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Organochlorinated pesticide contaminants in Golfo Dulce, Costa Rica

Alison L. Spongberg[1] and Penny Davis[2]
[1]Department of Geology, University of Toledo, Toledo, OH, 43606-3390, USA. E-mail: aspongb@geology.utoledo.edu
[2]Hull' & Associates, Inc., Toledo, OH, USA.

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Abstract: The organic contaminant load within the sediments of Golfo Dulce has so far gone unstudied. Concentrations of persistent pesticides were ascertained for comparison with future contaminant loads and for evaluation of response of biota to these compounds. Forty seven sediment cores were collected from the shores of Golfo Dulce, Costa Rica for quantification of persistent pesticide contamination, particle size distribution, and organic matter content. The gulf has to date had only minimal accumulations of pesticides. The deep anoxic fine-grained organic sediments in the northern portion of the gulf have had minimal impact from humans. However, evidence of pesticide metabolites, and aromatic hydrocarbons may indicate an accumulation of some contaminants and degradation of others in this zone. The Esquinas River sediments were found to contain numerous persistent pesticides, such as α,β,γ, and δ-BHC. The Coto-Colorado River sediments are coarser in texture, with low organic contents and may not retain pesticides efficiently. The pesticide load from this river may be transported great distances within the gulf. The Golfito area had little pesticide contamination, however, aromatic and diesel hydrocarbons were in great abundance in these sediments.

Key words: Organochlorinated pesticides, Golfo Dulce, Costa Rica, tropical estuary.

Golfo Dulce is a relatively undisturbed embayment located on the Pacific coast of Costa Rica. Deforestation, near-shore road construction, agriculture, gold mining, increased waste from population growth and tourism, and shipping now threaten the environment. Increases in agricultural production and heavy use of pesticides introduce heavy metals and synthetic organic compounds into the environment.

Several small rivers empty into the gulf carrying large amounts of particulate matter and associated contaminants. Because of the small size, restricted water circulation, and limited human impact on water quality, Golfo Dulce offers a unique opportunity to study the ecological impacts of the initial stages of coastal population growth in a tropical developing country. Unfortunately in other areas, development has resulted in increased pollution of restricted bays and waterways and subsequent unfavorable effects on indigenous wildlife. Often accumulation of toxic substances goes unnoticed until adverse effects are discovered.

Rarely is documentation of background or pristine levels of elements and compounds obtained prior to development. Therefore it was imperative that samples from Golfo Dulce be analyzed before further pollution occurred. This research documents the concentrations of certain organochlorinated contaminants which

are now present in Golfo Dulce and provides a record against which future measurements may be compared. This study provides a means to monitor the contributions of potentially harmful compounds into the water of the bay as development increases and populations near the gulf increase.

In the last several decades, a large variety and quantity of chlorinated pesticides have been introduced into the coastal areas of developing countries for agricultural use. While application and production of those compounds have been restricted or totally banned in developed countries, they are commonly used in other regions like Central America, South America, and Africa (Chapin & Wasserstrom 1981). Use of these chemicals has improved economies and lifestyles of residents. Yet their use has had adverse indirect effects, including pesticide resistance, environmental and health impairment, and high economic costs. The chemical toxicity of pesticides is partly responsible for this dichotomy. Their power to destroy pests makes them valuable tools, but this same lethal quality makes them potentially harmful to humans and the environment.

Other similar areas of the world can be used as examples of instances where pollution prevention and/or monitoring should have been used. Botello *et al.* (1994) studied the concentration and distribution of selected chlorinated pesticides in three coastal lagoons in the southeast Gulf of Mexico. Although many pesticides had previously been banned from use in Mexico, their presence was detected, indicating either their high persistence or recent illegal applications. Data indicated that environmental conditions may have caused pesticide transformation and degradation, especially in the cases of Aldrin transforming into Dieldrin and Endosulfan into the corresponding sulfate. In some cases, the metabolites were more toxic than their original components (McEwen & Stephensen 1979). Many researchers have noted that persistent pesticides could be identified in coastal area sediment in the USA, although its application was prohibited many years earlier. Concentration in shellfish was two-fold or more than in sediments in Mexican studies (Botello *et al.* 1994) and American studies (Marcus & Renfrow 1990, Mearns *et al.* 1988, Nadjek & Bazulic 1988). In Mexican oysters a trend of increasing pesticide concentration with time was observed (Botello *et al.* 1994). McEwen & Stephensen (1979) report different abilities of estuarine organisms to degrade DDT within the same ecosystem.

These reports clearly demonstrate that inland agricultural practices can affect water quality at great distances from their point of application. Many compounds applied in the central midwestern United States have been transported significant distances from their sites of application. There is a need for improved abilities to quantify the fate and transport of herbicides in river basins impacted by agricultural activities and to understand the complex hydrological and chemical relationships between groundwater and surface water, as well as the fate of these chemicals once discharged into bays and estuaries.

Unfortunately, development within Golfo Dulce has begun before sufficient 'background' data on uncontaminated conditions could be collected. Previous research has concentrated on biological evaluation and species distributions within Golfo Nicoya, Sierpe-Térraba, and Golfo Dulce (Wolff & Vargas 1994). The authors defined the baseline data for the oceanographic conditions (temperature, salinity) and invertebrate fauna on Golfo Nicoya and Golfo Dulce, however, the impact of pesticides has not been ascertained. Different environments as well as sediment types and compositions are known to vary in their buffering capacities and abilities to retain contaminants in toxic or non-toxic chemical forms. For example, sediments may adsorb heavy metals or organic contaminants, or facilitate their release in their toxic form. Anoxic sediments or chemical environments may be conducive to the breakdown of some contaminants into non-toxic forms through microbial or physical processes. The purpose of this research is to identify areas of pesticide contamination and sediment types or geochemical environments which contain them. These data will indicate the potential for contaminant accumulation or degradation should pollutant input increase in Golfo Dulce.

MATERIALS AND METHODS

Site Location: Golfo Dulce is an embay-

ment in southwestern Costa Rica (8°30' N., 83°16' W.) (Fig. 1) which measures 50km long by 10-15km wide. This bay is a fjord-like structure with depths slightly greater than 200m in the northern third. Anoxic conditions have been observed below depths of 100m within the bay. A 60-70m sill closes the mouth of the gulf (Wolff & Vargas 1994) restricting the interactions with the ocean. Shorelines are dominated by steep rocky slopes in the north and northeast. Large deforested areas dominate the west (Puerto Jiménez) and the east (Río Coto-Colorado). Steep mountains surrounding the gulf reduce water circulation which is apparently governed by the local wind regime. (Richards *et al.* 1971). Three main rivers are the source of fresh water and particulate matter into Golfo Dulce: Rincón, Esquinas, and Coto-Colorado.

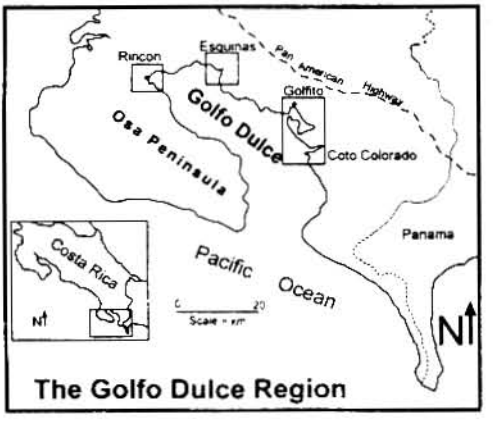

Fig. 1. Area map of the Golfo Dulce, Costa Rica region. Boxes indicate location of Figures 2-4.

The Osa Península lies on the western edge of Golfo Dulce and comprises the largest remaining coastal area of tropical rainforest in the Central American Pacific. Elsewhere general farming practices (domestic consumption and subsistence crops) are found in the area surrounding Golfo Dulce. Commercially grown crops including bananas, sugar, rice, cocoa, etc. are found in the Coto-Colorado watershed, while palm plantations are found in the Esquinas River basin.

The specific areas within Golfo Dulce where samples were taken include: the Rincón River mouth and a nearby deforested site, Esquinas River mouth, Puntarenitas, Golfito bay and port, and deep samples (20m to 200m) taken from within the bay itself (Fig. 2-4, Table 1). Samples were collected from almost the deepest reaches of Golfo Dulce including both oxic and anoxic regions. All sampling was done during low tide conditions.

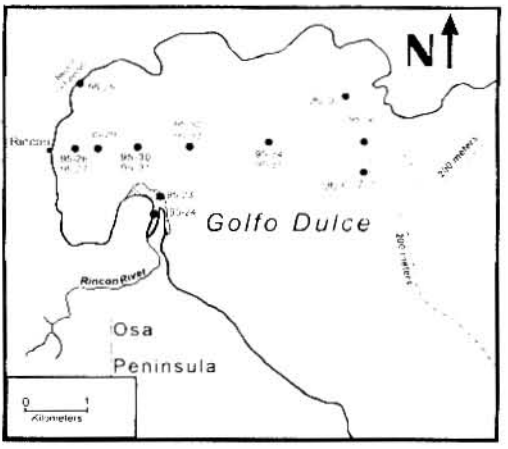

Fig. 2. 1995 and 1996 sample locations for the Rincón area and deep sediment cores, Golfo Dulce, Costa Rica.

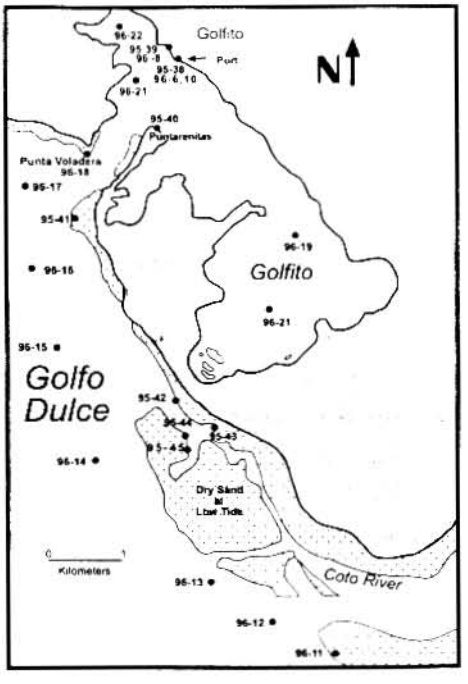

Fig. 3. 1995 and 1996 sample locations for the Golfito and Río Coto-Colorado areas, Golfo Dulce, Costa Rica.

TABLE 1

Sample Identification Numbers and Locations

Sample ID	Location
95-23B, 95-23J, 95-24B, 95-24J	Rincón River mouth
95-25B, 95-25J	Clear Cut
96-1 B, 96-2B	Esquinas River mouth
96-3B	Offshore Esquinas River, 70m
96-4B	Offshore Esquinas River, 40m
95-26B, 95-27B	20m core
95-29B1, 95-29B2	37m core
95-30B, 95-31B	60m core
95-32B, 95-33B	100m core
95-34B, 95-35B	100m core
95-36B, 95-37B	180m core
96-SB	25m core
96-6B	195m core
95-38B, 95-38J, 95-39B, 95-39J, 96-8B, 96-9B, 96-10B	Golfito port
96-19B	South end of Golfito Bay, 5m
96-20B	South end of Golfito Bay, 1,5m
96-21B	In front of Golfito loading docks, 15m
96-22B	North end of Golfito Bay, 35m
95-40B, 95-40J	Puntarenitas
96-18B	Punta Voladera, 14m
95-41B, 95-41J, 95-42B, 95-42J, 95-43B, 95-43J, 95-44B, 95-44J, 95-45J1, 95-45J2, 96-11B	Coto-Colorado River
96-14B	Offshore Coto-Colorado River, 7m
96-12B	Offshore Coto-Colorado River, 26m
96-15B	Offshore Coto-Colorado River, 35m
96-13B	Offshore Coto-Colorado River, 38m
96-16B	Offshore Coto-Colorado River, 70m
96-17B	Offshore Coto-Colorado River, 100m

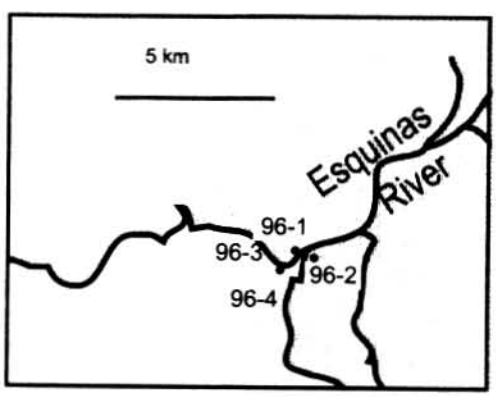

Fig. 4. 1996 sample locations for the Esquinas area, Golfo Dulce, Costa Rica.

For this study, 47 sediment samples (approximately 1-2kg each) were taken during two collection trips in January of 1995 (the dry season of Costa Rica) and May 1996 (after pesticide application). Shallow samples were obtained manually with a Plexiglas corer, (4.65cm I.D.). Deep samples were collected using a hand winch operated corer constructed of PVC pipe (5.5cm I.D.) and a heavy top weight. Positions were identified using GPS (Global Positioning System). Both techniques were highly successful in obtaining representative samples. Corers were scrubbed with water from the site prior to and after each sample was taken. Samples were placed into 500ml, wide-mouthed, amber glass jars and/or Kapak Scotchpak brand pint-sized heat-sealable pouches and then chilled. The amber jars were pre-cleaned with methylene chloride and methanol, then analyzed by GC/MS to ensure cleanliness. The samples were sealed in bags and/or jars and transported frozen to the University of Toledo, Toledo, Ohio. No preservatives were added to the samples, which remained frozen prior to analysis.

Particle size distribution was determined

using hydrometer and wet sieve analyses following ASTM Method D 422-63, Anonymous (1993). Samples from identical locations were combined as were the top and bottom of individual cores to produce the desired sample quantity. Total organic carbon of some samples was determined by oxidizing the sample in a muffle furnace for three hours at 500°C. After cooling, deionized water was added until saturation was reached. These saturated samples were then dried at 100°C overnight before weighing.

Pesticide analyses were performed on all samples from both collection trips. Samples from 1995, however, were analyzed differently from those collected in 1996. The 1995 data were inconclusive or questionable for pesticide evaluation and are not reported here. The 1995 data are used to qualitatively assess hydrocarbon input. Duplicate samples from 1996 were extracted and analyzed for confirmation. Initially, the organic fraction was extracted from a known quantity of sediment using methylene chloride in the Tecator Soxtec Extraction System HT 1043. Sulfur removal was accomplished during this extraction step using solvent cleaned copper strips.

A two step column chromatographic separation was used to segregate co-eluting compounds. Trials and refinement of several procedures resulted in the following protocol. The first step included a 1cm I.D. column filled successively with glass wool, sodium sulfate, florisil, and sodium sulfate. After saturating the column with solvent, the reduced methylene chloride extract was placed in the column and eluted with 0.5% diethyl ether in hexane. This produced extract F1 which was reduced to 3ml using a roto-evaporation unit. The columns were then eluted with 40% diethyl ether in hexane to produce extract F2. A second column contained the following sorbents: glass wool, sodium sulfate, fine acidized silica gel, coarse acidized silica gel, and sodium sulfate. After saturating the column with solvent, the reduced F1 extract was placed on the column and eluted with 0.5% toluene in hexane (S1). The column was lastly eluted with 25% diethyl ether in hexane (S2). The resulting three extracts were roto-evaporated to approximately 1ml, with iso-octane added as the keeper and analyzed for pesticides. Recovery efficiencies were greater than 85% for all compounds except heptachlor which was variable between 60-85%.

Ideally, the F2 extract isolates the following pesticides: δ-BHC, dacthal, dieldrin, and endrin. The S1 extract isolates the following compounds: hexachlorobenzene, heptachlor, o,p' DDE, mirex, and the 1242, 1248, 1254, and 1260 PCBs. S2 isolated the following compounds: α-BHC, β-BHC, γ-BHC, δ -BHC, oxychlordane, heptachlor epoxide, trans-chlordane, trans-nonachlor, cis-chlordane, o,p' DDE, p,p' DDE, o,p' DDD, cis-nonachlor, o,p' DDT, p,p' DDD, p,p' DDT, toxaphene, and methoxychlor.

Gas chromatographic analysis of the three extracts was performed on a Hewlett Packard 5890 II gas chromatograph equipped with an HP-5 MN Crosslinked 5% PH ME Siloxane capillary column and an electron capture detector. Inlet and detector temperatures were 205°C and 250°C, respectively. EPA Method 8081 was followed. Helium carrier gas was set to 6ml/min flow. Splitless injection was used. The oven was set to 100°C for two minutes, ramped at 15°C/min to 160°C, ramped at 5°C/min to a final temperature of 250°C, which was held for 10 minutes. Complete run time was 34 minutes. Analytical integration of the resulting peaks was limited to a minimum area count of 1000 using an RTE integrator. Detection limits are defined as the concentration corresponding to the area plus three standard deviations from the background readings at that time. Identification of pesticide peaks was accomplished by comparison with Supelco pesticide and PCB standards, as well as using sulfur as an internal standard. Sulfur is a natural component of almost all of the Golfo Dulce sediments and its entire removal was difficult. Therefore, the retention time for pesticide peaks of interest were compared with retention time of the sulfur peak to determine the slight variability in the manual injection technique.

Confirmation of standard peaks and most sample peaks was accomplished using a Hewlett Packard 6890 gas chromatograph equipped with an identical column and mass selective detector. The gas chromatographic method was identical to the previously described method. Data from this analysis were compared with the National Bureau of Standards library of 75 000 mass spectra for a

TABLE 2

Partical size Classification and Organic Carbon Content for Golfo Dulce Sediment Samples

Area	Water depth	Sample ID	Grain size classification	Percent organic carbon
Rincon	shore	95-23	Sandy clay	2.95, 2.63
Rincon	shore	95-24	Clayey silt	1.94, 1.79
Clear cut	shore	95-25	Sandy clay	0.49, 2.89
Esquinas River mouth	shore	96-1 B, 96-2B	Clayey silt	0.67, 1.32
Esquinas River	40m	96-4B	Silty clay	1.55
Esquinas River	70m	96-3B	Silty clay	1.56
Deep cores	20m	95-26, 95-27	Sandy clay	2.08, 3.44
Deep cores	25m	96-5B	Silty clay	3.05
Deep cores	37m	95-29	Sandy clay	3.36, 2.22
Deep cores	60m	95-30, 95-31	Sandy clay	4.44, 3.50
Deep cores	100m	95-32, 95-33	Silty clay	1.77, 1.98
Deep cores	150m	95-34, 95-35	Clay	2.52, 1.61
Deep cores	180m	95-36, 95-37	Silty clay	2.22, 0.70
Deep cores	195m	96-6B	Clay	2.37
Golfito	shore	95-38	Silty fine sand	1.38, 1.27
Golfito	shore	95-39	Silty fine sand	1.22, 1.32
Golfito	shore	96-8B	Silty fine sand	1.2
Golfito	shore	96-9B, 96-lOB	Silty fine sand	1.15
Golfito Bay, south end	5m	96-l9B	Silt	1.56
Golfito Bay, south end	1.5m	96-20B	Silt	1.49
In front of port	15m	96-21B	Silty clay	1.69
Golfito Bay, north end	35m	96-22B	Silty clay	1.26
Puntarenitas	shore	95-40	Fine sand	0.99, 1.18
Punta Voladera	14m	96-18B	Clayey silt	1.47
Coto-Colorado River	shore	95-41	Silty fine sand	1
Coto-Colorado River	shore	95-42	Clayey fine sand	0.93, 0.91
Coto-Colorado River	shore	95-43	Silty fine sand	1.13, 1.13
Coto-Colorado River	shore	95-44	Fine sand	1.11, 1.06
Coto-Colorado River	shore	95-45	Fine sand	0.18, 0.22
Coto-Colorado River	shore	96-11B	Finesand	0.3
Coto-Colorado River	7m	96-14B	Silty clay	1.56
Coto-Colorado River	26m	96-12B	Silty clay	2.02
Coto-Colorado River	35m	96-ISB	Silty clay	1.73
Coto-Colorado River	38m	96-13B	Silty clay	0.82
Coto-Colorado River	70m	96-16B	Silty clay	0.59
Coto-Colorado River	100m	96-17B	Silty clay	0.94

qualitative assessment of hydrocarbon contamination. These data also provided a qualitative evaluation of hydrocarbon content within the extracts.

RESULTS

Table 2 lists particle size data for the Golfo Dulce sediments. Grain sizes range from clay to fine sand. Samples obtained from the Coto-Colorado shore area were predominantly well sorted fine sands. Fine-grained sediments were recovered in 1996 offshore along the length of the sediment plume emerging from this watershed. A Secchi disc lowered into the water above this plume indicated that light was reduced to 1% at a depth of 30cm. Golfito offshore samples are moderately sorted fine sands, while the shore sediments are coarser grained. Deep core samples within the northern gulf are preferentially very fine-grained sediments. At the deep core location a Secchi disc could be lowered 5m before light was reduced to 1% penetration. Esquinas, Rincón, and the deforested area have moderate to poorly sorted silts and clays. A Secchi disc lowered into the water off Esquinas River to 15cm indicated that only 1% of light penetrated to that depth.

Percent organic carbon of each sample from

TABLE 3

Pesticide hits from Florisil 2 fraction, (ug pesticide per kg dry soil). Samples taken in 1996

Sample name	α-BHC	γBHC	β-BHC	δ-BHC	Heptachlor	Heptachlor epoxide	Aldrin	Dieldrin	Endrin	Endrin aldehyde	Endo-sulfan I	Endo-sulfan II	Endosulfan sulfate	pp-DDT	4 4'-DDE	4 4'-DDD
metabolites						*		*		*			*		*	*
96-1			**			**										
96-2																
96-3			**	**		**		**	**	**	**	**	2.87		**	**
96-4									**	**	**	**	8.10		**	**
96-5																**
96-6						2.06									4.07	
96-7																**
96-8		2.35										7.29			2.68	
96-9																**
96-10		2.96	0.85	1.99	1.31					3.31		3.06	2.24		**	**
96-11													**		**	**
96-12						1.21										
96-13																
96-14										**						
96-15										**						
96-16																
96-17												**				
96-18						6.37										
96-19																
96-20										**						
96-21																
96-22								**				**				
D.L.	1.10	1.50	0.75	0.90	1.00	1.20	1.00	1.00	3.00	1.60	1.80	2.00	1.80	4.60	2.50	3.20

* denotes pesticide degradation product (metabolite).

** denotes hit within10% of the detection limit.

TABLE 4

Pesticide hits from Silica Gel 1 fraction, (ug pesticide per kg dry soil). Samples taken in 1996

Sample name	α-BHC	γBHC	β-BHC	δ-BHC	Heptachlor	Heptachlor epoxide	Aldrin	Dieldrin	Endrin	Endrin aldehyde	Endo-sulfan I	Endo-sulfan II	Endosulfan sulfate	pp-DDT	4 4'-DDE	4 4'-DDD
metabolites						*		*		*			*		*	*
96-1	**	2.37	1.53	1.50				1.75	4.66	2.07			3.26			**
96-2	**	2.71	1.07	1.49							2.4				**	
96-3	**	**	**	**	**	**					**				**	
96-4	1.36	2.24	1.42	**	2.41	1.39					2.08	15.26		13.73	**	
96-5			1.69							**		**				
96-6								**								
96-7			**					**				**				
96-8			**			**		9.19				**		76.69		
96-9									2.76		2.38				**	
96-10								4.82								
96-11			**	**				**		**	**					
96-12																
96-13								**		**		**				
96-14																
96-15		15.23						**								
96-16								**							**	
96-17																
96-18								1.48								
96-19								**								
96-20																
96-21																
96-22								1.67								
D.L.	1.10	1.50	1.00	0.90	1.00	1.20	1.00	1.00	3.00	1.60	1.80	2.00	1.80	4.60	2.50	3.20

* denotes pesticide degradation product (metabolite)

** denotes hit within 10% of the detection limit.

TABLE 5

Pesticide hits from Sillca Gel 2 fraction (ug pesticide per kg dry soil). Samples taken in 1996

Sample name	α-BHC	γBHC	β-BHC	δ-BHC	Heptachlor	Heptachlor epoxide	Aldrin	Dieldrin	Endrin	Endrin aldehyde	Endo-sulfan I	Endo-sulfan II	Endosulfan sulfate	pp-DDT	4 4'-DDE	4 4'-DDD
metabolites						*		*		*			*		*	*
96-1	**	**						**				**	**		**	
96-2	**		**	**							**		**		**	**
96-3		**		**							**				**	
96-4	**	**	**	**		**		**				**				
96-5		**		**		**		**				**				
96-6								**					**			
96-7																
96-8												**		**		
96-9									**			**			**	
96-10		**						**								
96-11			**							**	**					
96-12																
96-13																
96-14												**				
96-15	1.11				2.20									13.34		
96-16															**	
96-17								**			**					
96-18			**				**							**	**	
96-19												**				
96-20											**	**			**	
96-21																
96-22			**									**				
DL.	1.10	1.50	1.00	0.90	1.00	1.20	1.00	1.00	3.00	1.60	1.80	2.00	1.80	4.60	2.50	3.20

* denotes pesticide degradation product (metabolite)

** denotes hit within 10% of the detection limit

Golfo Dulce are also listed in Table 2. Values range from 0.18% to 4.44%. Samples from the Coto River area and the Golfito area have lower fractions of organic carbon, averaging less than 1.5%. The Rincón River and deep water samples range from 1.7-4.5%.

Data for pesticide detection in the three extracts from the 1996 samples are given in Tables 3-5. Only the following pesticides were investigated: α, β, γ, and δ-BHC, heptachlor and metabolite heptachlor epoxide, aldrin and metabolite dieldrin, endrin and metabolite endrin aldehyde, endosulfan and metabolite endosulfan sulfate, DDT and metabolites DDD and DDE. Although other pesticides are known to be used in Costa Rica, the study to date has not included these. Although each extract should ideally isolate only certain compounds, the technique is often not exact. Therefore, all pesticide hits are noted, including those within 10% of the detection limit.

The BHC compounds were found in all samples from the Esquinas River mouth. Their appearance on almost all chromatograms was consistent on all repetitions. Concentrations range from barely detectable to 2.4µg/km. Recovery efficiencies for these compounds are high, averaging 85%. Samples from Esquinas showed hits from almost all other pesticide groups, including heptachlor and its epoxide, endosulfan and its sulfate, DDT metabolites, and dieldrin, and endrin aldehyde. One hit for DDT is noted, however, this hit could not be duplicated due to lack of sample. The two offshore samples contained the majority of these pesticides. This is consistent with finer grain size and higher organic content.

The deep core samples (96-5B, 96-6B) showed only minor hits of pesticide metabolites: heptachlor epoxide, 4, 4'-DDE, endrin aldehyde, dieldrin, endosulfan sulfate, as well as β, γ, and δ-BHC. The presence of metabolites in these sediments could be the effect of slow sediment transport to these remote locations, or to an ideal setting for pesticide breakdown. Chlorinated pesticides are known to biodegrade anaerobically. Therefore, these deep sediments would have the ideal physical and chemical parameters for pesticide degradation. More samples need to be analyzed from this area.

The sediments from the Coto-Colorado watershed show a scattered array of confirmed and/or duplicated pesticide hits. Metabolites with few parent compounds were identified. One rather large DDT detection (13µg/kg) was noted in 96-15B from a 35m depth. Although its metabolites were noted in other Coto-Colorado samples, no other DDT hits were identified. Sample 96-11B was taken slightly upstream in sandy sediments. The detection of more compounds, in higher concentrations despite the coarse texture indicates that the pesticides may be diluted as they enter the gulf.

Golfito Bay samples are similar to Coto-Colorado samples in pesticide content. Mostly metabolites of DDT and aldrin's metabolite dieldrin were detected. However, these samples showed the greatest presence of hydrocarbons which often obscured the pesticide data. High quantities of sulfur, aromatic and diesel range hydrocarbons, as yet unquantified were in all Golfito bay and port sediments.

DISCUSSION

Three areas of concern were originally identified within Golfo Dulce. The plume of sediment from Río Coto Colorado was expected to contain many persistent pesticides. The bay of Golfito was expected to contain high metal and hydrocarbon concentrations (to be presented in another paper). And, finally the northern samples were expected to be relatively free from anthropogenic contamination. However, organic and inorganic contaminants are commonly transported into and through aquatic systems while sorbed to sediment particles. The changing redox conditions in the northern gulf could affect pollutant bioavailability.

Several factors directly and indirectly influence the type and concentration of pollutants present in aquatic sediments. Surface reactions are very important to inorganic-sediment interactions and therefore, fine-grained sediments are the main site for retention of inorganic materials (Jenne *et al.* 1980). The potential and rate at which adsorption occurs are influenced by particle size distribution, organic matter content, mineralogy, clay type, cation exchange capacity and pH. Clay minerals, organic matter, and hydrated metal oxides are the major components for adsorption in soils and sediments (Pucknat 1981).

Particle size is indirectly related to clay and organic matter content, however, it is sometimes important to consider all particle size fractions. Goerlitz & Law (1974) examined six sediment samples for total chlorinated hydrocarbons in four size fractions (gravel, sand, silt, and clay) and found variable trends between contaminants and particle size.

The following discussion summarizes findings of this study in each sample location.

Rincón River: The Rincón River sediments represent a pristine area of Golfo Dulce which drains a sparsely populated watershed in the forested mountains of the Osa Peninsula in the northern portion of the gulf (Fig. 2). No industry and little commercial farming exist in this watershed. The river drains primarily forested mountains with low population densities. Therefore, sediments collected from this locality should contain little anthropogenic pollutant input.

Particle sizes ranged from sandy clay to clayey silt. The predominance of fine grained particles and moderate to high level of organic matter (1.79-2.95%) enhance the probability that sorbed contaminants would be detected, if present. Little to no aromatic hydrocarbon or pesticide compounds were detected at this site supporting the hypothesis of a clean watershed. Minor diesel hydrocarbons were detected probably from a combination of natural inputs and some slight anthropogenic inputs. Natural sources include plant and animal waxes and fatty acids. Anthropogenic input may include petroleum products, such as diesel fuel for boats used by the people living on the mountains of the Osa Peninsula. At the time samples were taken for this study, electricity was not present in the Rincón watershed area. Cooler evening temperatures in the highlands may encourage the need for diesel or gas powered heat sources.

Samples were also collected from an area with recent deforestation approximately one mile east of Rincón. This area has a low population density much like the Rincón region. A crude road, however, did exist above the deforested slope. Much of the soil had washed into Golfo Dulce. Bright red, iron oxidized, clayey fine sands were collected at the shoreline. Very little distribution of the sediment had occurred due to a lack of strong currents.

Organic carbon values varied substantially between the two samples collected at this site (0.49-2.89%). This difference in organic carbon correlated to the qualitative assessment of diesel hydrocarbon contamination. These compounds are likely from sources similar to the Rincón region. Anthropogenic influences would include fuel remnants from the machinery used to cut down the trees on the slope and heating fuels used by the local people.

Deep Water Cores: Golfo Dulce is anoxic at depth, however, occasional flushing with oxygen-enriched water sustains a relatively oxidized state in the basin (Richards *et al.* 1971). Thamdrup *et al.* (1996) found no accumulation of H_2S in pore waters in the anoxic regions. Nitrate-rich waters are found entering the bay at sill depth, and denitrification occurs at oxic and anoxic depths. The high rates of surface O_2 uptake suggests intense carbon cycling within the photic zone. Sediments immediately below oxygenated waters show strong irrigation and bioturbation and had carbon oxidation rates 5 to 10 times greater than the sediments in the deepest part of the basin. Those sediments underlying anoxic waters are laminated and composed of turbidites. In oxic regions about 50% of the carbon oxidation is dominated by sulfate reduction. About 100% of carbon oxidation is accounted for by sulfate reduction in anoxic regions.

Sediments from 20 to 200m depths were collected in the northwestern section of the bay offshore from the Rincón area. Particle size became finer with increasing depth. The 20m core was a clayey fine sand, while the remaining cores were clayey silts or silty clays. The 60m core had the highest organic carbon (3.5-4.4%) of all samples from both collection trips.

The deep core samples (96-5B, 96-6B) showed only minor hits of pesticide metabolites. The presence of metabolites only, and not parent compounds in these sediments could be the effect of either sediment transport rates slower than degradation rates of these pesticides, or to an ideal setting for pesticide breakdown in these deeper anoxic sediments. Light can only penetrate to 5m at these locations, therefore photodegradation will not occur. An oxygen probe measured 1.0% O_2 at

70m depth, decreasing to 0.5% at 110m to 195m. Chlorinated pesticides are known to biodegrade anaerobically. Therefore, if other necessary nutrients are available these deep sediments would have ideal physical and chemical parameters for pesticide degradation.

The deep core samples illustrate how fine-grained sediments settling in the bay may be a sink for some contaminants, while providing optimum conditions for the loss of other contaminants. Four of the five deepest cores (60, 100, 180, and 195m) had qualitatively high aromatic hydrocarbon concentrations, yet low diesel concentrations. This suggests that environmental parameters at this depth, such as pH, light, nutrients, or oxygen, may adversely affect the degradation of these compounds. Contrary to the chlorinated pesticides, the major degradation pathway for non-halogenated hydrocarbons is aerobic (Cole 1994). The combination of small particle size, moderate organic carbon content, and low oxygen conditions may enhance retention of these contaminants in deeper regions of Golfo Dulce. The hydrocarbons may accumulate to concentrations that pose health concerns as they remain undegraded in the environment and slowly dissolve into the water column.

The specific source of these compounds in Golfo Dulce is not known at this time. These hydrocarbon data are currently being quantified and evaluated.

Golfito: Golfito is the only major port within Golfo Dulce which handles a worldwide market exporting produce and lumber (Fig. 3). Gasoline and other fuels are stored nearby for use by ships and cars in the nearby town. At the time of collection several large oil (?) drums were visible along the shores. Pollution from hydrocarbons was expected in this area due to the extended presence of diesel burning ships.

Puntarenitas and Punta Voladera are located at the entrance into Golfito bay. The sediment load from the Coto-Colorado River could be seen offshore from these sparsely inhabited areas. Ships traveling to Golfito pass by these areas.

Sediments were collected on mudflats close to the port in Golfito and along a north-south transect in the central portion of Golfito Bay. The sediments were classified as silty fine sands with organic carbon ranging from 1.22-1.38%. The offshore samples were finer grained with no significant change in organic matter content.

Pesticides found in the Golfito samples were largely limited to metabolites. Dieldrin was commonly found, while several samples showed the presence of 4, 4'-DDD, 4, 4'-DDE, endrin aldehyde, and heptachlor epoxide. Aldrin, γ-BHC, and endosulfan were also detected. Farming done in the mountains surrounding Golfito would likely drain into the Esquinas or Coto-Colorado watersheds and be diverted from Golfito. Pesticides were not expected in the port unless they are a result of washing pesticide residue off produce before transportation by ship.

Most of these samples had high concentrations of sulfur and hydrocarbon compounds. Comparison to older standards gives values up to 200ppm for total polynuclear aromatic hydrocarbons. Considering that the smallest size fraction generally contains the highest concentration of contaminants, the very small clay/silt fraction of these sediments likely contains very high concentrations of pollutants. This small size fraction is used selectively by most biota for their food supply. Concern should be raised about these concentrations, and further investigation is needed, especially if this area is to be used for aquaculture.

The most likely source of hydrocarbons is incomplete combustion of petroleum products by ships and tourist boats using the port. Also, automobiles and trucks bringing supplies to port are more common in this area than other localities previously discussed. Oil spills from over-filling or leaky containers may also contribute somewhat to these high concentrations.

Esquinas River: The Esquinas River drains National Forest land and large palm plantations to the northeast. Only a few tributaries drain developed areas (Fig. 4). The BHC compounds were found in all samples from this area. Even though detected quantities were near the detection limit their appearance on almost all chromatograms was consistent on all repetitions. Concentrations range from barely detectable to 2.4μg/kg. Samples from Esquinas showed hits from almost all other pesticide groups, including heptachlor and its

epoxide, endosulfan and its sulfate, DDT metabolites, and dieldrin, and endrin aldehyde. The two offshore samples contained the majority of these pesticides. This is consistent with finer grain size and higher organic content.

Coto-Colorado River: The Coto-Colorado River drains a large agricultural watershed including large banana, pineapple, and palm oil plantations (Fig. 3). Extensive documentation indicates pesticide use with little enforced regulation at such farms (Dinham 1993; Thrupp 1988; Matthiessen & Weir 1989). Gillespie (1992) noted heavy use of pesticides in this area in the recent past. The Coto River area was selected in this study with the suspicion that pesticides would be found. Both sandy shoreline and clay-rich offshore sediments were sampled.

Sediments from 1995 were collected along sand flats exposed near the river mouth during low tide and along sand beaches northwest of the river. Puntarenitas lies on the tip of a peninsula between Golfo Dulce and Golfito Bay. This area was also sampled to evaluate the impact from Coto-Colorado sediment. The sediments were classified predominantly as fine sands. Organic carbon percentages were low ranging from 0.18-1.23%. No fine-grained samples were collected during the first sampling season. Pesticide analyses of these samples did not indicate their presence. The reasons to explain this include the possibility of no pesticides in this region, dilution below detection limits by the coarse grain size, or inadequate laboratory technique. Therefore, this area was resampled in 1996 to obtain finer grained samples from the sediment plume. These samples were analyzed for pesticides using the much superior protocol outlined above.

The 1996 sediments contained pesticide metabolites with few parent compounds. Concentrations for several compounds were much higher than in other areas. For example, 15.2µg/kg β-BHC, 1.11µg/kg α-BHC, 13.3µg/kg 4,4'-DDT and 2.2µg/kg heptachlor were found (duplicated and confirmed) in sample 96-16B, and 1.3µg/kg 4,4'-DDD was found in 96-14B. However, concentrations and number of hits was not as high as originally expected. Sample 96-11B was taken slightly upstream in sandy sediments. The detection of more compounds, in higher concentrations despite the coarse texture indicates that pesticides may be diluted and not retained in the sediments as they enter the gulf.

Mangrove forests from the Esquinas River basin, a lesser developed area, were compared with the Coto Colorado catchment where commercialization is occurring at a higher rate (Gillespie 1992). From 1961 to 1984, an 18% loss of primary forest in Esquinas River basin had occurred, while from 1963 to 1984 the human population increased over 100% from 14 745 to 33 251. These numbers reflect only a slight to moderate anthropogenic influence. There is a lack of written records indicating use of agricultural chemicals, however, Ministrio de Agricultura extension agents indicated that pesticides and other agricultural chemicals had been used in the area for the last decade. In the Coto Colorado watershed a 70% loss of primary forest from 1961 to 1984 with a population increase over 250% from 17 923 to 69 900 people had occurred. The first recorded introduction of pesticides into this floodplain was in 1954 when over 12,000 hectares were treated with dieldrin. Since that time, applications of fungicides, nematicides, herbicides, and chlorinated hydrocarbons has occurred on a regular basis. In 1973 a major banana plantation adopted biological control methods. Mangroves in the Coto-Colorado watershed have received direct and indirect anthropogenic influences correlated to agriculture and pesticide use.

The lack of pesticides found at Coto-Colorado in this preliminary study does not mean that they are not present in sediments of Golfo Dulce. Costa Rica registered over 1 200 pesticides in 1993 (García com. pers.). Their use has increased significantly over the last few years. Several factors can influence the lack of pesticides found, especially in the Coto-Colorado River area. As stated earlier, particle size distribution and organic content influence the potential for contaminant sorption. Samples taken from the Coto-Colorado River area were predominately low organic sands, which have a much lower affinity for organic pollutants. Pesticides may therefore be transported quickly out of the Coto-Colorado area to accumulate or be degraded elsewhere in the gulf or ocean.

In general, the pesticide contamination in the sediment samples in Golfo Dulce are well below levels noted in the studies referenced above. Whether these values represent pristine conditions or the onset of contamination is difficult to assess because no other studies have been conducted on relatively undeveloped, or tropical gulfs. Other studies have been conducted after obvious contamination has occurred. Many of the pesticide hits in this study are close to the detection limit, indicating only a minimal impact to date. Unfortunately, it is difficult to obtain accurate information on which pesticides are currently being used and at what rates. Nevertheless, the data indicate that certain areas within the gulf may be acting as sinks for contaminants. Although this preliminary study gives an initial picture of pesticide contamination in Golfo Dulce, a great need exists for more data to obtain a complete understanding of the basin. As the region develops these data can be used to assess future impact of pesticides on the sediment and water quality of the area.

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