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Sampling of Agrochemicals for Environmental Assessment in Rice Paddies: Dry Tropical Wetlands, Costa Rica

by Hugo A. Loaiciga and Timothy H. Robinson

Abstract

This paper presents results from a preliminary sampling strategy developed to track agricultural contaminants found in surface and subsurface media and used commonly in rice paddy cultivation in the dry, tropical forest coastal region of Guanacaste, Costa Rica. The emphasis is on the impact of eight indicator pesticides, five forms of nitrogen and phosphorus that are common nutrients found in fertilizers. After the field sampling strategy was developed, soil and water samples were collected twice: once during the beginning of the wet season and once during the initiation of the dry season. Hydrological parameters, soil classifications, agricultural product toxicology, irrigation and drainage networks, cultivated areas, land ownership, and pristine environments have been studied, mapped, and entered into a database in order to understand the spatial and temporal distribution of potential contaminants and their pending ecological degradation. Alternative crops and agricultural practices are suggested to reduce or eliminate impacts on biological preserves. Database development and basin characteristics have been entered into a Geographic Information System (GIS) that is capable of fully integrating suggested site modeling. Field sampling results indicate that proposed rice paddy cultivation in a relatively undisturbed basin is likely to have minimal impact on downstream biological preserves.

Introduction

The large delta region of the Tempisque and Bebedero Rivers in the northwestern province of Guanacaste, Costa Rica, contains favorable soils and growing conditions for the cultivation of rice. A continuous and reliable water supply to support irrigation of this crop is lacking in this tropical latitude (10° N, 84° W; see Figure 1), characterized by a strong dry (December-April) and wet (May-November) seasonal, cyclic climatic pattern. The Costa Rican agency responsible for irrigation projects, the National Ground Water Irrigation and Drainage Services (SENARA), has submitted a proposal to the International Development Bank to construct an irrigation canal that will bring more than 25 m³/s of water from a Caribbean watershed across the central Cordillera by conduit and open canal to the region under study. The assessment of the construction of the irrigation canal, referred to as the Western Canal, is complete. This interbasin water transfer across the continental divide is part of Costa Rica's largest irrigation undertaking to this date and is known as the Arenal-Tempisque Irrigation Project (Suarez et al. 1986). What follows is an analysis of the possible impact from the proposed development of 5163 hectares (1 hectare = 2.47 acres) located at Tamarindo Ranch, a province of Guanacaste, Costa Rica, which lie in the micro drainage of La Quebrada La Mula (La Mula Creek). SENARA hopes to develop the said area into rice paddies that would naturally discharge directly into the downstream

Palo Verde National Park, known for its wetland ecosystems and abundant waterfowl (Janzen 1983; Boza 1988). Major questions addressed by the study are (1) Can the development be done without negatively influencing the preserved lands of the Palo Verde National Park; and (2) If not, What would the likely impacts and possible alternatives be?

The evaluation of potential agrochemical contamination of these wetland ecosystems from the effluents of rice paddies requires a careful and comprehensive field sampling strategy for agrochemical concentrations in soils and effluent waters. Given the cyclical nature of pesticide and fertilizer application, it is difficult to acquire conclusive data through field sampling alone because contaminant peaks can be short and sporadic. By the construction of a Geographic Information System Database (ARC/INFO) (ESRI 1991), data generated by both field measurement and models can be archived, analyzed, and graphically displayed for high-quality output (Leipnik et al. 1993; Leipnik 1995). Field sampling was the primary focus of this study, but many of the input parameters for water quality modeling are provided and can be used with models of multiple component migration in future research efforts.

Water Quality Contamination Potential and Site Geology

Potential Migration Paths

The study area is situated just north and upslope from Palo Verde National Park and preserved wetland habitats in the northwestern region of Costa Rica (see Figure 1 for general location). The basin under study, La Quebrada La Mula, was an old cattle ranch that was once deforested for grazing but has lain fallow for many years, enabling second-growth forest to establish. If developed into rice paddies, the flat, central area of the basin will be terraced, making possible agricultural chemical migration from the paddies to the ecologically sensitive lagoons of the Park lands. The natural drainage of the La Quebrada La Mula Basin discharges stream effluent at the lower point in the region, El Bocano La Mula, a small ephemeral lake just inside the northern national park boundary. Once the lake has filled, water will overflow into the lower regions of the Tempisque River delta, the predominant regional hydrographic and fluvial feature. The receiving delta is parched with numerous perennial lagoons of various sizes. Estuarial marshlands also abound therein. This series of steps — namely, (i) effluent discharge from rice paddies, (ii) lake overflow, and (iii) fluvial transport through water bodies in the delta region — poses a potential contamination pathway to the wetland ecosystems.

Regional Geology

The geology of the study region is dominated by fluvial deposits throughout the upper reaches of the delta and marshy mangrove swamps near the river margins within 25 km of the confluence of the Bebedero and Tempisque Rivers and the Gulf of Nicoya, Pacific

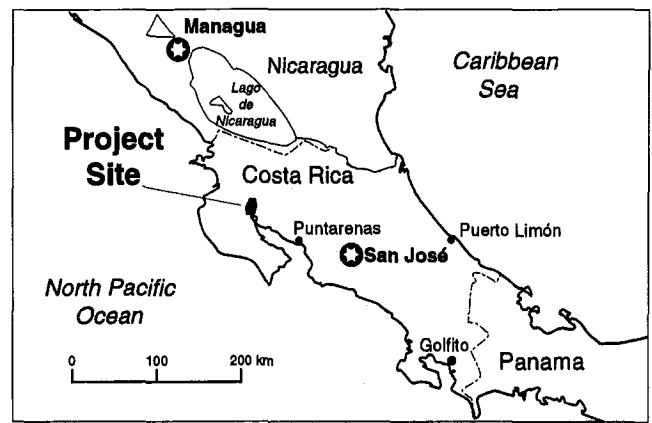


Figure 1. General view of project site.

Ocean. The depositional basin of the Tempisque Depression is bordered to the north by the Bagaces Formation, described as fluvial and sedimentary deposits interwoven with columnar basalt lava flows, and denotes the beginning of the volcanic pediment of the Central Cordillera of Costa Rica (Dengo 1962). The depositional basin is bordered on the south by the Liberia Formation, a fluvio-lacustrine deposit with some interbedding of granular rhyolite and pumice. Abrupt limestone buttes composed of reef deposits of homogeneous texture, the Barra Honda and Brita Formations, bisect the delta plain and provide for a natural break between the preserved and agricultural lands, through a conspicuous drop in topographic elevation in the area. The Brita Formation is distinguished by fine-textured and well-stratified volcanic lenses appearing within the limestone (Bergoeing 1983).

Exact cross sections of the study area do not exist, and well logs for the area are rare. Hence, site-specific information was difficult to gather. Table 1 presents hydrogeologic data and was generated from geologic reviews, scattered well logs (compiled by SENARA 1976-1986; 1989), and well data presented in the master

Formation Name	Aquifer Thickness (m)	Transmissivity (m ² /day)	Water Quality
Alluvium	60	60-320	Good to Mediocre
Liberia	100	10	Low pH and low TDS
Bagaces	350	77	Excellent
Brita	600	No data	Limited Data
Barra Honda	300	No data	Limited Data
Nicoya Complex	No data	66	Good

TDS: Total Dissolved Solids.

plan (Bel Ingenieria and Bookman-Edmonston Engineering Inc. 1978) for the entire Arenal-Tempisque Irrigation Project, of which the study area is a part. In spite of inherent limitations, the data in Table 1 is valuable for understanding the general hydrogeology of the study area.

Major water bearing formations are shown in Table 1, including transmissivity, flow capacity, stratigraphy, and water quality generalized indicators. From well logs collected by SENARA (1989) and field observations, these aquifers are, for the most part, not affected by near-surface events such as agriculture and irrigation infiltration and are primarily recharged along basin margins where outcropping occurs. Aquifer vulnerability from vertical contaminant migration is strongly impaired by the thick, impermeable clay lenses of the surficial alluvium that are prevalent in the depositional basin of the desired agricultural area.

Basin Soil Characteristics

Particle Size Distribution

Basin soil hydrologic parameters were established by sampling along five transects, each perpendicular to the stream course and equally spaced throughout the basin, as shown in Figure 2. Particle size distribution analyses for soils from the study area were carried out by hydrometer (Gee and Bauder 1986; Klute 1986), based on Stoke's Law (see, e.g., Hillel 1982). Samples were extracted from each apparent soil horizon at three separate soil pits dug along each transect shown in Figure 2. Results showed an average of 16 percent sand, 26 percent silt, and 55 percent clay for the A horizon; 10 percent sand, 27 percent silt, and 61 percent clay for the B horizon; and 14 percent sand, 15 percent silt, and 71 percent clay for the C horizon. PH was near 7 in the upper horizons and slightly alkaline at depth. Mean horizon temperatures did not vary over 2°C from the surface horizons at mean 30°C to 28°C at depth measured during daylight hours. The mean biotemperature in this life zone, classified as dry tropical forest, according to Holdridge (1967), is approximately 25°C. Mean annual rainfall is close to 1200 mm/yr (Hartshorn 1983).

Soil Classification

Soil pits were dug out along the transects, shown in Figure 2, one per transect, to a depth of approximately 1 meter. Soil samples were taken for each apparent soil horizon. The soils were classified according to the U.S. Department of Agriculture (USDA) soil classification scheme (see, e.g., Brady 1990). Of the 11 soil orders described in the classification, undoubtedly these soils are vertisols (Dudal and Eswaram 1988). Field observations and laboratory analyses revealed that they have minimal to no B horizon, are average in carbon content, have a particle size distribution high in clays, and have a massive structure with low hydraulic conductivity, stable temperature regime, and typical geographical location and pedon color. Working through the various

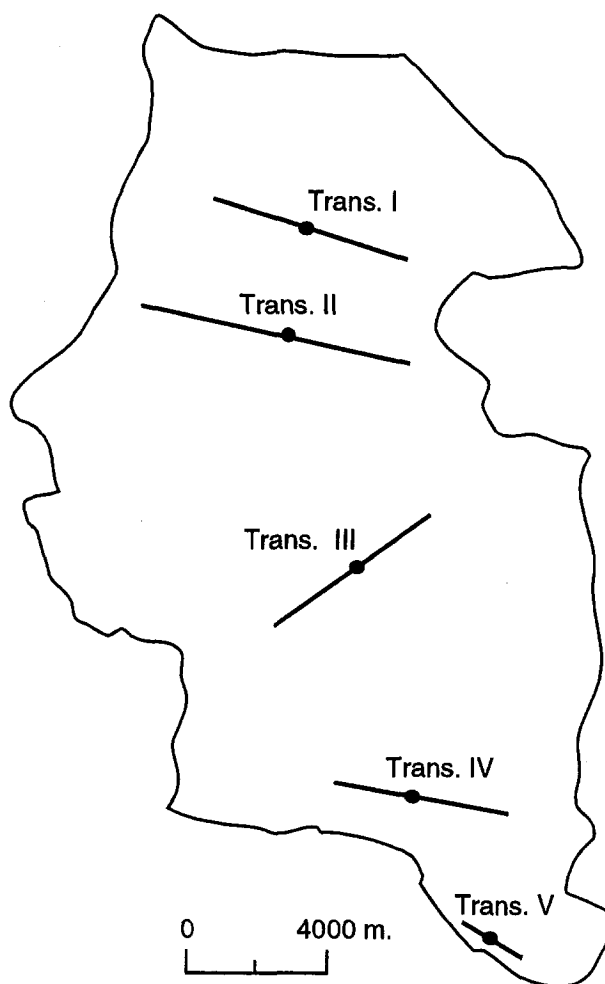


Figure 2. Transect locations in Quebrada La Mula Basin.

characteristics and descriptions in the USDA's soil taxonomy led to a classification of these soils as *type pelluserts*: fine, mixed, and isohypothermic.

Bulk Density

Bulk density of soil samples, shown in Table 2 by soil horizon, was calculated through field testing using a 100 mL-sample coring device that extracted soil samples without disrupting in situ conditions. The samples were run through a Daiki DIK-1120 Three-Phase Meter (Daiki Rika Kogyo Co. 1990) to test for bulk density, i.e., grams of the extracted soil over the in situ (bulk) volume. The field results, shown in Table 2, had standard deviations on the order of ± 10 percent of mean values. There appeared to be a general trend

Soil Horizon	I	III	IV	Average	Standard Deviation
A	1.42	1.26	1.19	1.29	0.13
B	1.64	1.35	1.34	1.44	0.22
C	1.59	1.41	1.10	1.37	0.18

See figure 2 for location of transects I, III, and IV.

of increasing bulk density with increasing depth for all sites sampled. Prior to the field tests, Vazquez (1972) had reported mean bulk densities of 1.27 gr/cc, 1.22 gr/cc, and 1.18 gr/cc for the horizons A, B, and C, respectively, from soil pits dug out some 50 km to the northwest of the study area, but still in the Tempisque River flood plain. The differences between those prior values and the values presented in Table 2 are attributed to soil differentiation over such distance.

Infiltration

Infiltration was studied along the central longitudinal axis of the basin to assist in the characterization of the basin soils and vadose zone properties. However, the focus of this project was off-site environmental degradation. For this reason, infiltration and hydraulic conductivity were studied more intensely toward the end of the drainage basin along transect IV (see Figure 2), where contaminants are likely to be released. Infiltration was measured using a double-ring infiltrometer (Burgy and Luthin 1956; Bouwer 1986), and the results for dry and wet season testing are as shown in Table 3. Because of the length of each test, man-hours needed, and other logistical and seasonal difficulties associated with infiltrometer measurements of infiltration rates, it was possible to acquire only part of the desired data according to the overall sampling design. The latter consisted of preplanned field measurements at three sites evenly distributed along the transects shown in Figure 2. The infiltrometer measurements were attempted, but either flooded conditions or large macropore cracks made the test impossible at various of the preplanned measuring sites. The successful measurements, however, indicated that infiltration rates decreased with topography toward the center of the basin and downstream along its central longitudinal axis toward the Palo Verde biological preserve. The lowest measured values were found to be 0.1 cm/hr and 1.6 cm/hr for the wet and dry seasons, respectively (see Table 3).

Hydraulic Conductivity

Hydraulic conductivity (K) measurements were conducted in two different ways. The first was done in situ, using an Eijkelkamp Hydraulic Conductivity Test Kit. The reverse Hooghoudt Method was applied, as field measurements were conducted under unsaturated conditions. Because large soil cracks were widely found in the area, it was felt that there was high probability for error in the upper soil horizons, as the water placed in the auger hole rapidly traveled laterally in the cracked soil zone and substantially slowed down in the non-cracked zone below. The in situ measurements of hydraulic conductivity indeed turned out to be too high, as shown in Table 4. To avoid the effects of cracks on conductivity under unsaturated conditions (and remembering that soil under rice paddies is flooded and saturated), soil samples for different horizons along transects IV and V were taken and flown back to the Vadose Zone Monitoring Laboratory (VZML) of the University of California at Santa Barbara (UCSB). These soils were

Transect	1		2		3	
	Dry ¹	Dry ¹	Wet ²	Dry ¹	Wet ²	Dry ¹
I						
cm/hr	-	-	1.7	-	-	-
m/day	-	-	0.4	-	-	-
IV						
cm/hr	4.4	1.6	0.1	2.7		
m/day	1.1	0.4	0.02	0.7		

¹December 1991
²August 1992
Refer to Figure 2 for location of transects.

Transect	Sample		
	1	2	3
IV			
cm/sec	0.0008	0.0005	0.0011
m/day	0.675	0.457	0.912
V			
cm/sec	0.0009	-	-
m/day	0.778	-	-

Refer to Figure 2 for location of transects.

Horizon	K	
	cm/hr	m/day
A	0.00045	0.39
B	0.000066	0.06
C	0.000028	0.02

dried, ground, and repacked to field-measured bulk densities to best simulate in situ conditions. Laboratory values of hydraulic conductivity of the repacked samples for all three horizons were then measured with constant head permeameters (Klute and Dirksen 1986); mean values are reported in Table 5. These latter estimates of K appear to be more consistent with field hydraulic characteristics of soils under saturated conditions.

Summary of Basin Hydrogeologic Characteristics

Clay content increased with depth farther downslope in the Quebrada La Mula Basin, toward the Palo Verde National Park, and toward its center. This is a naturally

occurring condition propitious for rice paddy water retention and for holding migratory contaminants on-site. The high clay percentage throughout the basin should produce slow migration of surface waters into the substrata and aquifers below. Low infiltration rates supported this conclusion, as contaminant migration into underlying aquifers would be negligible. The potential for aquifer vulnerability to migratory surface contamination in Quebrada La Mula Basin appears quite low when the soil is saturated.

Low hydraulic conductivity values indicated low ground water propensity to surface contamination given the slow movement of any contaminant plume. Ground water vulnerability appears to be an issue only in localized areas where clay aquitards may not be present. Macropores from soil cracks, characteristics of vertisols, could enable rapid movement of surface contaminants both vertically and horizontally through the soil profile when the soils are not saturated. If agricultural practices were modified to restrict agrochemical applications to rice paddies only after the fields have been flooded, the chance of rapid migration via macropores would be reduced or eliminated. If this idea were to be put into practice, analytical sampling could be limited to surface water and surface soils only.

Rice Paddy Cultivation

The majority of rice grown in the province of Guanacaste, Costa Rica, is in flooded fields or paddies. In contrast, there is some upland rice grown on the flanks of the Central Cordillera, but the amount of acreage is insignificant in comparison. The species of rice cultivated in paddies is *oryza sativa communis*, a medium-to long-grained white rice. The varieties most popular in Costa Rica are CR-1821, CR-5772, and CR-113, with the former being the most common (Sanabria 1988). These are hybrid varieties developed for Costa Rica. Other specialty varieties are grown, although their acreage is relatively small in comparison.

There are two cropping cycles per year. The dry and wet season cropping periods run from January to May and from July to November, respectively, given fluctuations in the climate cycle. Periods in between are used for field preparations and machinery repairs. The interval from planting to harvest ranges from 110 to 140 days, depending on the rice variety and the amount of sunlight (Monge 1989). Yields of rice range from 3 to 4 tons per hectare for the wet season and 5 to 6 tons per hectare for the dry season (Sanabria 1991). On average, the dry season yields are quite high, indicating favorable growing conditions in Guanacaste and relatively high use of fertilizers (Yagi 1993).

Throughout the Arenal/Tempisque Irrigation Project of Guanacaste there are hundreds of agrochemicals used for various crops at varying frequency. The following discussion focuses on the pesticides, herbicides, and fertilizers used in rice paddy cultivation, specifically in the area with the closest proximity to the microbasin La Quebrada La Mula and to three other basins cultivated with rice that were included in this study for com-

parative purposes. General agrochemical application amounts will set the background information for the ensuing sections on pesticide and nutrient characteristics. Agrochemical application exhibits a high variability from season to season and from farm to farm. The ensuing information was compiled from farm records kept at nearby Rancho Pelón de la Bajura (Loaiciga 1990) and from the rice paddy irrigation project managed by SENARA at the location of Bagatzi, adjacent to the study site (Ajun 1991).

Dry to wet seasonal variations in agrochemical application rates used for rice paddy cultivation are pronounced. During the summer or dry season crop, there are fewer incidents of plagues and blights. Therefore, fewer applications of fungicides and insecticides are needed. Many pervasive weeds such as *penoly mientor* grow vigorously in the paddies throughout these dry months because of the long hours of sunlight at these equatorial latitudes. Often they can be controlled by raising paddy water levels. Nevertheless, herbicide use in general is higher during the dry months of the year. Fertilizers are also applied at higher amounts during the summer to capitalize on favorable growing conditions. Farmers clean their drainage canals once a year. Cleaning is routinely done with machinery after application of a herbicide such as Paraquat, Round-Up, Gliforato, or Tordon 101 (Ajun 1991).

Actual field applications of agrochemicals were difficult to obtain since they vary from farm to farm, year to year. It is the rare farm that actually records its agrochemical use per unit area (hectare), and, more often than not, the rule is "apply when needed" for any agrochemical. Each farm sampled in the study used approximately the same products and amounts of applied product per unit area. Limited variation came with some of the more expensive agrochemicals because of cost and local specialized pest or weed problems. Rice yields also vary from season to season. For the dry season, yields can be as high as 8.0 tons per hectare and average 5.3 tons per hectare. During the wet season, the greatest yields are 6.8 tons per hectare with an average of 4.8 tons per hectare. The difference in seasonal rice yields is due to seasonal variations in the amount of sunlight (higher in the dry season) (Sanabria 1991).

Methodology

Field Sampling

A field sampling strategy was developed to understand the potential environmental impacts to the national park land of Palo Verde from applied agricultural products upstream. La Quebrada La Mula drainage basin was used as the control since it is a relatively pristine basin used for very limited cattle grazing and is under consideration as a potential rice paddy irrigation project. In other words, the soil and water chemical composition at La Quebrada La Mula Basin was the basis to establish background levels against which to compare the field concentrations found in areas where past agrochemical applications have occurred. After

establishing a sampling protocol, samples taken from Quebrada La Mula Basin were compared to water and soil samples extracted from three morphologically similar basins. All three basins were under rice paddy cultivation. Basin contaminants in each case would be expected to reach off-site ecosystems via effluent drainage canals. Therefore, the focus of the sampling design was on water and soil in the pathways of the effluent releases. Laboratory analyses of the samples were conducted to characterize pesticide and fertilizer residual present in the water and soils of principal effluent canals, which drain the selected basins. Sampling these canals presented the best chance of identifying the highest concentration of agrochemicals present in the drainage system from cultivated lands because the drainage canals are the principal pathways for contaminants. A map of contaminant concentration was then produced to demonstrate the spatial decay of agrochemical concentrations as one moves away from identified contaminant sources. A discussion of Geographic Information Systems (GIS) mapping in this study follows.

The three sampling basins to be compared to the control basin were carefully chosen for similarity in the following: (1) number of hectares in paddy rice cultivation; (2) exclusive rice cropping since initiation of the cultivation in each basin; and (3) rice paddy effluent leaving the farm via a principal drainage canal of comparable length. The basin sites chosen for comparative sampling — Pelòn de la Bajura, Rancho Horizonte, and Bagatzi — are all within 60 km of each other on the northern fringe of the floodplains of the Bebedero and Tempisque Rivers. By design, each basin site exhibited a wide variance in the number of years they have been under rice cultivation (i.e., 45, 15, and eight years for Pelòn de la Bajura, Rancho Horizonte, and Bagatzi, respectively). The variation of years under exclusive paddy cultivation allows for any buildup of residuals over time. In addition, to get an idea of residual decay with distance along the drainage canals in each of the three basins, sampling was done in three locations along their main canals: (i) the starting point of the canal; (ii) halfway to the discharge point; and (iii) just up channel from any tidal influences at the canal's termination. Vertical (paired) water samples of approximately 125 mL each were taken from 1 inch below the water surface to a few inches above the canal bottom, being careful not to take any surface water or saltating bedload sediment. The water samples were carefully handled to avoid extraneous contamination, packed in ice, and delivered for laboratory analysis within 24 hours of collection time. The purpose of this part of the sampling program was to catch contaminants wherever they might be traveling in the water column and mark the location of the water extractions for future study.

Soil samples were collected at the same channel cross sections as for the water samples using the same sample extraction protocol. Three partial extractions were taken in the soils forming the canal's bed in each basin: (i) 1 foot below the canal water level; (ii) 1 foot above the water level; and (iii) directly at the canal water level.

Soils were extracted with a quick-shot spade, inserted perpendicular into the soil surface and down 5 inches into the substrata. The three subsamples taken were then well mixed in a plastic sampling bag before being sealed, placed on ice, and transported to the analytical laboratories within 24 hours. Expediency was important, as sample degradation may be expected to occur immediately. Soil samples were paired (replicated) for comparing analytical results. It was believed that contaminants would most likely be present in the soil near the water level (i.e., 0 to 15 cm deep) and not deeper into the soil profile (see, e.g., Nixon and Pilson 1983; Hiltbold 1986). The results of the analytical work in the effluent channels were then compared to the control samples from Quebrada La Mula Basin to test for a gradation of pesticide/nutrient build-up in the canal soils, both toward the rice fields and with increased numbers of years under rice cultivation.

Sampling of both soil and water was to be conducted twice. The first round of sampling was to take place in December, which is the beginning of the dry season, or the close of the wet season cropping cycle. The second round of sampling was scheduled in August, within a month of the beginning of the winter (wet) season. The idea of spreading temporal sampling between dry and wet conditions was to capture seasonal contaminant fluctuations in soils and water, if these existed. The dry season sampling was to emphasize pesticide/herbicide sampling, while the winter round of sampling targeted primarily fertilizer nutrients, as the peak applications of these two types of agrochemicals coincide with the occurrence of dry or wet weather, respectively. Pesticides/herbicides are of interest because of their inherent toxicity. Nutrient inputs are important because of their potential for eutrophication of receiving waters and its associated algal growth and production of algal mats and anoxic conditions in eutrophic waters. As will be discussed later, the cost of analytical tests became prohibitive under the initial field sampling strategy just outlined, forcing some modifications in the course of the study.

GIS Application in the Sampling Study

The application of GIS in soil and ground water contamination studies is relatively new. For complex remediation and site characterizations extending over sufficiently large areas, the storage, manipulation, and display of subsurface pollution spatial/temporal data are greatly facilitated by GIS (Goodchild et al. 1993; Leipnik et al. 1993). The state of the art in the application of digital information systems and technology to subsurface remediation and monitoring has gone beyond data storage, manipulation, and display. Spatial decision support systems (SDSS) interface GIS with other ground water and contaminant transport models. SDSS bring together the capability to manage data and interface them with sophisticated numerical models to aid in subsurface remediation efforts (Leipnik 1995).

GIS was adopted in this study as a spatial environmental data manager. Base maps containing property

boundaries, along with hydrographic maps, soil maps, and sampling location maps (to cite just a few) were digitized and downloaded into the ARC/INFO (ESRI 1991) GIS (these color maps could not be reproduced herein). Each of these maps, called thematic maps, can be brought in to similar scales, overlaid, and combined to produce a variety of spatial representations of the study area, such as combined site location/hydrographic maps, for example. In this study, the following maps were digitized and fed into ARC/INFO: boundary of area defined by major rivers, boundary of project site, boundaries of the three biological reserves of the region, major rivers and streams present on topographic map sheets, streams within river boundaries, mountains within project site and adjacent areas, lakes within the project site and adjacent areas, transportation road network, geology of the project site, soils, land ownership within the river boundary, present and proposed irrigation and drainage canals, irrigation subdistricts of the Arenal-Tempisque Irrigation Project, and contaminant concentration spatial distributions (Robinson 1993). This extensive database will be used in future studies to interface the soil and hydrogeologic database with multicomponent mathematical models of nonpoint source pollution (see, e.g., Jamieson and Clausen 1988; Bonazountas and Wagner 1984) into a SDSS for rice paddy contamination assessment. The objective of this work, insofar as GIS is concerned, was to develop the aforementioned database and download it into ARC/INFO for mapping of contaminant plumes, carrying out proximity analysis of those contaminant plumes to sensitive ecosystems, and initiating the more involved process of developing the SDSS that will interface the spatial database cited above to contaminant transport models.

Laboratory Analysis for Pesticides

Having established a field sampling strategy, the next step was to identify the types of agrochemicals being used in the Cabuyo Irrigation Subdistrict (part of the greater Arenal/Tempisque Irrigation District) that encircles the project basin, La Quebrada La Mula. Identification of applied agrochemicals was essential to the subsequent establishment of a small group of indicator parameters on which to base contamination potential, rather than working with the entire set of analytes due to prohibitive costs, redundancy in terms of toxicity impacts, and relatively unequal potential impacts among the set of all applied agrochemicals. More than 175 agrochemicals (including pesticides, herbicides, and fertilizers) are regularly used throughout the Arenal/Tempisque Irrigation District according to a survey of SENARA records at their field office in the city of Cañas (Brizuela 1990; Sanabria 1988; SENARA 1989). Personal interviews with government extension agronomists and farmers in the areas immediately adjacent to the study basin resulted in a reduction of the most intensely used pesticides and herbicides in the specific area of interest at La Quebrada La Mula to 30. Pesticides/herbicides were originally singled out because of their toxicity. The list of these 30 agrochemicals was the

cornerstone in contractual agreements with two separate government analytical laboratories located in San Jose, Costa Rica. One of these two laboratories, at the Ministry of Agriculture, would test for concentrations of the 30 agrochemicals in soil and water samples, with similar tests to be made for verification by INCIENSA, the second governmental analytical laboratory. Sampling protocols were agreed upon by the principal investigators and authors of this paper and chemists from the test laboratories (The U.S. Dept. of Agriculture's 1987 *Agrochemical Handbook* served as a guideline for this study sampling protocol). A team was sent to the field and (replicated) samples were collected according to the agreed upon sampling protocol at the sites, as previously determined in the overall field sampling program previously described. A third paired set of water and soil samples was sent to the University of California at Santa Barbara (UCSB) for analysis of chosen agrochemicals and further investigation of nitrate-nitrogen and phosphate-phosphorus fertilizer concentrations.

Standard sample preservation, transport, and chain of command protocols were followed to ensure integrity of the samples. Laboratory results obtained at the two independent government laboratories in Costa Rica and at UCSB indicated concentrations below detection levels for the 30 selected pesticides in the analyzed soil and water samples. The analytical results obtained at the two laboratories in Costa Rica were shrouded with uncertainty, as those laboratories did not have enough experience in conducting analytical testing for chemically complex pesticides/herbicides. The pesticide concentrations obtained at UCSB were also nondetects across the board for all 30 pesticides and herbicides. The first round of sampling, therefore, did not support the hypothesis that agricultural practices resulted in potential hazardous concentrations of chemicals in the downstream waters and soils of the cultivated acreages.

A second round of field sampling was undertaken for verification of these initial results. It was determined, based on their environmental persistence, level of toxicity, and representativeness of groups of pesticides, that the list of 30 agrochemicals originally selected could be reduced to a more workable number of eight indicator agrochemicals. The decision analysis for the determination of key indicator agrochemicals was done in collaboration with researchers at the Department of Environmental Toxicology of the University of California at Davis, who have accumulated significant experience with rice paddy toxicologic studies conducted in the Sacramento River flood plain near Sacramento, California (Crosby 1991). The indicator list of eight selected pesticides/herbicides, shown in Table 6, was sent to various analytical laboratories in southern California for an estimate of the cost of laboratory analysis. Laboratory analysis for all the field samples for one round of sampling (i.e., either in dry or wet climate), and not including the analytical methodology development cost for two products that have never been tested before, amounted to nearly \$80,000, according to the lowest bid received

Table 6
Eight Indicator Pesticides/Herbicides

	Name		Cost/Sample	
	Alternate	Common	Water	Soil
Insecticide	Carbofuran	Furadan	\$150	\$195
	Cypermethrine	Ambush	175	195
	Methamidophos	Monitor	150	195
Herbicide	2-4-D	Hedonal	150	175
	Oxadiazon	Ronstar	200	200
	Thiobencarb	Bolero	150	175
Rodenticide	Brodifacoum	Klerat	200	200
Fungicide	Mancozeb	Dithane-M-45	115	115

from analytical laboratories contacted. This included testing for the eight selected indicators in soil and water samples in each of the three cultivated test basins — Pelòn de la Bajura, Rancho Horizonte, and Bagatzi — and at the control La Quebrada La Mula Basin. Sampling in dry and wet months, as called for in the original sampling strategy, would double the cost of analytical testing. The prohibitive cost of analytical testing required by focusing on pesticides/herbicides led the authors to redirect strategy and opt for the alternative of analyzing for selected nutrients (i.e., total nitrogen and phosphorus, nitrate-nitrogen, ammonium-nitrogen, and phosphate-phosphorus). This decision was not exclusively economically motivated, as pesticide/herbicide concentrations for the first samples were below detection level. It was recognized that eutrophication by nutrients and associated oxygen depletion of surface and soil water could pose the greatest risk to receiving waters. For the investment of resources needed in conducting additional environmental sampling and testing, fertilizer nutrients clearly offered the potential highest return in terms of significant impacts that could be discovered.

Laboratory Determination of Nutrients, Nitrogen, and Phosphorus

Agricultural fertilization introduces nutrients that can migrate to neighboring ecosystems. Fertilizers are known to promote excessive plant growth, thick algal mats, oxygen depletion by benthic organisms, and eutrophication. Farmers of the region use a variety of fertilizer formulas, usually referred to by percentage of weight of nitrogen (N), phosphorus (P), and potassium (K). Examples of typical formulas for N/P/K are 15-3-31, 10-30-10, and 26-0-26. The constituents with the highest potential impact are nitrogen and phosphorus. Hence, the analytical sampling focused on various forms of the two elements. These forms were nitrates ($\text{NO}_3\text{-N}$), ammonium nitrates ($\text{NH}_4\text{-N}$), total Kjeldahl nitrogen (TKN), phosphates ($\text{PO}_4\text{-P}$), and total phosphorus (TP). The sampling program for these five nutrients consisted of taking quadruple

sets of soil and water samples (with replicates) at each of the sampling basins (each basin included four sampling locations along its main drainage channels: the first at the inlet, two intermediate ones, and the fourth at the outlet), in the cultivated areas (Pelòn de la Bajura, Rancho Tamarindo, and Bagatzi), and at the control or background La Quebrada La Mula Basin. This was done during dry (December) and wet (August) months. Two sets of samples were sent to two independent analytical laboratories in Costa Rica (i.e., one set to each laboratory) and the other two sets of samples were analyzed at two different analytical laboratories at UCSB. This provided not only verification for consistency of analytical results, but also allowed us to average results obtained at each sampling cross section within each basin when analytical results were deemed consistent in terms of methodology, absence of systematic errors, and the like.

The laboratory procedure for analyzing $\text{NO}_3\text{-N}$ in soils using an extract ratio of 10 gr wet soil to 25 mL of water was implemented before passing the extractant through a copperized cadmium reduction column. The nitrate was then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine dihydrochloride. The resulting water solution has a magenta color, which is read at 520 nm. The $\text{PO}_4\text{-P}$ extraction for soils used an acid digest of a KC1 solution instead of water on a dry soil to a solution ratio of 5 gr to 25 mL followed by a modified molybdenum blue assay. Absorbances were read at 888 nm. Both soil water extracts were passed through a flow injection analyzer instrument applying spectrophotometry, where sample absorbances were matched to a concentration curve of standard samples of known amounts of $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$. For water analyses, the procedure was identical, with the exception of the extraction process. TKN follows the Kjeldahl Method of analysis for both water and soil. Soil extract is done through a digest of sulfuric acid. Through a series of dilutions and conversions between the ammonium cation and ammonia, water and soil samples are heated with salicylate and hypochlorite to produce a blue assay, at which point colorimetric chemistry can be applied to identify sample

concentrations of total nitrogen (MacBeth Division of Kollmorgen Instruments Corp. 1988). Total phosphorus is determined by using an acid digest with soils where the extractant is then analyzed with colorimetric chemistry at a ratio of 0.5 g soil to 10 mL acid solution (usually 4 parts HNO_3 and 1 part HClO_4). The procedure is the same for water samples as for soils, minus the extraction step. $\text{NH}_4\text{-N}$ is extracted from soil with a 2 M solution of KCl. The KCl extract is filtered, and the filtrate is analyzed for ammonia by the salicylate method. Ammonia is heated with salicylate and hypochlorite in an alkaline phosphate buffer, resulting in an emerald green solution. The intensity of color is proportional to the concentration of ammonia. The analysis for water samples is identical to that for soils with the extraction phase.

Results

The results for the first round of agrochemical sampling (30 pesticides/herbicides were considered) yielded nondetects across the board for all organic phosphates and chlorinated hydrocarbon pesticides and herbicides. As indicated previously, the reliability of laboratory results for this round of sampling was low, and, therefore, results were considered inconclusive as to the real environmental hazard of current agricultural practices in the study area. A verification of the first sampling results based on eight selected pesticides and herbicides was prevented by the high cost of associated analytical tests. Therefore, fertilizer concentrations became the focus of the study. These are easily categorized into phosphorus, nitrate, and ammonium compounds and prone to fairly straightforward chemical testing. Based on the negative results for pesticides/herbicides, it was realized that nutrients' potential for eutrophication of receiving waters as well as for creating anoxic conditions in soil water made these fertilizers the primary environmental risk associated with agrochemical application practices in the area.

Table 7 shows the complete analytical results for fertilizer sampling. These results indicate that the concentrations of fertilizers in soil and water in the cultivated acreages were not significantly different from those in the control basin. As was the case for pesticides, there does not seem to be an accumulation of agrochemicals in the soils or above-background agrochemical residuals in effluent waters, either for pesticides/herbicides or fertilizers. Table 7 is set up with the five nutrient constituents placed across the top with water and soil sample results in separate columns, and down the right side are the sampling location sites, the control basin, and the three active rice-growing basins. The intention was to demonstrate a decline in contaminant levels as one moves away from the rice paddy and down the drainage canal and an increase in the residual soil contamination with an increase in the number of years continuously cultivating rice. Irrigation water freshly arriving to the farm was also analyzed for the same

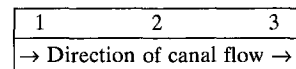
constituents to provide a comparison and a baseline of water quality. These results are labeled with a "O" in the location column of Table 7.

Appearing in the columns under $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ for water are data arrays marked by the month during which the samples were taken. The August sampling (1992) was done one to two months into the wet season cropping cycle, and the December sampling (1991) was done in the early stages of the dry season.

To better understand the data presented, reference values have been provided for comparison as well as the results from irrigation inlet water samples taken during the 1992 sampling. There is only one U.S. EPA standard for the nutrients studied. Nitrates in drinking water have a maximum concentration of 714 μM (micro Molar) or 10 mg/L (U.S. EPA 1991). Evidently, the acquired data are several orders of magnitude lower than the standards. For ammonium nitrate ($\text{NH}_4\text{-N}$), the U.S. EPA health advisories or Suggested No-Adverse-Response Levels (SNARLS) have proposed a maximum concentration level of 126 μM $\text{NH}_4\text{-N}$ (Marshack 1991). This value is substantially higher than the values shown for that column of Table 7. In addition, three other constituents common to nutrient pollution incoming at Goleta Valley Waste Water Treatment Plant (WWTP, Goleta, California) for sludge are shown at the bottom right of Table 7 (Goleta Valley Sanitary District 1992). These reference levels for nutrients demonstrate how low the nutrient values of the field samples were for both soil and water.

The results across the nutrient data summary in Table 7 indicate little to no current environmental impact in the canal waters or soils from rice paddy nutrients. It appears that no nutrient buildup from sorptivity exists in the canal soils and that the effluent waters were comparable to the waters entering the fields at the irrigation inlet canals. The residence time is short for the five nutrients studied in water and soil. A possible explanation for the soil results could be the large volume of water flowing in the canals, which, in effect, would wash the soils of any contaminants on a continuous basis. Agrochemicals might also be rapidly biodegraded in these warm tropical climates with high levels of solar irradiance. In addition, water moves relatively quickly down the drainage canals, making it difficult to catch any contaminant peaks in the surface effluents. In summary, no consistent trend with position along the canals was found in any of the sampled basins. This could be due to high spatial and temporal variability of contaminant distributions not captured by the field sampling scheme or to insufficient number of replicates that could have hindered more detailed characterization of contaminant concentration at the selected sampling sites. An enlarged sampling scheme for nutrients and other agrochemicals might reveal contamination to downstream wetlands not discovered by our study. The cost of conducting such a study would be significant (perhaps nearing \$0.5 million for a definitive spatial and temporal characterization of major agrochemicals), and

Table 7
Residuals in Soil and Water from Agrochemical Fertilizers
Limnology and Marine Science Laboratories, UCSB
SENARA / UCSB



Location	Yrs*	pH**	NO3-N				NH4-N		TKN		PO4-P				TP		
			Water		Soil		Water	Soil	Water	Soil	Water	Soil		Water	Soil		
			μM	$\mu\text{mol-N/g (dry)}$	μM	$\mu\text{mol-N/g (dry)}$	μM	$\mu\text{mol-N/g (dry)}$	μM	$\mu\text{mol-P/g (dry)}$	μM	$\mu\text{mol-P/g (dry)}$	μM	$\mu\text{mol-P/g (dry)}$			
Quebrada la Mula	0		(Dec.)	(Aug.)	(Dec.)	(Aug.)					(Dec.)	(Aug.)	(Dec.)	(Aug.)			
(Control)	1*	7.1	12.1	0.1	0.14	<0.007	1.9	0.08	<179	40.8	0.7	5.9	0.04	0.3	<48	9.3	
	2**	6.9	23.6	0.1	0.05	0.007	0.7	0.05	<179	59.9	0.9	10.8	0.04	1.2	<48	13.6	
	3***	7.5	7.1	0.2	0.08	<0.007	1.1	0.69	<179	126.2	0.5	1.7	0.02	1.2	<48	23.5	
Bagatzl	0	8	7.9	ND	1.2	ND	ND	0.5	ND	<179	ND	ND	3.3	ND	ND	<48	ND
	1		8.0	9.3	1.5	0.04	0.007	1.8	0.84	<179	68.3	0.4	3.5	0.01	0.4	<48	13.0
	2		7.5	5.7	0.9	0.02	0.008	18.0	0.06	<179	26.7	0.6	4.4	0	0.1	<48	5.7
	3		7.5	5.0	0.9	0.02	0.01	15.7	0.46	<179	141.7	0.4	4.2	0.01	0.4	<48	14.2
Rancho Horizonte	0	15	7.3	ND	1.6	ND	ND	1.7	ND	<179	ND	ND	1.2	ND	ND	<48	ND
	1		7.2	23.6	2.4	0.08	0.007	2.2	0.36	<179	12.5	1	2.8	0.02	0.2	<48	8.3
	2		7.0	30.0	2.7	0.05	<0.007	0.9	0.14	<179	17.5	0.6	0.9	0	0.2	<48	11.2
	3		7.1	36.4	3.2	0.04	<0.007	0.9	0.87	<179	32.9	0.3	3.2	0.01	0.4	<48	11.6
Pelon la Bajura	0	45	7.7	ND	0.5	ND	ND	0.5	ND	<179	ND	ND	1.7	ND	ND	<48	ND
	1		8.1	15.0	2.8	0.04	0.008	27.9	0.23	<179	86.2	0.7	1.1	0.06	1.0	<48	19.0
	2		7.9	ND	1.5	0.08	<0.007	1.6	0.11	<179	54.6	0.9	1.5	0.05	0.4	<48	11.6
	3		8.1	3.6	0.8	0.07	<0.007	1.6	0.14	<179	12.6	0.5	0.8	0.06	0.2	<48	7.2

All samples were paired and the average recorded above.

- * Years cultivating rice.
- ** Water only, measured in the field with a Hanna Instruments pH meter.
- * Irrigation canal inlet waters (only).
- * Sample taken near rice field.
- ** Sample taken half the distance between "1" and "3".
- *** Near the discharge point of the drainage canal.
- TKN Total Kjeldahl nitrogen
- NO3-N Nitrate nitrogen
- NH4-N Ammonium nitrate
- PO4-P Phosphate phosphorus
- TP Total Phosphorus
- Y EPA Drinking Water Standard:
EPA Suggested Health advisories, SNARLS NO3-N: 10 mg/L or 714 μM
- YY Nutrient levels for Goleta Valley WWTP, California
NH4-N: 126 μM
Sludge from treatment plant:
NH4-N: 205 $\mu\text{mol/g}$
TKN: 1964 $\mu\text{mol/g}$
TP: 1571 $\mu\text{mol/g}$
- ND No data.
- μM Micro molar.

that level of investment appears unjustified based on our preliminary work. Our work suggests that effluent discharge into the streams of the lower La Quebrada La Mula draining into the ecological reserve of Palo Verde National Park might only have the effect of increasing the amount of water entering the lagoons and marshland environments, with no apparent impact on water quality.

Summary and Conclusions

The delta plains of the Tempisque and Bebedero Rivers in Costa Rica provide excellent agricultural opportunities for large-scale farming. The need to bring vast tracts of this area under cultivation does not come

without its environmental price tag. Loss of pristine habitats and irreplaceable ecosystems calls for careful development planning to minimize ecological impacts and preserve sensitive and unique landscapes. The proposed agricultural development of the micro basin La Quebrada La Mula is a controversial issue due to the basin's adjacency and hydrologic connection with the Palo Verde National Park. Approximately three-quarters of the basin of La Quebrada La Mula (5163 hectares) is charted for rice paddy development. The land will be divided into 10 hectare parcels and sold to low income farmers.

Studies of the basin hydrogeology found classic vertisol (typic pellustersts, fine mixed, and ishypothermic)

low hydraulic conductivity values of less than 0.12 m/d to a depth of 1.5 meters, low infiltration rates of 0.02 to 0.4 m/d wet to dry season, and a wide spatial extent of fine-grained, clay-rich soils (specifically, vertisols). With this in mind, a sampling strategy was developed to study the environmental impact from paddy effluent carrying agrochemicals. The research undertaken compared soil and water samples from the principal drainage canals of the three nearby cultivated basins, all with varying years of exclusive rice cultivation (Pelòn de la Bajura, Bagatzi, Rancho Horizonte), to the relatively undisturbed La Quebrada La Mula Basin.

Two rounds of sampling were conducted, each following the sampling strategy and protocol. The results of the two rounds, the first looking at pesticides and the second at nutrients, suggest that rice paddy effluent does not carry significant amounts of contaminants to produce identifiable peaks in either water or soil analytical test results. Insofar as agrochemical concentrations are concerned, effluent waters from the three farms are similar to that of the streams of La Quebrada La Mula based on our sampling results. The proposed agricultural development of the micro basin appears to have little or no adverse effects, through the mechanism of nutrient and pesticide transport in surface and ground waters, on the preserved lands of the Palo Verde National Park.

The sampling strategy of this study adequately addressed the questions posed by the goals of the research project. However, the absence of more frequent sampling raises questions about the impact of rice paddy cultivation in the study area, since agrochemical applications in paddy rice are sporadic, and contaminant discharge off-site occurs in condensed peaks with substantial periods of clean water in between (Scardaci et al. 1987). For the rice fields of the Arenal/Tempisque Irrigation Project, it is the occasional field discharge that could bring pervasive concentrations of agrochemicals, whether they be nutrients from fertilizers or pesticides, to the downstream environments. More comprehensive and better supported conclusions could be drawn by either increasing the temporal frequency and/or the spatial coverage of field sampling. This would allow, in addition, the calibration of multicomponent transport models, with a resulting overall better characterization of the time/space distribution of agrochemicals in and around the study area.

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