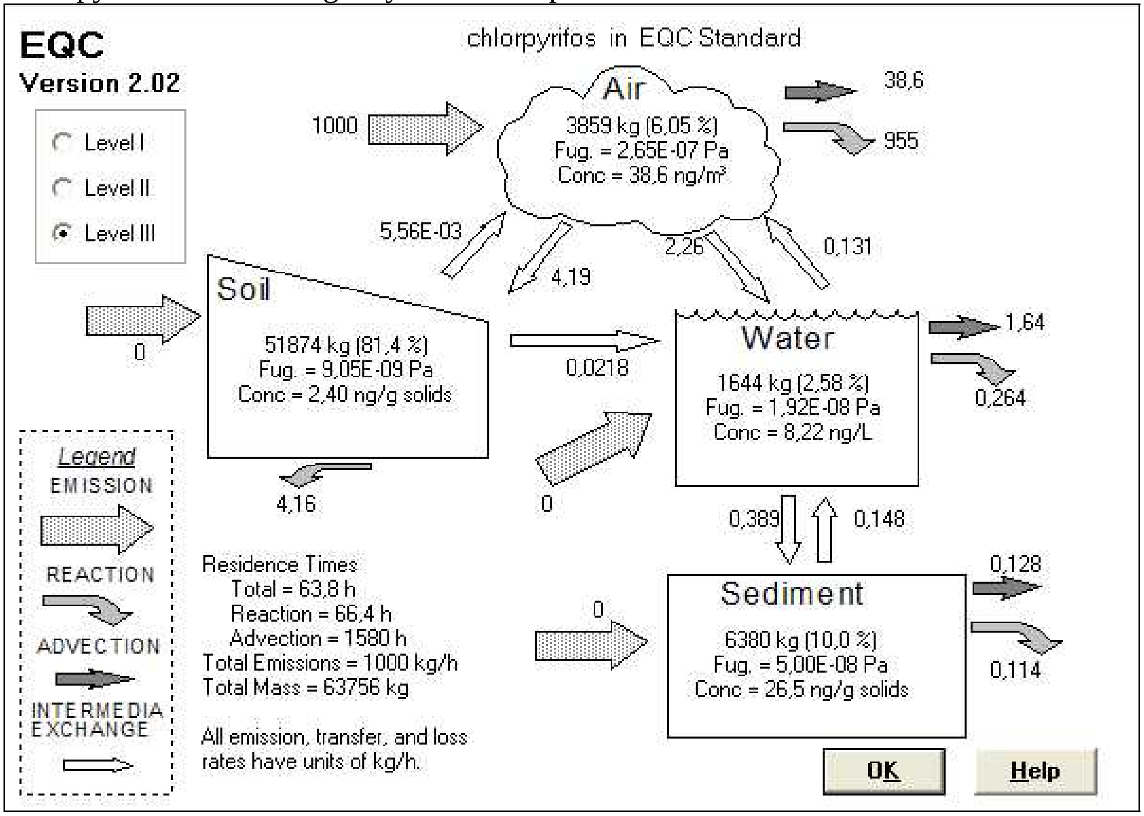
chlorpyrifos in EQC Standard

○ Level I
● Level II
○ Level III

Fugacity = 2,38E-07 Pa
Residence Times
Total = 1443 h
Reaction = 1525 h
Advection = 26757 h
Total Emission = 1000 kg
Total Mass = 1,44E+06 kg

All loss rates have units of kg/h.

Chlorpyrifos: Level 3 Fugacity Model Output



EQC
Version 2.02

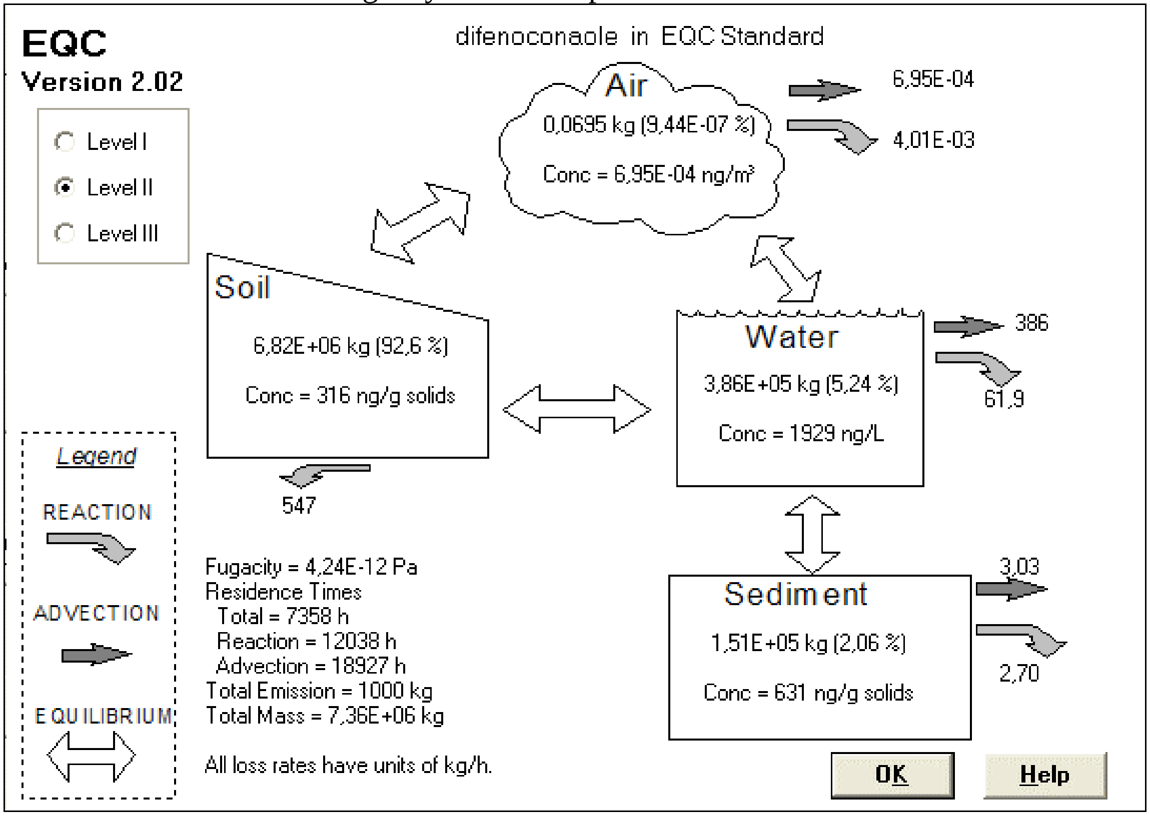
chlorpyrifos in EQC Standard

○ Level I
○ Level II
● Level III

Residence Times
Total = 63,8 h
Reaction = 66,4 h
Advection = 1580 h
Total Emissions = 1000 kg/h
Total Mass = 63756 kg

All emission, transfer, and loss rates have units of kg/h.

Difenoconazole: Level 2 Fugacity Model Output



○ Level I
● Level II
○ Level III

Air: 0,0695 kg (9,44E-07 %)
Conc = 6,95E-04 ng/m³

Soil: 6,82E+06 kg (92,6 %)
Conc = 316 ng/g solids

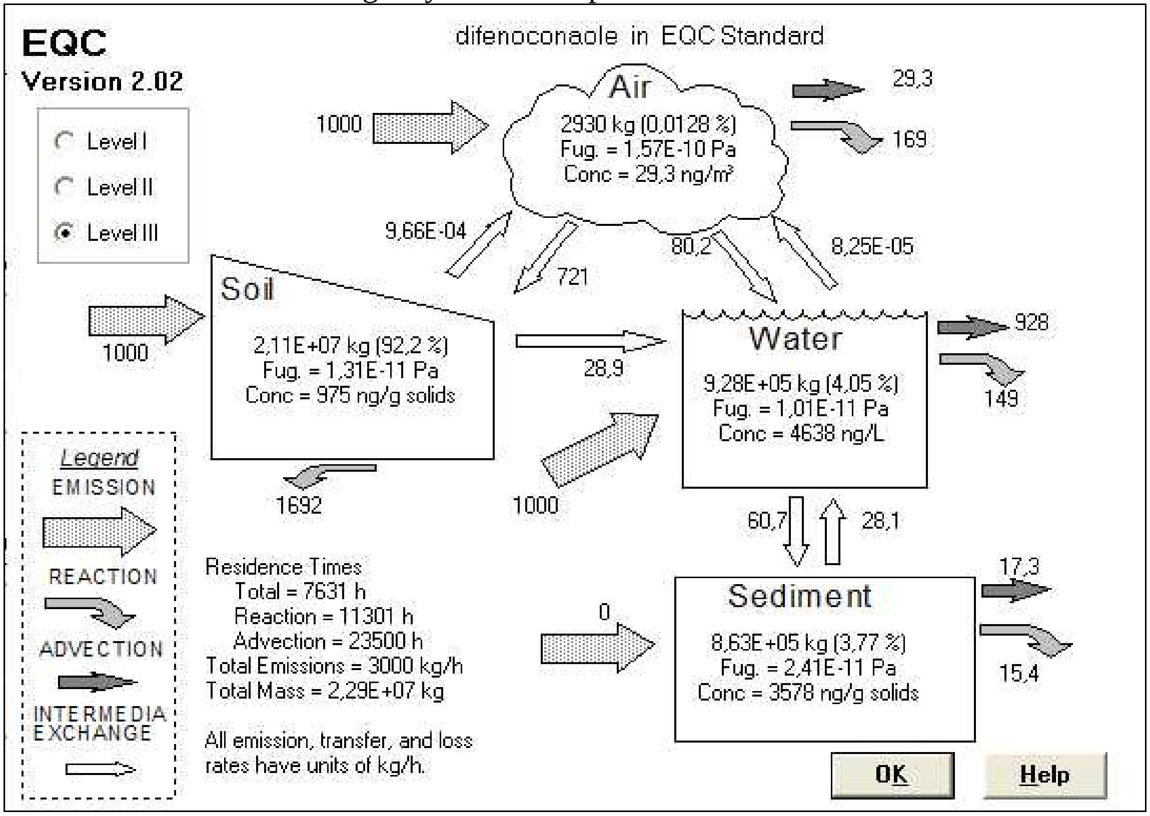
Water: 3,86E+05 kg (5,24 %)
Conc = 1929 ng/L

Sediment: 1,51E+05 kg (2,06 %)
Conc = 631 ng/g solids

Fugacity = 4,24E-12 Pa
Residence Times
Total = 7358 h
Reaction = 12038 h
Advection = 18927 h
Total Emission = 1000 kg
Total Mass = 7,36E+06 kg

All loss rates have units of kg/h.

Difenoconazole: Level 3 Fugacity Model Output



○ Level I
○ Level II
● Level III

Air: 2930 kg (0,0128 %)
Fug. = 1,57E-10 Pa
Conc = 29,3 ng/m³

Soil: 2,11E+07 kg (92,2 %)
Fug. = 1,31E-11 Pa
Conc = 975 ng/g solids

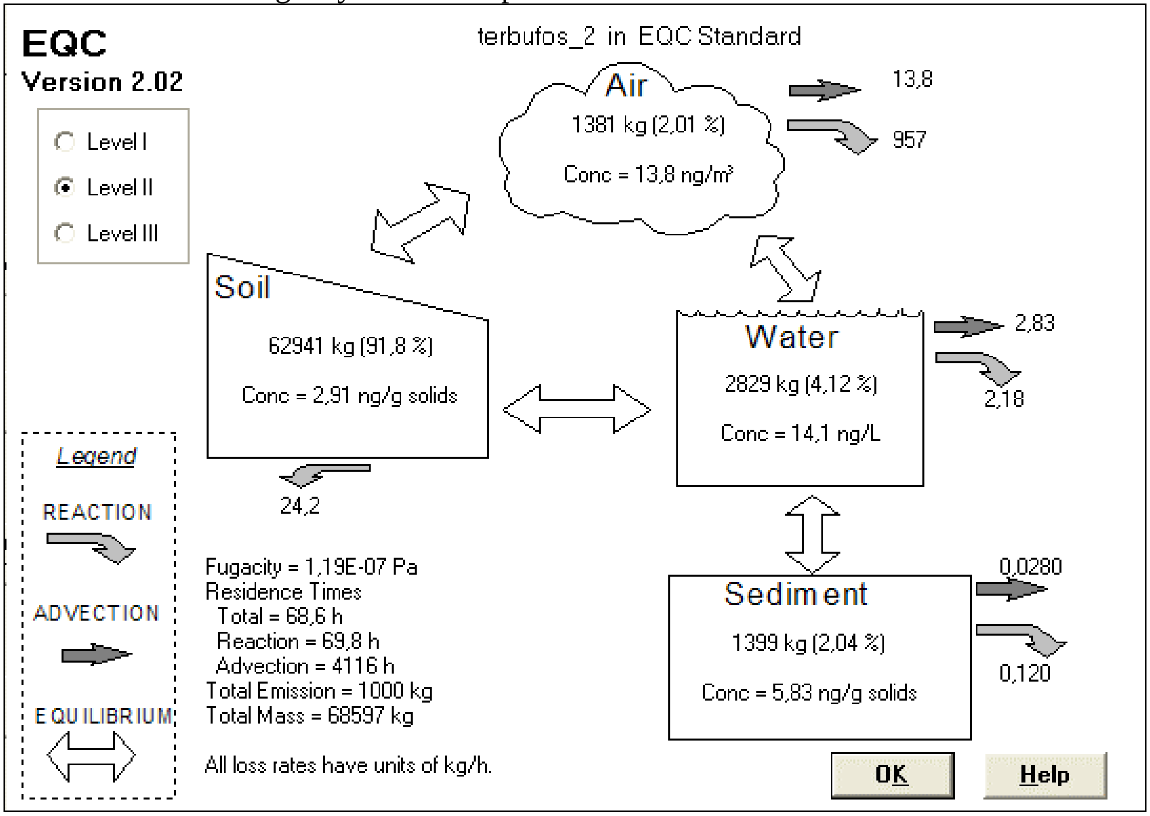
Water: 9,28E+05 kg (4,05 %)
Fug. = 1,01E-11 Pa
Conc = 4638 ng/L

Sediment: 8,63E+05 kg (3,77 %)
Fug. = 2,41E-11 Pa
Conc = 3578 ng/g solids

Residence Times
Total = 7631 h
Reaction = 11301 h
Advection = 23500 h
Total Emissions = 3000 kg/h
Total Mass = 2,29E+07 kg

All emission, transfer, and loss rates have units of kg/h.

Terbufos: Level 2 Fugacity Model Output

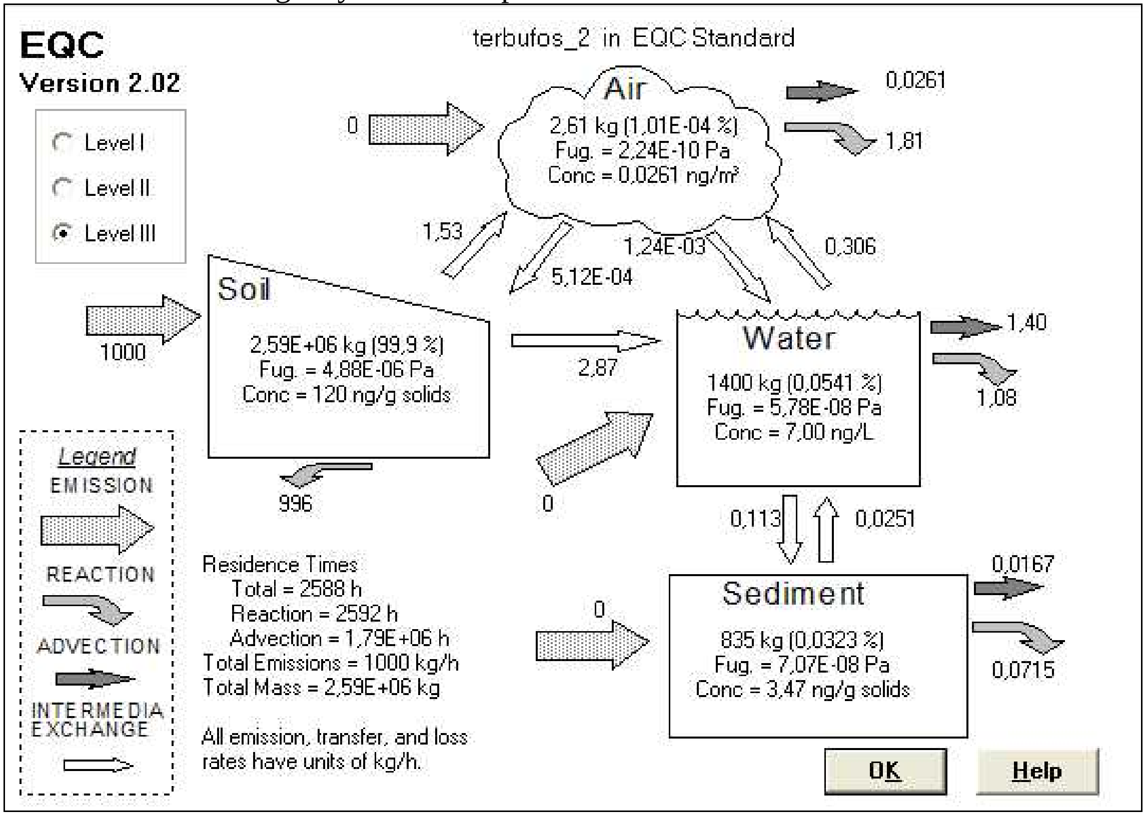


○ Level I
● Level II
○ Level III

Fugacity = 1,19E-07 Pa
Residence Times
Total = 68,6 h
Reaction = 69,8 h
Advection = 4116 h
Total Emission = 1000 kg
Total Mass = 68597 kg

All loss rates have units of kg/h.

Terbufos: Level 3 Fugacity Model Output



○ Level I
○ Level II
● Level III

Residence Times
Total = 2588 h
Reaction = 2592 h
Advection = 1,79E+06 h
Total Emissions = 1000 kg/h
Total Mass = 2,59E+06 kg

All emission, transfer, and loss rates have units of kg/h.

Predicted Environmental Concentrations (PECs) based on three drift fraction (DF) scenarios for a generic m^3 of water body based on one month application rates in the four production systems of Sixaola watershed.

Monthly Application	Intensive Banana (IB)	Intensive Plantain (IP)	Moderate Plantain (MP)	Low-Intensity Plantain (LP)
Chlorpyrifos				
Dose/month (g/ha)	720	720	480	400
PEC (μg/L) per DF				
100% Entry (DF=1)	72	72	48	40
Fugacity II (DF=0.0137)	0.99	0.99	0.66	0.55
Fugacity III (DF= 0.026)	1.87	1.87	1.25	1.04
Difenoconazole				
Dose/month (g/ha)	500	250	250	0
PEC (μg/L) per DF				
100% Entry (DF=1)	50	25	25	0
Fugacity II (DF=0.052)	2.62	1.31	1.31	0
Fugacity III (DF= 0.041)	2.03	1.01	1.01	0.00
Terbufos				
Dose/month (g/ha)	2500	2500	2500	2500
PEC (μg/L) per DF				
100% Entry (DF=1)	250	250	250	250
Fugacity II (DF=0.041)	10.3	10.3	10.3	10.3
Fugacity III (DF= 0.00054)	0.135	0.135	0.135	0.135

Appendix B: Study Site Stream Characteristics

Site Name	**Gandoca**	**Cana**	**Sandbox**	**Sixaola**	**Suretka/Margarita**	**Shirolita**	**Drinking Water**	**Aviarios Rescate**
Stream Type	Coastal lagoon	Banana Canal	Floodplain Stream	Large river - downstream	Large river - upstream	Floodplain Stream	Sixaola wells (2)	Oxbow of Estrella River
Production Regime	None	Intensive Banana	Intensive Plantain	Intensive Banana	Intensive Plantain	Moderate Plantain	Intensive B & P	Intensive Banana
# Water Samples	5	15	5	6	5	5	5	5
# SPMD months	1	3	1	2	1	1	0	0
Field Averages								
Temp C°	30.04	26.25	26.88	23.83	21.56	26.68	27.63	26.96
EC(mS/cm)	37.70	0.27	0.18	0.11	0.10	0.21	0.86	0.20
Salinity (ppt)	24.10	0.13	0.08	0.06	0.05	0.10	0.43	0.14
DO (%)	62.11	72.54	93.14	97.78	98.77	92.44	41.50	70.00
DO (mg/L)	4.03	5.85	7.43	8.14	8.72	7.40	3.30	5.52
pH	7.78	7.31	7.58	8.25	7.05	7.08	6.71	7.17
V (m/s)	N/A	0.08	0.29	0.87	0.96	0.34	N/A	0.00
Est. Width (m)	N/A	18.85	4.15	132.53	56.25	9.58	N/A	5.75
Est. Depth (m)	N/A	1.43	0.17	2.98	4.25	0.37	N/A	1.30
Est Q(m3/s)	N/A	3.12	0.24	337.19	248.83	1.49	N/A	0.00
TSS (g/L)		0.092	0.002	0.234		0.011		
Field Snapshot								
Time of Day	1:00 p.m.	11:30 a.m.	10:00 a.m.	11:00 a.m.	8:30 a.m.	8:00 a.m.	12:00 p.m.	4:00 p.m.
Temp C°	27.9	28.8	26.8	28.1	23.1	24.1	28.9	29.7
EC (mS)	18.59	0.26	0.19	0.14	0.14	0.21	0.16	0.48
Salinity (ppt)	11.96	0.12	0.09	0.06	0.07	0.10	0.07	0.23
Flow (m3/s)	0.0	0.0	0.10	105.0	56.2	0.0	0.0	0.0
DO (%)	41.3	70.0	118.8	104.0	112.0	86.1	53.0	111.8
DO (mg/L)	2.9	4.6	9.0	7.7	9.4	6.6	3.5	7.45
pH Field	7.4	7.7	8.7	7.8	8.2	7.9	6.6	7.8

Site Name	**Gandoca**	**Cana**	**Sandbox**	**Sixaola**	**Suretka/Margarita**	**Shirolita**	**Drinking Water**	**Aviarios Rescate**
Snapshot LAB								
pH Lab	7.3	7.7	8.1	7.7	8.0	7.9	6.9	8.0
EC(mS)	2.26	0.26	0.20	0.14	0.15	0.22	0.16	0.47
Alkalinity	53.6	97.8	69.7	60.4	69.7	108.8	76.5	170.9
Hardness	263.3	97.2	70.5	53.8	60.1	93.6	63.7	158.5
Ca (mg/L)	23.3	26.8	19.0	16.5	18.5	27.2	16.4	39.6
Mg (mg/L)	49.82	7.38	5.61	3.09	3.41	6.23	5.51	14.49
K (mg/L)	15.96	2.73	1.92	0.96	0.98	2.09	0.33	2.66
Na (mg/L)	382.21	12.14	11.57	5.40	5.67	7.70	8.03	41.16
Cl^-(mg/L)	629.34	12.28	5.37	0.77	2.30	3.84	3.07	33.77
$PO4^{-3}$ (mg/L)	0.49	0.34	0.18	0.16	0.09	0.20	0.20	0.49
$NH4^+$-N (mg/L)	0.05	0.23	0.05	0.04	0.05	0.06	0.08	0.05
$NO3^-$-N(mg/L)	0.05	2.10	N.D.	0.03	0.02	0.03	N.D.	0.05
Sediments (0.425 mm)								
% N	0.31	0.13	0.07	0.16	0.02	0.12	N/A	N/A
% C	4.26	1.50	0.54	1.79	0.16	1.27	N/A	N/A
% S	0.85	0.06	0.04	0.06	0.02	0.07	N/A	N/A
Fish Diversity								
Total Species		12	13			15		
Dominant species		*Poecilia gillii* *Astyanax* *Aeneus* *Awaous banana*	*Poecilia gillii* *Sicydium spp.* *Astyanax* *Aeneus* *Agonostomos monticola*			*Poecilia gillii* *Astyanax* *Aeneus*		

Appendix C: Selected Acute and Chronic Toxicity Values

Pesticide	Acute 96 hr LC50	Chronic MATC	Species Type	Species Name	Reference
Chlorpyrifos	µg/L	µg/L			
	0.30	0.100	Daphnia	*Daphnia magna. longispina*	Barron and Woodburn 1995, Van Wijngaarden et al. 1993
	0.07		Amphipod	*Rhepoxynius abronius*	Barron and Woodburn 1995, PAN 2007
	0.08		Shrimp	*Paratya australiensis*	PAN 2007, Olima and Pablo 1997
	0.40		Fish: Tidewater Silverside	*Menidia peninsulae*	PAN 2007, Borthwick et al. 1985
	0.19		Marine Amphipod	*Gammarus palustris*	PAN 2007, Leight and Van Dolah 1999
	0.05		California Freshwater FAV		Siepmann and Finlayson 2002
	0.03		California Saltwater FAV		Siepmann and Finlayson 2002
		0.004	Marine shrimp	*Mysidopsis bahia*	Barron and Woodburn 1995
		0.014	California Freshwater FCV		Siepmann and Finlayson 2002
		0.009	California Saltwater FCV		Siepmann and Finlayson 2002
Difenoconazole	µg/L	µg/L			
	770		Daphnia	*Daphnia magna*	Agriliance MSDS
	150		Opossum Shrimp	*Americamysis bahia*	PAN 2007
	800		Fish: Rainbow Trout	*Oncorhynchus mykiss*	IRET 1999
	410		Sheepshead minnow	*Cyprinodon variegatus*	PAN 2007
		8.70	Daphnia Early Life Stage	*Daphnia Magna*	Agriliance MSDS
		5.60	Fish Early Life Stage	*Pimephales promelas*	Agriliance MSDS
Terbufos	µg/L	µg/L			
	0.31		Daphnia	*Daphnia magna*	EcotoxNet 2007, IRET 1999
	0.22		Opossum Shrimp	*Americamysis bahia*	PAN 2007
	0.17		Scud	*Gammarus pseudolimnaeus*	PAN 2007, Howe et al.1994
	0.77*		Bluegill Sunfish	*Lepomis macrochirus*	USEPA 1999* Time not reported
	1.80		Bluegill Sunfish	*Lepomis macrochirus*	USEPA 1999
		1.40**	Rainbow Trout	*Oncorhynchus mykiss*	USEPA 1999 ** Estimated
		0.048	Daphnia	*Daphnia magna*	USEPA 1999
		0.030	Daphnia	*Daphnia magna*	USEPA 1999

Appendix D: Acute and Chronic Risk Quotients for Stream Sites

Acute Risk Factors (N/D = pesticide was not detected in samples so no risk calculation)
Observed or predicted environmental concentration/acute no effect concentration

Study Site	**Cana**	**Sixaola**	**Margarita**	**Sandbox**	**Shirolita**
Production	Intensive	Intensive	Intensive	Intensive	Moderate
Regime	Banana	Banana	Plantain	Plantain	Plantain
Chlorpyrifos Risk					
PEC1 (DF1=100%)	3333.75	225	400	128625	17137.5
PEC 2 (DF2 = 1.3%)	46.25	2.5	5	1761.25	235
PEC3 (DF3 = 2.6%)	86.25	6.25	10	3337.5	667.5
Field Water Average	N/D	N/D	N/D	N/D	N/D
SPMD Average	0.0041	0.0004	0.0002	0.0002	0.0002
Difenoconazole Risk					
PEC1 (DF1=100%)	6.349	0.083	0.074	23.807	4.762
PEC2 (DF2 = 5.2%)	0.333	0.005	0.004	1.247	0.249
PEC3 (DF3 = 4.0%)	0.257	0.003	0.003	0.964	0.193
Field Water Average	0.333	N/D	N/D	N/D	0.2000
SPMD Average	0.0000	N/D	N/D	N/D	N/D
Terbufos Risk					
PEC1 (DF1=100%)	5446.47	367.65	653.53	210058.82	42017.65
PEC2 (DF2= 4.1%)	224.12	15.29	27.06	8652.94	1731.18
PEC3 (DF3 = 0.05%)	2.94	0.18	0.35	113.53	22.35
Field Water Average	N/D	N/D	N/D	N/D	N/D
SPMD Average	0.0008	0.0004	N/D	N/D	N/D

Chronic Risk Factors (N/D = pesticide was not detected in samples so no risk calculation)
Observed or predicted environmental concentration/chronic no effect concentration

Study Site	**Cana**	**Sixaola**	**Margarita**	**Sandbox**	**Shirolita**
Production	Intensive	Intensive	Intensive	Intensive	Moderate
Regime	Banana	Banana	Plantain	Plantain	Plantain
Chlorpyrifos Risk					
PEC1 (DF1=100%)	6667.5	450	800	257250	34275
PEC 2 (DF2 = 1.3%)	92.5	5	10	3522.5	470
PEC3 (DF3 = 2.6%)	172.5	12.5	20	6675	1335
Field Water Average	N/D	N/D	N/D	N/D	N/D
SPMD Average	0.0082	0.0009	0.0004	0.0004	0.0004
Difenoconazole Risk					
PEC1 (DF1=100%)	17.005	0.223	0.198	63.768	12.755
PEC2 (DF2 = 5.2%)	0.891	0.013	0.011	3.341	0.668
PEC3 (DF3 = 4.0%)	0.689	0.009	0.009	2.582	0.516
Field Water Average	0.89	N/D	N/D	N/D	0.54
SPMD Average	0.00004	N/D	N/D	N/D	N/D
Terbufos Risk					
PEC1 (DF1=100%)	3086.3	208.3	370.3	119033.3	23810.0
PEC2 (DF2= 4.1%)	127.0	8.7	15.3	4903.3	981.0
PEC3 (DF3 = 0.05%)	1.7	0.1	0.2	64.3	12.7
Field Water Average	N/D	N/D	N/D	N/D	N/D
SPMD Average	0.0004	0.0002	N/D	N/D	N/D

Appendix E: Quebrada Cana Fish Kill Data

Three fish kills were personally observed in the Quebrada Cana (October 29 2005, May 1 2006, and May 29 2006), although local community members have reported many more at the same site over the 18 month study period. A summary of field measurements made during the latter two events are reported below.

Minimum Species mortality** (Taxa and maximum body length observed)

Family Name	**Species Observed**	**Common Name**	**Noted Body Length**
Palaemonidae	*Macrobrachium spp.*	camarón negro	10 cm
Palaemonidae	*Macrobrachium spp.*	camarón claro	8 cm
Eleotridae	*Gobiomorus dormitor*	gauvina	30 cm
Centropomidae	*Centropomus spp.*	snook o sábalo	20 cm, 55 cm, 1 meter
Haemulidae	*Pomadasys crocro*	ronco o roncador	5 cm
Eleotridae	*Eleotris spp.*	pez perro	10 cm

** Two fish species (Poecilia gillii - family Poeciliidae and Astyanax aeneus- family Characidae) were observed surviving by repeatedly sucking air from the surface.

	May 1 2006	May 29 2006
Time of day	12:30 p.m.	9:30 a.m.
Temperature °C	29.0	27.9
Dissolved Oxygen (mg/L)	4.5	5.25
Conductivity (mS)	0.259	0.336
Salinity (ppt)	0.12	0.16
pH	7.7	7.7
Hardness (mg $CaCO_3$/L)	97.2	
Calcium (mg/L)	26.75	
Magnesium (mg/L)	7.3	
Potassium (mg/L)	2.7	
Sodium (mg/L)	12.14	
Chloride (mg/L)	12.3	
Phosphate (mg/L)	0.36	
Ammonium (mg/L)	0.23	
Nitrate (mg/L)	2.18	
Stream width (m)	26	25
Stream depth (m)	3.0	2.1
Flow velocity (m/s)	0.0	0.0
SPMD * - Chlorpyrifos μg/L	Not sampled	0.0000075
SPMD *- Difenoconazole μg/L	Not sampled	0.00001
SPMD * - Terbufos μg/L	Not sampled	0.00002
Water Grab Sample Difenoconazole μg/L	Not sampled	0.3

* Time-weighted average for 4 day (96 hr) SPMD samplers (Chapter 3) using Rs=5.0 L/d