DFID Natural Resources Systems Programme

DFID NRSP PROJECT R7668 (REPORT 6)

IMPACT AND AMELIORATION OF SEDIMENT AND AGRO-CHEMICAL POLLUTION IN CARIBBEAN COASTAL WATERS

Environmental survey of agro-chemicals in the land water interface of St Lucia

July 2002

This activity of the project *Impact and amelioration of sediment and agro-chemical pollution in Caribbean Coastal Waters* was funded by the United Kingdom Department for International Development (DFID - NRSP LWI R7668). The conclusions and recommendations given in this report are those considered appropriate at the time of preparation. They may be modified in the light of further knowledge gained at subsequent stages of the Project. The findings of this report do not necessarily reflect the opinions or policies of DFID, MRAG Ltd, CEHI or any other institution with which it may be associated.

Authors:

Andrew Lewis
Caribbean Environmental Health Institute
The Morne
Castries
St Lucia, WI

Nicole Esteban
MRAG Ltd
47 Princes Gate
London SW7 2QA
UK

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

EXECUTIVE SUMMARY

- Recent literature reviews have shown that there have been few studies conducted on the fate of agro-chemicals in the Caribbean in general, and St Lucia in particular, and there is a need to assess fate of these chemicals to inform policy decisions on administration and management.
- A snapshot environmental survey was conducted in three watersheds in St Lucia in November 2001. The aim of the survey was to assess the fate of agro-chemicals (selected pesticides and fertilisers) in water, sediment and biota along the length of the watershed, from plantations in the upper catchment to point of entry in coastal waters.
- The survey took place towards the end of the rainy season in order to avoid any short-term fluctuations in baseline levels due to flooding. For validation purposes, samples were analysed in two laboratories in St Lucia and the UK.
- The selection of pesticides for analysis was based on import levels of pesticides to St Lucia during 1998 and 1999 as well as a prioritisation of those pesticides based on a toxicity review.
- Results show that pesticide levels in samples were below minimum detectable limits for the selected pesticides except for one tissue sample (crab tissue from a mangrove forest in Mamiku watershed), which contained Diazinon at 0.158mg/kg concentration.
- Both participating laboratories (CEHI and CSL) produced identical results for all samples, with the exception of the presence of Diazinon in one crab tissue sample which was detected by CSL (Mamiku Station 3) and not by CEHI.
- With regard to fate of fertilisers in the environment, results showed that potassium levels were high in two watersheds and also in sea moss. It was thought that this high loading was due to use of potassium-based fertilisers, and that sea moss may act as a natural sink for potassium ions. However, there has been no systematic study of fertilisers and their impact on nutrient levels in the St Lucian environment prior to this survey and there was therefore no baseline for comparison of our results.
- There is need for a more comprehensive agro-chemical monitoring programme in St Lucia paying close attention to application rates/frequency and weather patterns. A monitoring programme has been designed for the purpose of seeking funding.

LIST OF ACRONYMS

CCA	Caribbean Conservation Association
CEHI	Caribbean Environmental Health Institute
CSL	Central Science Laboratory, UK
DDE	1,1'-(2,2,dichloro-ethenylidene)-bis (4-chlorobenzene)
DDT	1,1'- (2,2,2 trichloroethylidene)-bis (4-chlorobenzene)
DFID	UK Department for International Development
EU	European Union
GC-MSD	Gas Chromatography with Mass Selective Detector
HPLC	High Performance Liquid Chromatography
KAPB	Knowledge, Attitude, Practices and Behaviour
LC_{50}	Lethal Concentration$_{50}$ (concentration of a material which will kill 50% of the test subjects when administered as a single exposure
LD_{50}	Lethal Dose$_{50}$ (amount of material which will kill 50% of test subjects in one dose)
LIMS	Laboratory Information Management System database
LOD	Limit of Detection
MAFF	Ministry of Agriculture, Forestry and Fisheries, St Lucia
MRAG	Marine Resources Assessment Group Ltd
NRSP	Natural Resources Systems Programme
US	United States
USEPA	United States Environmental Protection Agency
USFDA	United States Food and Drug Administration
UWI	University of the West Indies
WHO	World Health Organisation
WIBDECO	Windward Islands Banana Development Corporation

1 INTRODUCTION

Saint Lucia, like many other Caribbean States is heavily dependent on agricultural produce to sustain its economy through exports and to feed its population. This has led to an increase in the level of agro-chemicals introduced annually to the farming sector in order to improve production. Agro-chemicals, which include pesticides and fertilisers, may be defined as:

"Any substance or mixture of substances of natural or synthetic origin, used to stimulate or regulate the growth of, or to control the pests of agricultural, horticultural or plantation crops and domesticated livestock" (Hammerton and Reid 1985 cited in Vienneau 1997).

Pesticides may be further defined as any substance or mixture of substances intended to guard against, destroy or control pests (Hennao *et al*, 1993). Pesticides are very important in agriculture and public health programmes as they are used to control insects, weeds, and other undesirable organisms such as nematodes. However, pesticides are toxic to non-target organisms, including human beings. Pesticides can be divided into different classes according to their function. For example, there are insecticides, herbicides, fungicides and nematicides, which kill insects, weeds, fungi and nematodes respectively. These classes of pesticides are further divided into groups according to their chemical structure. Thus there are organochlorines (e.g. lindane), carbamates (e.g. carbofuran), organophosphates (e.g. pirimiphos-methyl) and pyrethroids (e.g. cypermethrin).

There has been a widespread increase in the use of pesticides worldwide. With this increase in chemical usage, concerns have been raised over the long-term effects of these chemicals on humans and the environment. The large quantities of pesticides being used invariably leads to the accumulation of pesticides in the environment. The presence of these residues in the environment often results in damage to the environment. Developing countries like St. Lucia are at greater risk from the effects of increased pesticide use than more developed countries as developing countries often lack the legislation and control over chemical pesticides (Vienneau, 1997).

Fertilisers are added to farming systems to stimulate growth. In general, fertilisers are not usually considered as being dangerous to human health. There is currently a paucity of studies into the environmental impacts of fertiliser use in St Lucia and the wider Caribbean. Agricultural fertilisers are generally considered to play a major role in eutrophication. (Ferguson *et al.*, 1996). Fertilisers have also been linked to methaemoglobinaemia ("Blue baby syndrome") in infants and stomach cancer in adults (Addiscott, 1996).

There have been few studies conducted on the impact of pesticides in the Caribbean. Studies on the fate, breakdown, transport, bioaccumulation and human health effects have primarily been conducted in temperate countries where they are produced. Many studies are funded by the pesticide manufacturing industry, which has the resources to publicise these studies or suppress unfavourable results (Cox, 1998 cited in Dasgupta and Perue, 2002). It is therefore important that independent studies be carried out in tropical climates.

This snapshot survey of agro-chemicals in St Lucia forms part of the environmental monitoring activities of a three year research project[1]. The results of this survey is intended to contribute to the estimation of the fate of agro-chemicals in the environment with particular emphasis on the land-water interface and impacts on the marine environment. Sample analyses were carried out by Caribbean Environmental Health Institute (CEHI), St Lucia and the Central Science Laboratory (CSL), UK.

1.1 St Lucia

1.1.1 Geography

St Lucia is situated in the Eastern Caribbean between Martinique to the North and St Vincent to the South. Its geographic coordinates are 13^{o} 53' N and 60^{o} 68' W. The island has a total land area of 620km^{2}, with approximately 158km of coastline (United States CIA, 2001). St. Lucia is very mountainous with its highest peak being Mt Gimie, which rises 950m (3,117ft) above sea level (CCA, 1991). The major river systems in St. Lucia include Roseau, Troumassee, Fond D'Or, and Cul de Sac (Woudneh, 1999).

The island is of volcanic origin and its soils are derived from volcanic andesites, basalts and dacites (CCA, 1991). Approximately half of St. Lucia is covered by andesite-derived soils. These soils are generally acidic, found on slopes up to 40^{o}, exhibit low to medium fertility and are susceptible to erosion. More fertile alluvial soils are found in valleys such as Roseau, Cul-de-Sac, Troumassee, Fond D'Or and Marquis. These areas are used extensively for agricultural cultivation.

1.1.2 Agricultural Sector

Bananas account for more than 80% of total agricultural production with coconuts, vegetables, avocadoes and breadfruits making up the rest (Department of Statistics, 2001). It is estimated that approximately 36.4km^{2} of land in St. Lucia is under banana production (Little *et al.*, 2001). The crop is cultivated mainly in fertile valleys such as Roseau, Cul-de-Sac and Troumassee. However, significant quantities of bananas are also produced on steep slopes. This increases the risk of soil erosion, as the root system of banana plants is ineffective against soil erosion..

The monocultural production of bananas in St. Lucia has serious environmental implications. This leads to a severe depletion of natural nutrients leading to increased fertiliser use. Monocultural production systems are also prone to pest infestation and therefore often require heavier pesticide use. The recent diversification programme, and impact of changes in the international trade regime for bananas, has resulted in a decreased production of bananas and diversification to other crops such as horticulture

1.1.3 Pesticide Importation and use

For the period June 1999 – May 2000, 1,289,587kg of solid pesticides and 43,142L of liquid pesticides were imported into St. Lucia (see Table 1.1). Nematicides accounted for most of the solid pesticides imported, while herbicides and insecticides accounted for almost all liquid pesticides.

[1] *Impact and Amelioration of Sediment and Agro-chemical Pollution on Caribbean Coastal Waters* (DFID NRSP LWI Project R7668).

The most widely used herbicides are Gramoxone (paraquat) and Touchdown (Glyphosate-trimesium). Mocap (ethoprophos) and Fungaflor (imazalil) are the most heavily used nematicide and fungicide used respectively. There was a significant increase in the quantity of Ethoprophos imported into St. Lucia in 1999 (Dasgupta and Perue, 2001). Checks with the St Lucia Pecticide Control Board indicated that this was due to stockpiling of the pesticide and not the result of nematode infestation. This is corroborated by the fact that subsequent to 1999 there have been minimal imports of ethoprophos.

Table 1.1 Quantities and categories of pesticides imported into St. Lucia (June 1999 – May 2000)[2]

Pesticide	Solid pesticide (kg)	Liquid pesticide (l)
Insecticide	43,574	273,580
Fungicide	23,890	3,396
Herbicide	13	156,897
Nematicide	1,217,799	12
Rodenticide	4,310	151
Tickicide	1	106
Total	1,289,587	434,142

There is a large number of insecticides approved for use in St. Lucia of which Demon TC, a pyrethroid, and Diazinon appear to be most popular among those approved for agricultural purposes. Insect pests do not appear to be a major factor in the primary agricultural crop (banana) and thus the largest contributor to insecticide imports are household insecticides particularly Baygon. Table 1.2 below lists the most commonly used pesticides in the agricultural sector in St. Lucia.

Table 1.2 List of the most commonly used pesticides in the agricultural sector in St Lucia[3]

Pesticide	Active Ingredient	Class
Fungaflor	Imazalil	Fungicide
Furadan	Carbofuran	Fungicide
Gramoxone	Paraquat	Herbicide
Miral	Isazophos	Nematicide
Mocap	Ethoprophos	Nematicide
Primicid	Pirimiphos-ethyl	Insecticide
Roundup	Glyphosate	Herbicide
Touchdown	Glyphosate-trimesium	Herbicide
Vydate	Oxamyl	Insecticide/nematicide

[2] Source: Proceedings of the 5th Meeting of the Coordinating group of Pesticide Control Boards of the Caribbean (CGPC).
[3] Source: Adapted from Woudneh, 1999.

1.1.4 Fertiliser importation

Fertiliser imports into St. Lucia for the period 1995 – 1999 are shown in Table 1.3.

Table 1.3 Fertiliser imports into St. Lucia 1995 – 1999[4]

Year	Ammonium Nitrate (tonnes)	Ammonium Sulphate (tonnes)	Urea (tonnes)	Others (tonnes)
1995	17	334	31	6730
1996	7	-	9	8027
1997	38	2	18	5760
1998	-	-	1650	2913
1999	2	-	1404	4486

1.1.5 Environmental Fate

A significant portion of all pesticides used in agricultural production eventually reaches the soil. Even when agro-chemicals are applied directly to plant foliage, the soil is a major recipient, reservoir and site of potential degradation (Aharonson, 1987). Robinson (1997) suggested that agro-chemicals enter the soil and water environments through the action of workers in four primary ways:

1. Directly by application to control soil and water-inhabiting pests;
2. Through fall-out of upward drift from aerial spraying and dusting operations;
3. From run-off of spray droplets from plant surfaces, either by themselves or along with precipitation to the soil, and erosion and run-off from agricultural lands to water; and
4. From remains of plants and animals.

In St. Lucia, the potential for pesticide pollution is high given the frequency and intense use of pesticides, coupled with inappropriate handling, disposal and storage methods (Woudneh, 1999). The distribution of pesticide residues in the environment following application is dependent on a number of factors. Water solubility, soil sorption, volatilisation, bioaccumulation and rate of degradation all influence the mobility and transport of these chemicals. Initial distribution is heavily influenced by application method, weather conditions, soil type, topography, vegetation and proximity to bodies of water. Robinson (1997) suggested that movement of pesticides on the soil surface is usually accelerated by:

1. Steep topography;
2. Low soil permeability; and
3. High rainfall.

[4] Source: St Lucia Ministry of Agriculture, Forestry and Fisheries - Agricultural Statistical Report 1999.

Highly soluble pesticides tend to be more rapidly leached. In sandy soils, leaching of water-soluble chemicals has been enhanced by periods of heavy rainfall (Aharonson, 1987). Soils that weakly absorb pesticides and have a rapid infiltration rate facilitate groundwater pollution to a greater extent than soils that strongly absorb pesticides and have a slow infiltration rate (CEHI, 1998). The adsorption of pesticides to organic matter and clay increases their persistence in the environment, thus pesticides remain longer in soils with a high organic or clay content than in soils with low organic/clay content. Table 1.4 indicates the potential for selected pesticides used in St Lucia to persist in the environment. The soil sorption coefficient describes the tendency of a pesticide to bind to soil.

Table 1.4 Properties of some commonly used pesticides in St Lucia[5]

Pesticide	Pesticide movement rating	Soil half life (days)	Water solubility (mg/l) at 20-30°C	Soil sorption coefficient
Carbofuran	Very high	50	351	22
Ethoprophos	High	25	750	70
Glyphosate	Extremely low	47	900,000	24000
Imazalil	Very low	150	1400	4000
Isazophos	High	34	69	100
Oxamyl	Low	4	282,000	25
Paraquat	Extremely low	1000	620,000	1000,000
Pirimiphos-ethyl	Moderate	45	93	300

Temperature and sunlight are important factors affecting the persistence of pesticides. The high temperatures and sunny days experienced in the Caribbean favour the solubility, volatilisation, photolysis and hydrolysis of pesticides in the environment. Whereas photolysis is limited to the soil surface, hydrolysis is an important reaction throughout the whole system. Hydrolysis is also important in determining the potential for pesticide contamination of groundwater. This is due to the fact that, unlike root zone degradation, volatilisation, and photo-degradation, hydrolysis is a mitigating process that can occur at any point in the soil, subsoil, and saturated zone environments (Aharonson, 1987).

Micro-organisms also play an important role in the transformation and degradation of agro-chemicals in soil. For example, microbial degradation of carbaryl in soil has been identified as an important pathway leading to its reduction in soil (Ripley and Chau, 1982).

In soil, fertilisers containing inorganic nitrogen and wastes containing organic nitrogen are first decomposed to give ammonia, which is then oxidised to nitrite and nitrate. Surplus nitrates readily move with groundwater (USEPA, 1987). Whether nitrates continue to move downward and into groundwater depends on underlying soil and/or bedrock conditions as well as depth to groundwater. If depth to groundwater is shallow and the underlying soil is sandy, the potential for nitrates to enter groundwater is relatively high. The fate of nitrates in soil is also influenced by the presence of high or low water tables, the amount of rainfall and the presence of organic material (WHO, 1996). Nitrification and denitrification may also occur in

[5] Source: Oregon State University Extension Pesticide Properties Database, 1994.

surface water depending on pH and temperature. However, uptake of nitrogen by plants account for most of the nitrate reduction in soils.

2 MATERIALS AND METHOD

2.1 Selection of pesticides for analysis

The project team worked in collaboration with the Ministry of Agriculture, Forestry and Fisheries (MAFF), Department of Agriculture and has been provided with lists of pesticides imported to St Lucia (1998-1999) by the Secretary of the Pesticides Control Board (PCB), Mr Guy Mathurin (Table 2.1). The data were analysed for priority pesticides by MRAG Ltd using a toxicity review prepared for the project by the Department of Chemistry at the University of the West Indies (UWI), Mona Campus in Jamaica (Dasgupta and Perue, 2002).

Table 2.1 Pesticide imports to St Lucia, 1998-1999

Category	Brand Name	AI chemical	Unit	1998	1999	Total
Fungicide	Cuprosan 311 SD	copper oxychloride	Kg	1.5	0.7	2.2
		Maneb	Kg	0.5	0.2	0.7
		Zineb	Kg	0.5	0.6	1.1
	Fungaflor 75 SP	Imazalil	Kg	1620.0	11932.0	13552.0
	Mancozeb 80% WP	Mancozeb	kg		87.5	87.5
	Phyton 27	ammonium formate	litres	0.1	9.0	9.1
		copper sulphate pentahydrate	litres	0.2	13.7	13.9
		sodium sulphate alquiletoxi	litres	0.1	3.2	3.3
	Ridomil MZ 72 WP	Mancozeb	kg	1600.0		1600.0
		Metalaxyl	kg	200.0		200.0
	Tilt 250 EC	Propiconazole	litres		682.5	682.5
	Trimiltox-Forte	copper calcium sulphate	kg	1.5		1.5
		copper carbonate	kg	0.8		0.8
		copper oxychloride	kg	2.3		2.3
		Mancozeb	kg	2.0		2.0
	Vectra	Bromaconazole	litres		1.4	1.4
Herbicide	2-4 D Amine	dichlorophenoxyacetic acid	litres	56.9		56.9
	Fusilade	fluazifop-p-butyl	litres	12.8	3.0	15.8
	Gramocil	Diuron	litres	1477.6	4666.8	6144.4
		Paraquat	litres	2955.2	9333.6	12288.8
	Gramoxone	Paraquat	litres	5820.0	13158.0	18978.0
	Reglone	Diquat	litres	12.0	1216.8	1228.8
	Talent	Asulam	litres		1291.1	1291.1
		Paraquat	litres		64.6	64.6
	Touchdown	glyphosate-trimesium	litres	3913.0	14517.1	18430.1
Insecticide	Actellic	pirimiphos-methyl	litres	28.0		28.0
	Actellic 50 EC	pirimiphos-methyl	litres		42.0	42.0
	Admire 2 Flowable	imidacloprid	litres	1.3		1.3
	Basudin	diazinon	litres	1.2	54.0	55.2
	Diazinon	diazinon	litres	86.6		86.6
	Diazinon 14G	diazinon	kg		1.7	1.7
	Diazinon 48 EC	diazinon	litres		49.5	49.5
	Dursban	chlorpyrifos	litres		33.6	33.6
	Dursban PT 270	chlorpyrifos	litres	0.3	0.9	1.2
	Karate	lambdacyhalothrin	litres	10.9		10.9
	Karate 2.5 EC	lambdacyhalothrin	litres		6.8	6.8
	Malathion	diazinon	litres		76.9	76.9
		malathion	litres	90.5		90.5
	Malathion ULV 91	diazinon	litres		17.2	17.2
	Sevin 5%	Carbaryl	kg	27.0		27.0
	Sevin 5% WP	Carbaryl	kg		24.3	24.3
	Sevin 80 Dust	Carbaryl	kg		90.4	90.4
	Sevin 85 S	Carbaryl	litres		18.5	18.5
	Sevin 85 WP	Carbaryl	kg	235.5	6.4	241.9
	Tambo 440 EC	cypermethrin	litres	80.5	16.4	96.9

Category	Brand Name	AI chemical	Unit	1998	1999	Total
		profenofos	litres	805.2	163.8	969.0
	Thiodan 50 WP	endosulfan	kg		4.5	4.5
	Trigard	cyromazine	kg	3.8	11.3	15.0
Nematicide	Furadan 10G	carbofuran	kg	9000.0	9280.3	18280.3
	Miral 10G	isazofos	kg	7330.0	2220.0	9550.0
	Mocap 10G	ethoprophos	kg	6480.0	102085.2	108565.2
	Rugby	cadusafos	kg		1080.0	1080.0
	Vydate L	oxamyl	litres	2744.4	1865.0	4609.4

The list of imported pesticides (Table 2.1) was used to determine pesticides for analysis (as detailed in Table 2.2). It was not been possible to analyse all priority pesticides due to budgetary and laboratory constraints. The majority of pesticides were analysed by both CEHI and the UK laboratory (Central Science Laboratory, CSL), however minor variation occured due to differing equipment availability. Table 2.2 indicates nutrients that were analysed to estimate fate of fertilisers in the environment (nitrate, nitrite, potassium, phosphorous). Fertiliser constituents were ascertained with information collated from the Extension Services of MAFF during a project workshop held at the Still Plantation in Soufriere on 26th June 2001 (Kenward et al., 2001).

Table 2.2 List of agro-chemicals analysed

Agro-chemical	Group	Priority	Lab tests	Sampling regime
Nutrients				
Nitrate	Nutrients	H	CEHI only	Water, sediment, fish/invert, algae
Nitrite	Nutrients	H	CEHI only	Water, sediment, fish/invert, algae
Potassium	Nutrients	H	CEHI only	Water, sediment, fish/invert, algae
Phosphorous	Nutrients	H	CEHI only	Water, sediment, fish/invert, algae
Group 1: organo-chlorine pesticides				
Endosulfan	Organo-chlorine	H	CEHI + CSL	Water, sediment, fish/invert, algae
Imazalil	Organo-chlorine	L/M	CEHI + CSL	Water, sediment, fish/invert, algae
Chlorpyrifos	Organo-chlorine	M	CEHI + CSL	Water, sediment, fish/invert, algae
Group 2: carbamate pesticides				
Oxamyl	Carbamate	H	CEHI + CSL	Water, sediment, fish/invert, algae
Carbaryl	Carbamate	L	CEHI + CSL	Water, sediment, fish/invert, algae
Carbofuran	Carbamate	L	CEHI + CSL	Water, sediment, fish/invert, algae
Group 3: organo-phosphate pesticides				
Ethoprophos	Organo-phosphate	H	CEHI + CSL	Water, sediment, fish/invert, algae
Diazinon	Organo-phosphate	L	CEHI +	Water, sediment, fish/invert,

Agro-chemical	Group	Priority	Lab tests	Sampling regime
			CSL	algae
Malathion	Organo-phosphate	L	CEHI + CSL	Water, sediment, fish/invert, algae
Pirimiphos-methyl	Organo-phosphate	L	CEHI + CSL	Water, sediment, fish/invert, algae
Cadusafos	Organo-phosphate	L/M	CEHI + CSL	Water, sediment, fish/invert, algae
Isazofos	Organo-phosphate	M	CEHI + CSL	Water, sediment, fish/invert, algae
Profenofos	Organo-phosphate	M	CEHI + CSL	Water, sediment, fish/invert, algae
Group 4: bipyridinium compounds				
Paraquat	Bipyridinium	H	CEHI + CSL	Water only (CEHI), Water, fish/invert, algae (CSL)
Diquat	Bipyridinium	M	CEHI + CSL	Water only*
Other groups of pesticides				
Metalaxyl	Acylalanine	L	CEHI + CSL	Water, sediment, fish/invert, algae
Cypermethrin	Pyrethroid	L/M	CEHI + CSL	Water, sediment, fish/invert, algae
Lambdacyhalothrin	Pyrethroid	L	CEHI + CSL	Water, sediment, fish/invert, algae
Cyromazine	Triazine	L	CEHI + CSL	Water, sediment, fish/invert, algae
Propiconazole	Triazole	M/H	CEHI + CSL	Water, sediment, fish/invert, algae
Diuron	Urea	L	CEHI + CSL	Water, sediment, fish/invert, algae

2.2 Location of watersheds

2.2.1 Selection of watersheds

The selection of watersheds was discussed at a number of meetings held with various institutions and governmental bodies during November 2000 (Kenward and Mees, 2000). Most people agreed that banana production had the highest impact on watersheds in terms of agro-chemicals and land-use. Three watersheds have been chosen with a variety of agricultural uses and pressures, as described below:

Watershed 1: Soufriere (17.2 km²)

This is a low impact watershed situated on the windward side of the island with high levels of precipitation. There is limited commercial farming and low banana production (MB); the main agricultural crops are root vegetables (dasheen, yams) which use a high amount of fertilisers (NPK). This watershed is critical due to the fringing reef along this coastline. This is the sedimentation research site of York University and thus important to include in the agro-chemical component of the project.

Watershed 2: Roseau (49.1 km²)

This river basin is located in the banana belt of St Lucia and is well known to be heavily impacted by agriculture, principally by banana production. The construction of a high dam has considerably reduced water flow in the river. Banana cultivation is year-round using aerial- and ground spraying. The Forestry Department has produced a report detailing a significant decrease in birds (St Lucia aurial hedgefeeder) due to aerial spraying.

Figure 2.1 Location of study watersheds

Watershed 3: Praslin/Mamiku/Patience (16 km²)
This site has been selected to contrast with the other study locations; it has different coastal and climatic characteristics from Watersheds 2 and 3 as it is on the Atlantic side of the island with much lower levels of rainfall. Two watersheds drain into Praslin Bay, which has no coral reef, however there is a mangrove stand with sea moss cultivation. There is a virtual absence of banana cultivation (except at Mamiku Estate) and the presence of diverse fruit, vegetable and flower cultivation. It is believed that the impacts of these crops are an important area of study since banana production is on the decline in St Lucia and they represent expected future trends in agriculture. Sampling of this watershed will include seamoss which is farmed in Praslin Bay.

2.2.2 ***Locations of sampling sites in Roseau, Soufriere and Mamiku watersheds***

One of the objectives of the project workshop held with extension officers from MAFF Department of Agriculture (Kenward *et al.*, 2001) was to collate information about farming practices (crop type, soil conservation, irrigation, etc) and general location in the three study watersheds. Subsequent to the project workshop, surveys were made of the watersheds to select appropriate monitoring stations. Table 2.3 summarises information collected about the watersheds and describes selected monitoring stations.

Table 2.3 Study watersheds: monitoring station locations and description

Mamiku Watershed area: 16.0km²	Boundaries: forested ridges either side of Mamiku valley. Main towns/villages are Mamiku, Mon Repos, Patience and La Pointe
Station 1 (upper valley)	N 13°52.408’ W 60°55.766’ The river is fast flowing with some deep, still ponds. Water is sampled from centre of the river at the surface. Bottom sediment is sand. Crops on surrounding steep banks are coconut (immediately adjacent), banana, mango, tertiary forest, wild ferns and vines. Further away are cultivated dasheen and yams
Station 2 (mid valley)	N 13°51.912’ W 60°54.520' The river becomes a series of mini waterfalls with some deeper, stagnant pools with sandy bottoms. There is a private water intake point near the sampling point and the pool here is turbid. The sampling point for water is mid stream, surface and for sediment is at the bottom of the stagnant pool near the intake point. The area is surrounded by uncultivated/minor cultivation slopes and is perhaps an abandoned plantation. There are cows and an empty pigsty. No crops adjacent to the river but coconut, mango, bananas, guavas and secondary bush further away on the slopes.

Station 3 (lower valley)	N 13°52.199' W 60°53.849' Banana plantations continue almost to the shoreline and along the river until it becomes a mangrove forest. The river has a very slow flow and is very turbid with muddy river banks. The sampling point is mid stream on the surface of the water. Station 3 tissues were 9 crabs caught in traps in the river.
Station 4 (shore)	N 13°52.616' W 60°53.443' Sampling was conducted close to the site of sea moss culture around the island in the middle of Praslin Bay. Bottom sediment in the bay is fine sand with some sea grass. Station 4 tissues were cultured species (sea moss) and wild molluscs (11 red topshells, 9 chiton, 3 nudibranchs, 55 whelks) which were collected from western (closest to river) side of the island (0-4m depth).
Roseau Watershed area: 49.1km²	Boundaries (main towns/villages are Millet, Dame de Traversay, Durandeau, Sarot, La Treille, Vanard, Jacmel, Jean Baptiste, Morne, Door, Blair, Peru, Fond Manger, Collie town, Massacre, Roseau Distillery, Derriere Lagoon, Bois dined, La Croix Main got): • Upper watershed - from the forest reserve to Mont Gamier • Southern boundary - down the Venus/Anise La Rayed ridge to Roseau • Northern boundary – down the Ladle Carrot ridge to Margot
Station 1 (upper valley)	N 13°54.686' W 60°59.835' One of the main tributaries of the Roseau river passes through the Park Estate and this station is just below the Estate. The river is shallow and mainly bedrock and pebbles either side. There are spates of rapids then slower sections with pebbles and sand at bottom. Cultivation: dasheen, breadfruit, bananas, cocoa, coconut, tertiary forest and tree crops.
Station 2 (mid valley)	N 13°55.721' W 60°59.485' This location is just below the confluence of tributaries to the main river below the village of Durandeau. The river is slow flowing with average 0.25m depth and deep silty pools. The LHS bank is a wide, low embankment with reeds whereas RHS is steep with banana and vines. Further from river, this is an area of cultivation of bananas, coconut palms, mango trees, pineapple, mixed vegetables (chilli peppers, tomatoes).

Station 3 (lower valley)	N 13°57.353' W 61°01.237' The lower valley is intensively farmed with large banana plantations along both banks of the river. Sampling site is by the main coastal road bridge next to the school. The banks have a gentle gradient.
Station 4 (shore)	N 13°57.776' W 61°01.950' At the outlet of Roseau River there is a narrow beach (with fishing boats) and no visible reef. The sampling point was adjacent to the sedimentation trap north of the river (direction of current) along the coastline which is rocky, descending steeply to 4.0m. Station 3 tissues were aquatic green macrophytes/algae (similar to Ulva lactuca) (1 sample) and fish (juvenile Tilapia) and crustacean (cray fish) (1 sample). Station 4 tissues were molluscs (5 whelks, 3 rough tops, 10 small conch), crustacea (1 hermit crab) and fish (3 goatfish, 1 parrotfish).
Soufriere Watershed area: 17.2km²	Boundaries: Forested ridges either side of Soufriere valley. Main towns/villages are Soufriere, Ruby, La Perle, Zenon, Cressland, Diamond, Esperance, Fond St Jacque, Toraille, Belvedere, Migny, St Phillip.
Station 1 (upper valley)	N 13°50.362' W 61°00.929' Sampling site on Jeremy/James River (main tributary of Soufriere River) just above Migny village. The river flow is rapid and there is sediment accumulation on both river banks (silt, sand). The river bottom is mostly composed of boulders. Around the river is an area of cultivation of mixed vegetables (dasheen, celery, parsley, cucumber, tomato, cabbage). We spoke to a farmer who uses Gramoxone after clearing field and before planting crop.
Station 2 (mid valley)	N 13°50.258' W 61°01.678' Site below confluence of main tributaries to Soufriere river. The river flow is rapid with large boulders and silt/sand accumulated along the banks. Very steep banks adjacent to river with farming of breadfruit, citrus, pawpaw, coconut, pumpkin, banana, root crops and secondary forest (bush, vines, ferns). Lots of pools with sediment in the river. Access to river just below main road junction.
Station 3 (lower valley)	N 13°51.405' W 61°03.367' Sampling station along the straightened section of the river through Soufriere town adjacent to constructed channel/dam with riprap on one side (playing fields) and vegetated slope on the other. Lots of Tilapia fish in the dammed section of the river (sampled for Station 3 tissues).

Station 4 (shore)	N 13°51.485' W 61°03.815' Much of Soufriere Bay is protected by fringing reef with sediment below the reef crest. Sampling was conducted adjacent to sediment traps monitored by York to the north side of the main bay (direction of longshore current flow). Station 4 tissues are molluscs (9 slugs, 3 cowries, 68 rough tops

2.3 Sampling procedures

CEHI is the regional institution with pesticide analytical capabilities and conducted sampling and the majority of analyses. Collaboration was organised so that all samples are collected by the project research assistant (Nicole Esteban) and CEHI. As detailed above (see Table 2.2), CEHI analysed two of the replicate samples. A third replicate was sent to a UK ISO-certified laboratory (CSL, MAFF) for analysis. This verification will aid CEHI in their quality control.

2.3.1 Sampling design

As detailed in Table 2.3, sampling at all three watersheds took place in four locations: the upper catchment, mid catchment, estuarine outlet and coastal reef/lagoon. At each monitoring station, 3 matrices were sampled: water, sediment and tissue (fish/invertebrate). The possibility of contaminated drinking water was also highlighted by several institutions (Water Resources Management Unit, WASCO) and it was decided to include drinking water extraction points when sampling. Sampling of drinking water extraction points was conducted in collaboration with WASCO (Mr Raphael Eudovique). Sampling of species farmed by aquaculture (Praslin/Mamiku: seamoss in Praslin Bay) was also been included in the survey. The sampling design matrix is shown in Table 2.4. Wherever possible, all matrices were analysed for individual chemicals, however it was not possible to analyse for certain groups of chemicals in sediment (e.g., Diquat and paraquat).

Table 2.4 Sampling design for three watersheds in St Lucia (Soufriere, Roseau, Praslin/Mamiku)

Stations	**Matrices**			
	Water	**Sediment**	**Fish/invert**	**Algae**
Farm	3	3	0	0
Mid course	3	3	0	0
Estuary	3	3	3	0
Reef	3	3	3	0
Drinking water abstraction point	3	0	0	0
Aquaculture	0	0	1	1
CSL (1 replicate/station)	15	12	7	1
CEHI (2 replicates/station) [6]	30	24	14	2

[6] The exception is paraquat, which will be analysed by CEHI (2 replicates of water only) and UK lab (1 replicate of water, 3 replicates of tissues)

Total	**45**	**36**	**21**	**3**

2.3.2 Sampling methodology

All sampling took place during 26 November through 1 December 2001. Sampling was carried out by the project researcher, Nicole Esteban in association with CEHI and WASCO (drinking water abstraction point only). Samples were transported to the CEHI laboratory. One-third of samples were prepared for onward transportation to CSL laboratory in the UK. Samples were hand delivered to CSL by Nicole Esteban in order to ensure that samples were kept chilled (water samples in glass bottles) or frozen (all other samples). Sampling methodology for the different matrices varied and is described in the next section.

Water

The vertical profile of sampling is important, as some pesticides are non-soluble in water and so form a film on the surface. Water was thus sampled from the surface of the water column. A total of 3 litres (2 litres for CEHI and 1 litre for CSL) was collected at each monitoring station. 1.5 litres was collected into glass bottles (some pesticides diffuse into plastic, e.g., cypermethrin) and 1.5 litres was collected into plastic bottles (other pesticides plate out or adsorb onto glass, e.g., paraquat). Stations 1-2 were freshwater, station 3 was freshwater/brackish and station 4 was seawater. Solvent (Hexane HPLC) was added into glass bottles to prevent water insoluble compounds from plating onto glass (e.g. cypermethrin).

Sediment

It is preferable to sample sediment with small grain sizes (e.g., organic-rich mud, clay) as pesticides diffuse to the organic portion of sediments. Approximately 300 grams of sediment (200 grams for CEHI and 100 grams for CSL) was sampled from the surface at the side of the rivers. Sediment was collected from station 4 (reef) by SCUBA. In the case of Soufriere and Roseau, sediment was collected from a location next to sediment traps laid by the University of York.

Tissues

Sessile invertebrates (e.g., mussels, clams) were collected in preference to fish as they could be taken from a fixed location. Invertebrates also have lower fat content and fat-soluble pesticides are therefore more easily detectable in their tissues. Where it was not possible to find invertebrates, it was necessary to collect fish. In this case, a local fisherman came out on the boat and set traps at the stations to catch reef-resident species (surgeonfish, goatfish, damselfish). Approximately 300 grams of tissues were required for analytical purposes (200 grams for CEHI and 100 grams for CSL).

3 RESULTS AND DISCUSSION

Samples collected from the three watershed areas, Mamiku, Roseau, Soufriere were analysed for a number of pesticides and nutrients. The pesticide levels in all the samples analysed were below detection limit except for Diazinon found in a tissue sample at Mamiku station 3 by CSL. The diazinon concentration obtained was 0.158 mg/kg.

Detailed results obtained from analysis of split samples carried out at CEHI and CSL are presented in Appendix 1 and Appendix 2 respectively. Both laboratories obtained similar results with respect to the pesticide analyses undertaken except for Diazinon found in tissue samples collected at Mamiku station 3, which was detected only by CSL. This was attributed to a difference in extraction procedures utilised by the laboratories as well as possible inhomogeneity of the tissue sample. CSL used a Soxhlet extraction procedure involving a 12-15 hour extraction time. This allowed a very long contact time of the sample with the solvent thereby increasing extraction efficiency. CEHI's extraction technique involved blending of the tissue samples with solvent for a few minutes each time, which may not have allowed for adequate extraction. Although every effort was made to ensure the homogeneity of samples analysed by both laboratories, this may have also been a source of error. Tissue samples were blended with a small quantity of dichloromethane and the sample split and sent to each laboratory. Instrumentation may have also played a role in the result obtained by CSL. A Gas Chromatograph – Mass Spectrometer (GCMS) was utilized by CSL while CEHI used a Gas Chromatograph with Flame Photometric Detector.

The overall results obtained by both laboratories suggested that pesticide contamination was not found at this time. However, it should be mentioned that this study was a one-time survey, which may not have adequately considered all the factors that would affect the presence of pesticides in the environment. Given the nature of some of the pesticides involved in this study, it may have also been useful to test for metabolites, which was not a part of this survey. Previous studies have detected the presence of ethoprophos and pirimiphos-ethyl in the environment, particularly in the Roseau river, which is situated in a heavily cultivated banana region (Woudneh, 1998; CEHI, 1998). The results obtained in this study may have been due to a variety of factors. Over the past five years there has been a steady decline in the banana industry in St. Lucia. This has led to a decrease in the acreage under cultivation and by extension the amount of agro-chemicals being used. Improved pest and pesticide management practices by farmers may have also resulted in less chemicals being used. At the time of sampling St. Lucia was emerging from a dry period, which would have reduced the risk of water contamination from runoff. It should also be noted that it was not known how recently, if at all, were pesticides applied in the regions selected for this study. It is therefore essential that such a study be repeated at other times of the year and that long-term monitoring programmes should be established.

The results obtained for phosphates and nitrates could not be directly linked to fertiliser use as baseline data was lacking. The nitrate levels in water for the samples tested ranged between 0.10 – 0.90 mg/l NO^{3-} while the phosphate levels in water samples fell between 0.02 and 0.30 mg/l PO_4^{3-}. The nitrate levels obtained were well below the WHO drinking water guideline value of 50 mg/l. No guideline values could be obtained for phosphates in either natural waters or drinking water. A previous study of nitrates and phosphates in water done by CEHI (Singh and Lewis, 1996) in the Soufriere River produced similar data for nitrates to those obtained in this study.

(Singh and Lewis, 1996) found nitrates in the range 0.04mg/l to 1.5mg/l. The phosphate levels found by Singh and Lewis were generally higher (0.1 - 1.9 mg/l PO_4^{3-}) than the levels detected in this present study. No studies could be identified for nitrates and phosphates in soil in St. Lucia.

The potassium levels in water samples in all the watersheds were less than 20mg/l for stations 1 to 3. However, values of 1850mg/l, 1230mg/l and 591mg/l were obtained for Mamiku station 4, Roseau station 4, and Soufriere station 4 respectively. Station 4 samples were collected at the coast or in mangroves leading out to sea. The values obtained at these Stations exceeded the natural levels of potassium seawater of 410 mg/l (The University of Sheffield and WebElements Ltd, 2002). This was attributed to fertiliser use particularly in the Roseau Watershed.

Information obtained from the Ministry of Agriculture, Forestry and Fisheries, St. Lucia (L. McDonald, pers. comm.) indicated that the potassium levels in soils of St. Lucia were generally between 156 – 1173 mg/kg. These values were exceeded at Roseau stations 1 and 2, and also at Soufriere stations 2 and 4. The highest value, 5710.4 mg/l was obtained at Roseau station 4. This may have been due to the use of potassium-based fertilisers in the heavily cultivated Roseau area. However, further studies are needed before more concrete conclusions are made. Soufriere station 4 also contained significant levels of potassium (3932 mg/kg). While it could not be confirmed, it was thought that in addition to potassium from fertilisers, the potassium levels in the Soufriere area might also have been the result of volcanic soils typically found in this region.

The potassium level in sea moss was extremely high (1.567×10^5 mg/kg). The reasons for this high value could not be ascertained. However, it was thought that sea moss may act as a natural sink for potassium ions.

From the discussion above it can be seen that there is limited data on the fate of agro-chemicals the St. Lucian environment. In particular, soil and tissue studies are lacking. Although there are a few studies available on St. Lucian waters, much more work needs to be done in this area. Both targeted research and more long-term monitoring programmes need to be established to enable better assessment of the impact of agro-chemicals on the environment.

4 REFERENCES

Addiscott, T.M. 1996. Fertilisers and Nitrate Leaching. In: *Agricultural Chemicals and the Environment*. Edited by R.E. Hester and R. M. Harrison, I-24. Cambridge, Royal Society of Chemistry.

Aharonson, N. 1987. Potential Contamination of Ground Water by Pesticides. In: *Pure and Applied Chemistry*, Vol. 59, No. 10, pp. 1419 – 1446, IUPAC

Boodram, N. 2002. Fate of agro-chemicals in the land water interface, with reference to St Lucia. Research report for DFID LWI R7668. St Lucia, CEHI.

CCA, 1991. *St. Lucia Environmental Profile*. St. Michael, Barbados. Caribbean Conservation Association.

CEHI, 1998. *Pesticide Pollution in the Windward Islands*. Castries, CEHI.

Dasgupta, T. and Perue, C. 2002. *Review of Agro-chemical Toxicity for the Caribbean*. UWI, Mona.

Edwards, P.E. 2002. Fate of agro-chemicals in the land water interface, with reference to Jamaica and the wider Caribbean. Research report for DFID LWI R7668. Jamaica, UWI Mona.

Henao, S.; Finkelman, J.; Albert, L.; de Koning, W. 1993. Pesticide and Health in the Americas, PAHO/WHO.

Ferguson, A.J.D.; Pearson, M.J. and Reynolds, C.S. 1996. Eutrophication of Natural waters and Toxic Algal Blooms. In: *Agricultural Chemicals and the Environment*. Edited by R.E. Hester and R. M. Harrison, I-24. Cambridge, Royal Society of Chemistry.

Little, V.; Ambrose, E.; St. Hill, T.; and Magloire, L. 2001. *Analysis of the Options for Controlling Yellow Sigatoka (leafspot) disease of bananas in St. Lucia*. Castries, IICA.

Kenward, N. 2001. Sampling programme for agro-chemical in St Lucian coastal waters. November 2001. London, MRAG Ltd.

Kenward, N., Mees, C.C. and Simpson, L. 2001. Agro-chemical workshop. Still Plantion, Soufriere. June 2001. London, MRAG Ltd.

Ripley, B.D. and Chau, A.S.Y. 1982. Carbamate Pesticides. In: *Analysis of Pesticides in Water: Nitrogen Containing Pesticides.* Vol.3, CRC press, Boca Raton.

Singh, J. G. and Lewis, A. 1996. *Environmental and Coastal Resources Project-Water Quality Monitoring at St. Lucia local site*. Castries, CEHI

University of Sheffield and WebElements Ltd, UK]. Document served: Tuesday 30th July, 2002 URL:http://www.webelements.com/

United States Central Intelligence Agency*. World Factbook 2001.*[Online] Updated 2001/03/05 URL:http://www.cia.gov/publications/factbook

Vienneau, D. 1997. *An Assessment of Available Information on Environmental impacts of Chemical Pesticides Used in CARICOM states of the Caribbean Region*. Masters Thesis, Dalhousie University, Halifax, Nova Scotia

Woudneh, M.B. 1998. *Pesticide Pollution Assessment in the Roseau Valley, St. Lucia*. Castries, CEHI

Woudneh, M.B. 1999. *Pesticides in St. Lucian Waters*. Castries, CEHI

WHO, 1996. *Guidelines for Drinking Water Quality*. Vol. 2nd Edition, Geneva

APPENDIX 1 – CSL ANALYSIS RESULTS

PGD-84
THE ANALYSIS OF ENVIRONMENTAL SAMPLES FROM ST. LUCIA

CENTRAL SCIENCE LABORATORY

Study No: **PGD-84**

Study title: **ANALYSIS OF ENVIRONMENTAL SAMPLES FROM ST. LUCIA**

Sponsor:	Marine Resources Assessment Group (MRAG) 47, Princes Gate London SW7 2QA
Study Director:	Sheonaidh Mc Gaw
Test Facility:	Central Science Laboratory Sand Hutton York YO41 1LZ United Kingdom Tel No: 01904 462000 ext 3410 Fax No: 01904 462253
Period of investigation:	December 2001 – May 2002
Date of issue of report:	see signature of Study Director
No. of pages in report:	30

Authentication

I declare that from the receipt of samples at the test facility this non-regulatory work was conducted following the procedures described herein, and in accordance with the OECD Principles of Good Laboratory Practice subject to the following exceptions:

i. the study was not subject to monitoring by the CSL Quality Assurance (QA) Unit.

ii. the results reported were not subject to monitoring by the CSL QA Unit.

iii. the HPGPC cleanup of fish samples was performed outside the GLP compliant area.

However, the test facility was subject to facility and process audits by the CSL QA Unit and the work and results were also subject to rigorous analytical quality control (AQC). This report represents a true and accurate record of the results obtained.

Signed .....Date.....

Sheonaidh McGaw
Study Director
Central Science Laboratory, York

Signed .....Date.....

Dr M F Wilson
Head of Pesticides Group
Central Science Laboratory, York

Signed .....Date.....

R. Glass, Contract Manager, Central Science Laboratory, York

SUMMARY

1. Environmental samples (water, fish and other aquatic organisms, and sediment) were delivered by Nicole Esteban of MRAG on the 3/12/01. These samples were entered onto the Laboratory Information Management System (LIMS) on the 6/12/01.

2. All samples are negative apart from one fish tissue sample (sample number 33171, MRAG reference Mamiku Station 3), which has a small residue of Diazinon at 0.158 mg/kg.

CONTENTS

INTRODUCTION

1.1 Samples were delivered by Nicole Esteban on the 3rd December 2001. A total of 21 samples were received; 6 samples of a pre-blended mixture of fish and other sea creatures, 12 sediment samples, 13 water samples (2 portions of each sample – 1 portion in a glass bottle and the other in a plastic bottle), 1 sample of sea moss and 1 sample of algal biomass. The latter 2 samples have been referred to throughout this project as algae.

1.2 *Summary of analyses*

1.2.1 All samples were analysed by GC-MSD for the following residues :
Endosulfan, Endosulfan Sulfate, Imazalil, Chlorpyrifos, Ethoprophos, Diazinon, Malathion, Pirimiphos-methyl, Cadusafos, Isazofos, Profenofos, Metalaxyl, Cypermethrin, Lambda-Cyhalothrin, Cyromazine and Propiconazole.

1.2.2 All samples were analysed by HPLC with post-column derivatisation and a fluorescence detector for the following residues :
Oxamyl, Carbaryl and Carbofuran.

1.2.3 The water samples were analysed by HPLC with a diode-array detector for Paraquat and Diquat. Fish and algae were analysed by HPLC with a diode-array detector for Paraquat.

1.3 A total of 3 replicate analyses was performed for each sample. For all analyses except for Paraquat and Diquat, 2 of the replicates were performed and reported by the laboratory in St. Lucia (CEHI). All 3 replicate analyses for Paraquat and Diquat were performed at CSL. The results from CEHI do not form part of this report.

EXPERIMENTAL

Sampling

2.1 Samples were collected between the 24th November and the 1st December 2001. They were delivered to the laboratory on the 3rd December 2001 and booked into the Laboratory Information Management System (LIMS) on the 6th December 2001. All samples apart from water samples in glass bottles were stored at -20°C. Water samples in glass bottles were stored at 5-10°C.

2.2 Water samples in glass bottles and plastic bottles were given separate laboratory numbers. A small volume of Dichloromethane was added to the water samples in glass bottles before being transported to the UK.

2.3 Fish samples were blended at a laboratory in St. Lucia (CEHI) and divided into 3 portions; 2 portions for analysis by CEHI and the third portion for analysis by CSL.

Methodology

Multi-residue analysis of fish samples for compounds outlined in section 1.2.1. See tables 1 and 2 of the appendix for a summary of results.

3.1 Method reference MRAG01

5 g of sample were ground up with an equivalent weight of sand and atleast five times the sample weight of anhydrous Sodium Sulfate. The mixture was Soxhlet extracted into Diethyl Ether for 12-15 hours. The extract was made up to 100 ml once extraction was complete. A 20 ml portion of the Ether extract was blown down to just dryness and re-dissolved in 2 ml of 1:1 Cyclohexane: Ethyl Acetate. 1ml was cleaned up by Gel Permeation Chromatography (GPC). The cleaned up extract was evaporated to dryness and re-dissolved in 2 ml of 1:1 Hexane:Ethyl Acetate and analysed by Gas Chromatography with a Mass Selective Detector (GC-MSD). A DB-5ms column was used for the analysis of all but the more polar compounds (method MRAG01(a)) and a DB-1701 column was used for the more polar compounds (namely Cyromazine and Imazalil) (method MRAG01 (b)).

Multi-residue analysis of algae for compounds outlined in section 1.2.1. See tables 3 and 4 of the appendix for a summary of the results.

3.2 Method reference MRAG02

5 g of sample were weighed out and 1.5 g of Sodium Hydrogen Carbonate and 40 ml of Ethyl Acetate were added. Samples were placed in a water bath at 30°C for 30 minutes. Samples were homogenised for 1 minute at 20,500 rpm using an ultraturrax homogeniser and filtered through ~25g of anhydrous Sodium Sulfate. Another 40 ml of Ethlyl Acetate was added to the samples the homogenising repeated. The filtrates were combined and the resultant extracts were made up to 100 ml. A 10 ml portion of the Ethyl Acetate extract was evaporated to just dryness and re-dissolved in 2 ml of 1:1 Hexane:Ethyl Acetate. This was analysed by GC-MSD using a DB-5ms column for the analysis of all but the most polar compounds, method MRAG02(a) and using a DB-1701 column for the more polar compounds (namely Cyromazine and Imazalil), method MRAG02(b).

Multi-residue analysis of sediment samples for compounds outlined in section 1.2.1. See tables 5 and 6 of the appendix for a summary of the results.

3.3 Method reference MRAG03

9-10 g of sample were ground up with three to five times the sample weight of anhydrous Sodium Sulfate. The mixture was Soxhlet extracted into Diethyl Ether for 12-15 hours. The extract was made up to 100 ml once extraction was complete. A 10 ml portion of the Ether extract was blown down to just dryness and re-dissolved in 2 ml of 1:1 Hexane: Ethyl Acetate and analysed by GC-MSD. A DB-5ms column was used for the analysis of all but the more polar compounds, method MRAG03(a) and a DB-1701 column was used for the more polar compounds (namely Cyromazine and Imazalil), method MRAG03 (b).

Multi-residue analysis of water samples for compounds outlined in section 1.2.1, apart from the more polar residues (namely Cyromazine and Imazalil). See table 7 of the appendix for a summary of the results.

3.4 Method reference MRAG04

Samples were transported and stored with added Dichloromethane in glass bottles. HPLC grade water was used as a blank and for recoveries. 5 g Sodium Chloride was dissolved in each sample. Prior to extraction by partitioning 3 times with 200 ml of Dichloromethane for 2 minutes. The Dichloromethane extracts were evaporated to dryness, re-dissolved in 2 ml of 1:1 Hexane:Ethyl Acetate and <1 g anhydrous Sodium Sulfate added. The extracts were analysed by GC-MSD using a DB-5ms column.

Multi-residue analysis of water samples for polar residues outlined in section 1.2.1 (Cyromazine and Imazalil). See table 8 of the appendix for a summary of the results.

3.5 Method reference MRAG05

Water samples transported and stored in plastic bottles were used. HPLC grade water was used for the blank and for recovery checks. 10 ml of sample was measured into a graduated test tube, put on a dri-block at 90°C and evaporated to dryness. Residues were re-dissolved in 1 ml 1:1 Hexane:Ethyl Acetate and analysed by GC-MSD using a DB-1701 column.

Multi-residue analysis of fish samples for compounds outlined in section 1.2.2. See table 9 of the appendix for a summary of the results.

3.6 Method reference MRAG06

See section 3.1 for extraction details, as the same extracts were used for the multi-residue and for the carbamate analyses. 10 ml of the Ether extract was evaporated to dryness, re-dissolved in 2 ml of HPLC grade water and filtered through a 0.45µm PTFE disc filter. 50 µL of the extract was analysed by HPLC with post-column derivatisation using a Phenyl-Inertpak column and a fluorescence detector.

Multi-residue analysis of algae samples for compounds outlined in section 1.2.2. See table 10 of the appendix for a summary of the results.

3.7 Method reference MRAG07

See section 3.2 for extraction details, as the same extracts were used for the multi-residue and for the carbamate analyses. 10 ml of the Ethyl Acetate extract was evaporated to dryness, re-dissolved in 2 ml of HPLC grade water and filtered through a 0.45µm PTFE disc filter. 50 µL of the extract was analysed by HPLC with post-column derivatisation using a Phenyl-Inertpak column and a fluorescence detector.

Multi-residue analysis of sediment samples for compounds outlined in section 1.2.2. See table 11 of the appendix for a summary of the results.

3.8 Method reference MRAG08

See section 3.3 for extraction details, as the same extracts were used for the multi-residue and for the carbamate analyses. 20 ml of the Ether extract was evaporated to dryness, re-dissolved in 4 ml of HPLC grade water and filtered through a 0.45µm PTFE disc filter. 1500 µL of the extract was analysed by HPLC with post-column derivatisation using a Phenyl-Inertpak column and a fluorescence detector.

Multi-residue analysis of water samples for compounds outlined in section 1.2.2. See table 12 of the appendix for a summary of the results.

3.9 Method reference MRAG09.
Water samples transported and stored in plastic bottles were used for the carbamate analysis. A 4 ml portion of the sample was filtered through a 0.45µm disc filter and 1500µL of sample was analysed by HPLC with post-column derivatisation using a Phenyl-Inertpak column and a fluorescence detector.

Multi-residue analysis of fish and algae samples for compounds outlined in section 1.2.3. See tables 13, 14 and 15 of the appendix for a summary of the results.

3.10 Method reference MRAG10.
2.5 g sample was homogenised by an ultraturrax homogeniser at 10,000 rpm for 1 minute with 10 ml of a solution of 10 % Trichloroacetic acid (TCA) in water, then centrifuged for 10 minutes. The supernatant was decanted off, the homogenisation was repeated and the supernatants combined for each sample. The extract was then cleaned up on a Waters Sep-Pak Plus tC18 Environmental cartridge. Paraquat was eluted from the clean-up cartridge with 10 ml of a solution of 10% methanol, 90% water containing 0.1% Orthophosphoric acid. The cleaned-up sample was then put through a second clean-up, on a 150 mg Oasis MCX cartridge. Paraquat was eluted with 2 ml of a solution of 1M Ammonium Chloride in 1:1 Methanol:Water. This final cleaned up solution was diluted with 0.5 ml water and 2 ml of a 250 mM solution of Sodium Octanesulfonate in 1% aqueous Orthophosphoric acid (at pH 3). Samples were analysed by HPLC (100µL injection) on a Phenomenex Columbus column using a photodiode array detector.

Multi-residue analysis of water samples for compounds outlined in section 1.2.3. See tables 16, 17 and 18 of the appendix for a summary of the results.

3.11 Method reference MRAG11.
Sea water blank was prepared by making a solution of 2.5 % Sodium Chloride in HPLC grade water. 100 ml of sample were cleaned up on a 60 µg Oasis MCX cartridge. Paraquat and Diquat were eluted with 2 ml of a solution of 1M Ammonium Chloride in 1:1 Methanol:Water. This final cleaned up solution was diluted with 0.5 ml water and 2 ml of a 250 mM solution of Sodium Octanesulfonate in 1% aqueous Orthophosphoric acid (at pH 3). Samples were analysed by HPLC (100µL injection) on a Phenomenex Columbus column using a photodiode array detector.

RESULTS AND DISCUSSION

4.1 All results have been summarised in table form in the appendix.

4.2 All samples are negative, apart from sample 33171 (Mamiku station 3) in which a residue of Diazinon at 0.158 mg/kg was found. Several of the fish and algae tissues and two of the sediment samples exhibited peaks in the multi-residue GC-MSD screen. Confirmation of these residues by comparing the relative ion ratios for each of these suspected residues to that of a recovery have ruled these samples out as “false positives”. These have been marked on the results tables for reference.

4.3 The results for the analysis of fish tissues for Malathion can not be used. Although the samples were cleaned up by GPC, there was an extremely large interference peak of similar retention to Malathion. This peak was present in all ions collected for Malathion.

4.4 Interferences have caused problems in some samples, particularly for the spikes at lower concentrations (for example, see tables 1, 3, and 4). In these instances, the LOD has been raised to that of the higher recovery. In some cases, interferences, particularly at the lower spiking level, have enhanced the recoveries.

4.5 Note that the recoveries for Oxamyl and Carbaryl in sediment are very low. The soil used for spiking probably contains some clay and it may be that these residues have stuck on to the clay particles in the soil. The worst recovery is recovery 1 for Oxamyl, which is 4%. However, the LOD achieved on the HPLC sediments run is 0.0001 mg/kg. This is 50 times less that the LOD aimed for (0.05 mg/kg). If there were a residue at a LOD of 0.05 mg/kg and only 4% recovery was achieved, then this would equate to a LOD on the HPLC run of 0.002 mg/kg. Because a LOD of 0.001 mg/kg was achievable in this HPLC run, we would still be able to see any residues at the 0.05 mg/kg LOD. Therefore, although in table 10 a LOD of 0.001 mg/kg has been reported, the LOD should be raised to 0.05 mg/kg for all carbamates.

APPENDIX

Table 1 – Results of fish analyses using method MRAG01(a), run number 16806

			Results, expressed as <LOD in mg/kg					
MRAG ref			Roseau station 3	Roseau station 4	Mamiku station 3	Mamiku station 4	Soufriere station 3	Soufriere station 4
Lab sample no.			33169	33170	33171	33172	33173	33174
	%rec1	%rec2						
Residue								
Ethoprophos	119	221	<0.050	<0.051	<0.044	<0.049#	<0.047	<0.050
Cadusafos	103	156	<0.050	<0.051	<0.044	<0.049	<0.047	<0.050
Diazinon	120	201	<0.050	<0.050#	0.044**	<0.049	<0.046	<0.050
Isazofos	80	183	<0.049	<0.050	<0.044	<0.048	<0.046	<0.049#
Metalaxyl	62	207	<0.051	<0.052	<0.045	<0.050	<0.048#	<0.051
Pirimiphos-Methyl	128	251	<0.050	<0.050	<0.044	<0.049	<0.046	<0.050
Malathion	151	306						
Chlopyrifos	104	182	<0.050	<0.050	<0.044	<0.048	<0.046	<0.050
Endosulfan I	232	125	<0.050	<0.050	<0.044	<0.048#	<0.046#	<0.050#
Profenofos	376	176	<0.050	<0.051	<0.045#	<0.049	<0.047	<0.051
Endosulfan II	120	182	<0.050#	<0.050	<0.044	<0.049#	<0.046	<0.050#
Propiconazole	184	385	<0.050#	<0.050#	<0.044#	<0.048#	<0.046	<0.050#
Endosulfan Sulfate	147	159	<0.059	<0.060	<0.053#	<0.058	<0.056#	<0.060#
Lambda-cyhalothrin	143	266	<0.050	<0.050	<0.044	<0.049	<0.047	<0.050
Cypermethrin	N/a*	215	<0.248	<0.252	<0.220	<0.243	<0.232	<0.249

* rec 1 not visible above the noise. Hence LOD raised to that of rec 2.

Peaks found in original screen. Not confirmed as additional ions are either missing or failed on relative peak ion ratios

Note : Interference in the form of a very large co-elutant peak at the retention time for Malathion. This is also present in all 3 ions used. Hence no useful information can be obtained for malathion.

** Sample is positive for diazinon. Residue is 0.158 mg/kg

Table 2 – Results of fish analyses using method MRAG01(b), run number 17598

			Results, expressed as <LOD in mg/kg					
MRAG ref			Roseau station 3	Roseau station 4	Mamiku station 3	Mamiku station 4	Soufriere station 3	Soufriere station 4
Lab sample no.			33169	33170	33171	33172	33173	33174
	%rec1	%rec2						
Residue								
Cyromazine	123	101	<0.023	<0.024#	<0.021	<0.023	<0.022	<0.023
Imazalil	109	111	<0.024	<0.025#	<0.022	<0.024#	<0.023	<0.024

Peaks found in original screen. Confirmation based on ion ratios indicate that these samples are negative. However sample 33170 has failed on only the one ion ratio.

Table 3 – Results of algae analyses using method MRAG02(a) run number 16806

			Results, expressed as <LOD in mg/kg	
MRAG ref			Roseau station 3, algal biomass	Mamiku seamoss
Lab sample no.			33167	33168
	%rec1	%rec2		
Residue				
Ethoprophos	159	149	<0.050	<0.050
Cadusafos	71	66	<0.051	<0.051
Diazinon	*	89	<0.251	<0.251
Isazofos	297	125	<0.050	<0.050
Metalaxyl	62	101	<0.051	<0.051
Pirimiphos-Methyl	208	109	<0.050	<0.050
Malathion	198	113	<0.050	<0.050
Chlopyrifos	200	114	<0.050	<0.050
Endosulfan I	56	78	<0.050	<0.050
Profenofos	*	66	<0.255	<0.255
Endosulfan II	127	72	<0.050	<0.050
Propiconazole	264	94	<0.050	<0.050
Endosulfan Sulfate	160	71	<0.060	<0.060
Lambda-cyhalothrin	159	99	<0.050	<0.050
Cypermethrin	*	97	<0.251	<0.251

* Rec. 1 is either not visible above the baseline or there is an interfering peak in the of similar area to rec. 1, hence the LOD has been increased to that of rec. 2
Note that there are some matrix effects enhancing % recovery values for rec. 1

Table 4 – Results of algae analyses using method MRAG02(b) run number 17598

			Results, expressed as <LOD in mg/kg	
MRAG ref			Roseau station 3, algal biomass	Mamiku seamoss
Lab sample no.			33167	33168
	%rec1	%rec2		
Residue				
Cyromazine	131	152	<0.023	<0.023
Imazalil	78	41	<0.025	<0.025

Table 5 – Results of sediment analyses using method MRAG03(a) run number 16806

			Results	expressed	as	<LOD	in mg/kg			
MRAG ref			Roseau station 1	Roseau station 2	Roseau station 3	Roseau station 4	Mamiku station 1	Mamiku station 2	Mamiku station 3	Mamiku station 4
Lab sample no.			33153	33156	33157	33158	33159	33160	33161	33162
	%rec1	%rec2								
Residue										
Ethoprophos	60	105	<0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cadusafos	71	119	<0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Diazinon	120	117	<0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Isazofos	108	94	<0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05#	<0.05
Metalaxyl	179	159	<0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Pirimiphos-Me	76	110	<0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Malathion	103	106	<0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Chlopyrifos	96	77	<0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Endosulfan I	*	100	<0.28	<0.25	<0.25	<0.25#	<0.26	<0.24	<0.25	<0.25
Profenofos	71	110	<0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Endosulfan II	120	91	<0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Propiconazole	112	88	<0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Endosulfan Sulfate	197	101	<0.07	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06#	<0.06
Lambda-cyhalothrin	115	84	<0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cypermethrin	116	86	<0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

* Interference peak in blank of similar area to that of recovery 1, hence rec. 1 can not be used and LOD has been raised to that of LOD 2.
# Peaks noted in screening run. On checking the ion ratios, samples were found to be negative

Table 5 (cont'd) – Results of sediment analyses using method MRAG03(a) run number 16806

	Results	expressed	as <LOD	in mg/kg
MRAG ref	Soufriere station 1	Soufriere station 2	Soufriere station 3	Soufriere station 4
Lab sample no.	33163	33164	33165	33166
Residue				
Ethoprophos	<0.05	<0.05	<0.05	<0.05
Cadusafos	<0.05	<0.05	<0.05	<0.05
Diazinon	<0.05	<0.05	<0.05	<0.05
Isazofos	<0.05	<0.05	<0.05	<0.05
Metalaxyl	<0.05	<0.05	<0.05	<0.05
Pirimiphos-Me	<0.05	<0.05	<0.05	<0.05
Malathion	<0.05	<0.05	<0.05	<0.05
Chlopyrifos	<0.05	<0.05	<0.05	<0.05
Endosulfan I	<0.25	<0.25	<0.25	<0.25
Profenofos	<0.05	<0.05	<0.05	<0.05
Endosulfan II	<0.05	<0.05	<0.05	<0.05
Propiconazole	<0.05	<0.05	<0.05	<0.05
Endosulfan Sulfate	<0.06	<0.06	<0.06	<0.06
Lambda-cyhalothrin	<0.05	<0.05	<0.05	<0.05
Cypermethrin	<0.05	<0.05	<0.05	<0.05

Table 6 – Results of sediment analyses using method MRAG03(b) run number 17340

			Results	expressed	as	<LOD	in mg/kg			
MRAG ref			Roseau station 1	Roseau station 2	Roseau station 3	Roseau station 4	Mamiku station 1	Mamiku station 2	Mamiku station 3	Mamiku station 4
Lab sample no.			33153	33156	33157	33158	33159	33160	33161	33162
	%rec1	%rec2								
Residue										
Cyromazine	229	51	<0.11	<0.10	<0.10	<0.10#	<0.10	<0.10	<0.10	<0.10
Imazalil	539	123	<0.11	<0.10	<0.10	<0.10	<0.11	<0.10	<0.10	<0.10

	Results	expressed	as	<LOD
MRAG ref	Soufriere station 1	Soufriere station 2	Soufriere station 3	Soufriere station 4
Lab sample no.	33163	33164	33165	33166
Residue				
Cyromazine	<0.10	<0.10	<0.10	<0.10
Imazalil	<0.10	<0.10	<0.10	<0.10

Interference peak in the screen. Ion ratios are different from the recovery, hence negative.

Table 7 – Results of water analyses using method MRAG04 run number 16549

			Results	expressed	as	<LOD in	µg/L		
MRAG ref			Vieux Fort Treat. Plant Beausejour	Roseau station 1	Roseau station 2	Roseau station 3	Roseau station 4	Mamiku station 1	Mamiku station 2
Lab sample no.			33123	33126	33127	33128	33129	33130	33131
	%rec1	%rec2							
Residue									
Ethoprophos	72	85	<1.0	<0.9	<1.0	<0.8	<1.0	<1.0	<1.0
Cadusafos	78	94	<1.0	<0.9	<1.0	<0.8	<1.0	<1.0	<1.0
Diazinon	76	92	<0.9	<0.9	<1.0	<0.8	<1.0	<1.0	<1.0
Isazofos	83	100	<0.9	<0.9	<1.0	<0.8	<1.0	<1.0	<0.9
Metalaxyl	93	103	<1.0	<0.9	<1.0	<0.9	<1.0	<1.0	<1.0
Pirimiphos-Me	71	86	<0.9	<0.9	<1.0	<0.8	<1.0	<1.0	<1.0
Malathion	88	96	<1.0	<0.9	<1.0	<0.8	<1.0	<1.0	<1.0
Chlopyrifos	83	96	<0.9	<0.9	<1.0	<0.8	<1.0	<1.0	<1.0
Endosulfan I	90	93	<0.9	<0.9	<1.0	<0.8	<1.0	<1.0	<1.0
Profenofos	98	94	<1.0	<0.9	<1.0	<0.8	<1.0	<1.0	<1.0
Endosulfan II	106	103	<0.9	<0.9	<1.0	<0.8	<1.0	<1.0	<1.0
Propiconazole	92	95	<0.9	<0.9	<1.0	<0.8	<1.0	<1.0	<1.0
Endosulfan Sulfate	119	88	<1.1	<1.1	<1.2	<1.0	<1.2	<1.2	<1.1
Lambda-cyhalothrin	97	105	<0.9	<0.9	<1.0	<0.8	<1.0	<1.0	<1.0
Cypermethrin	127	129	<0.9	<0.9	<1.0	<0.8	<1.0	<1.0	<1.0

Table 7 (cont'd) – Results of water analyses using method MRAG04 run number 16549

		Results	expressed	as	<LOD	in µg/L
MRAG ref	Mamiku station 3	Mamiku station 4	Soufriere station 1	Soufriere station 2	Soufriere station 3	Soufriere station 4
Lab sample no.	33132	33133	33134	33135	33136	33137
Residue						
Ethoprophos	<1.0	<1.0	<1.0	<1.0	<1.0	<0.9
Cadusafos	<1.0	<1.0	<1.0	<1.0	<1.0	<0.9
Diazinon	<1.0	<1.0	<1.0	<0.9	<1.0	<0.9
Isazofos	<1.0	<1.0	<1.0	<0.9	<1.0	<0.9
Metalaxyl	<1.0	<1.0	<1.0	<1.0	<1.0	<0.9
Pirimiphos-Me	<1.0	<1.0	<1.0	<0.9	<1.0	<0.9
Malathion	<1.0	<1.0	<1.0	<1.0	<1.0	<0.9
Chlopyrifos	<1.0	<1.0	<1.0	<0.9	<1.0	<0.9
Endosulfan I	<1.0	<1.0	<1.0	<0.9	<1.0	<0.9
Profenofos	<1.0	<1.0	<1.0	<1.0	<1.0	<0.9
Endosulfan II	<1.0	<1.0	<1.0	<0.9	<1.0	<0.9
Propiconazole	<1.0	<1.0	<1.0	<0.9	<1.0	<0.9
Endosulfan Sulfate	<1.2	<1.2	<1.2	<1.1	<1.2	<1.1
Lambda-cyhalothrin	<1.0	<1.0	<1.0	<0.9	<1.0	<0.9
Cypermethrin	<1.0	<1.0	<1.0	<0.9	<1.0	<0.9

Table 8 – Results of water analyses using method MRAG05 run number 17340

				Results	expressed	as	<LOD in	µg/L	
MRAG ref				Vieux Fort Treat. Plant Beausejour	Roseau station 1	Roseau station 2	Roseau station 3	Roseau station 4	Mamiku station 1
Lab sample no.				33138	33139	33140	33141	33143	33144
	%rec1	%rec2	% rec. 3						
Residue									
Cyromazine	174	123	85	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2
Imazalil	137	107	72	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6

		Results	expressed	as	<LOD in	µg/L	
MRAG ref	Mamiku station 2	Mamiku station 3	Mamiku station 4	Soufriere station 1	Soufriere station 2	Soufriere station 3	Soufriere station 4
Lab sample no.	33145	33146	33147	33149	33150	33151	33152
Residue							
Cyromazine	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2
Imazalil	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6

Table 9 – Results of fish analyses using method MRAG06 run number 16528

			Results	expressed	as	<LOD in	mg/kg	
MRAG ref			Roseau station 3	Roseau station 4	Mamiku station 3	Mamiku station 4	Soufriere station 3	Soufriere station 4
Lab sample no.			33169	33170	33171	33172	33173	33174
	%rec1	%rec2						
Residue								
Oxamyl	96	96	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Carbofuran	83	78	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Carbaryl	40	37	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04

Note : Poor recovery for carbaryl.

Table 10 – Results of algae analyses using method MRAG07 run number 16528

			Results	expressed	as	<LOD in	mg/kg	
MRAG ref			Roseau station 3	Roseau station 4	Mamiku station 3	Mamiku station 4	Soufriere station 3	Soufriere station 4
Lab sample no.			33169	33170	33171	33172	33173	33174
	%rec1	%rec2						
Residue								
Oxamyl	80	83	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Carbofuran	83	83	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Carbaryl	72	72	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04

Table 11 – Results of sediment analyses using method MRAG08 run number 16353

			Results	expressed	as	<LOD	in mg/kg			
MRAG ref			Roseau station 1	Roseau station 2	Roseau station 3	Roseau station 4	Mamiku station 1	Mamiku station 2	Mamiku station 3	Mamiku station 4
Lab sample no.			33153	33156	33157	33158	33159	33160	33161	33162
	%rec1	%rec2								
Residue										
Oxamyl	4	20	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Carbofuran	58	73	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Carbaryl	20	49	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

	Results	expressed	as <LOD	in mg/kg
MRAG ref	Soufriere station 1	Soufriere station 2	Soufriere station 3	Soufriere station 4
Lab sample no.	33163	33164	33165	33166
Residue				
Oxamyl	<0.001	<0.001	<0.001	<0.001
Carbofuran	<0.001	<0.001	<0.001	<0.001
Carbaryl	<0.001	<0.001	<0.001	<0.001

Note that the recoveries for sediment are very low, particularly for Oxamyl and Carbaryl. This is 50 times below the LOD aimed for. Take the worst case scenario, i.e. a recovery of 4%. If only 4% of residue is extracted at the requested limit of detection 0.05 mg/kg, this would equate to a limit of detection of 0.002mg/kg. We would therefore still be able to see any residues at the requested limit of detection of 0.05 mg/kg. It would therefore be advisable to raise the LOD for all samples to that of the originally requested value of 0.05 mg/kg as originally requested for all 3 analytes.

Table 12 – Results of water analyses using method MRAG09 run number 16209

	Results	expressed	as	<LOD in	µg/L	
MRAG ref	Vieux Fort Treat. Plant Beausejour	Roseau station 1	Roseau station 2	Roseau station 3	Roseau station 4	Mamiku station 1
Lab sample no.	33138	33139	33140	33141	33143	33144
Residue						
Oxamyl	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Carbofuran	<0.49	<0.49	<0.49	<0.49	<0.49	<0.49
Carbaryl	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50

		Results	expressed	as	<LOD in	µg/L	
MRAG ref	Mamiku station 2	Mamiku station 3	Mamiku station 4	Soufriere station 1	Soufriere station 2	Soufriere station 3	Soufriere station 4
Lab sample no.	33145	33146	33147	33149	33150	33151	33152
Residue							
Oxamyl	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Carbofuran	<0.49	<0.49	<0.49	<0.49	<0.49	<0.49	<0.49
Carbaryl	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50

Note : No recovery checks included as analysis was by direct injection of water samples onto the HPLC.

Table 13 – Results of batch 1 fish and algae analyses using method MRAG10 run number 17331

			Results	expressed	as	<LOD	in	mg/kg
MRAG ref			Roseau station 3 fish	Roseau station 4 fish	Mamiku station 3 fish	Mamiku station 4 fish	Soufriere station 3 fish	Soufriere station 4 fish
Lab sample no.			33169	33170	33171	33172	33173	33174
	%rec1	%rec2						
Residue								
Paraquat	92	96	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

	Results expressed as <LOD in mg/kg			
MRAG ref			Roseau station 3 algal biomass	Mamiku Sea Moss
Lab sample no.			33167	33168
	%rec1	%rec2		
Residue				
Paraquat	224	114	<0.05	<0.05

Table 14 – Results of batch 2 fish and algae analyses using method MRAG10 run number 17409

			Results	expressed	as	<LOD	in	mg/kg
MRAG ref			Roseau station 3 fish	Roseau station 4 fish	Mamiku station 3 fish	Mamiku station 4 fish	Soufriere station 3 fish	Soufriere station 4 fish
Lab sample no.			33169	33170	33171	33172	33173	33174
	%rec1	%rec2						
Residue								
Paraquat	*	61	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25

	Results expressed	as <LOD in mg/kg		
MRAG ref			Roseau station 3 algal biomass	Mamiku Sea Moss
Lab sample no.			33167	33168
	%rec1	%rec2		
Residue				
Paraquat	*	68	<0.25	<0.25

- Recoveries slightly lower for this batch, hence rec. 1 cannot be seen above the baseline. LOD therefore raised to that of rec. 2 i.e. 0.25 mg/kg.

Table 15 – Results of batch 3 fish and algae analyses using method MRAG10 run number 17472

			Results expressed as <LOD in mg/kg					
MRAG ref			Roseau station 3 fish	Roseau station 4 fish	Mamiku station 3 fish	Mamiku station 4 fish	Soufriere station 3 fish	Soufriere station 4 fish
Lab sample no.			33169	33170	33171	33172	33173	33174
	%rec1	%rec2						
Residue								
Paraquat	80	68	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25

	Results expressed as <LOD in mg/kg			
MRAG ref			Roseau station 3 algal biomass	Mamiku Sea Moss
Lab sample no.			33167	33168
	%rec1	%rec2		
Residue				
Paraquat	*	52	<0.25	<0.25

* Due to a reduction in response from the first to the third run, the lowest standard used for the calibration has been increased to a concentration above the expected final concentration for rec. 1. Hence the LOD has been increased to the lowest measurable recovery, i.e. rec. 2.

Table 16 – Results of batch 1 water analyses using method MRAG11 run number 17409

				Results	expressed	as	<LOD in	µg/L	
MRAG ref				Vieux Fort Treat. Plant Beausejour	Roseau station 1	Roseau station 2	Roseau station 3	Roseau station 4	Mamiku station 1
Lab sample no.				33138	33139	33140	33141	33143	33144
	% rec1	% rec2	% rec3						
Residue									
Paraquat	*	*	63	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Diquat	*	130	95	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0

		Results	expressed	as	<LOD in	µg/L	
MRAG ref	Mamiku station 2	Mamiku station 3	Mamiku station 4	Soufriere station 1	Soufriere station 2	Soufriere station 3	Soufriere station 4
Lab sample no.	33145	33146	33147	33149	33150	33151	33152
Residue							
Paraquat	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Diquat	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0

* Due to a reduction in standard response, the lowest standard used for the calibration has been increased to a concentration above the expected final concentration for rec. 2. Hence the LOD has been increased to the lowest measurable recovery, i.e. rec. 3

Table 17 – Results of batch 2 water analyses using method MRAG11 run number 17447

				Results	expressed	as	<LOD in	µg/L	
MRAG ref				Vieux Fort Treat. Plant Beausejour	Roseau station 1	Roseau station 2	Roseau station 3	Roseau station 4	Mamiku station 1
Lab sample no.				33138	33139	33140	33141	33143	33144
	% rec1	% rec2	% rec3						
Residue									
Paraquat	*	168*	114	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Diquat	*	148*	107	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0

		Results	expressed	as	<LOD in	µg/L	
MRAG ref	Mamiku station 2	Mamiku station 3	Mamiku station 4	Soufriere station 1	Soufriere station 2	Soufriere station 3	Soufriere station 4
Lab sample no.	33145	33146	33147	33149	33150	33151	33152
Residue							
Paraquat	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Diquat	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0

* Due to a reduction in standard response, the lowest standard used for the calibration has been increased to a concentration above the expected final concentration for rec. 2. Hence the LOD has been increased to the lowest measurable recovery, i.e. rec. 3

Table 18 – Results of batch 3 water analyses using method MRAG11 run number 17472

				Results	expressed	as	<LOD in	µg/L	
MRAG ref				Vieux Fort Treat. Plant Beausejour	Roseau station 1	Roseau station 2	Roseau station 3	Roseau station 4	Mamiku station 1
Lab sample no.				33138	33139	33140	33141	33143	33144
	% rec1	% rec2	% rec3						
Residue									
Paraquat	*	165*	113	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Diquat	*	173*	110	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0

		Results	expressed	as	<LOD in	µg/L	
MRAG ref	Mamiku station 2	Mamiku station 3	Mamiku station 4	Soufriere station 1	Soufriere station 2	Soufriere station 3	Soufriere station 4
Lab sample no.	33145	33146	33147	33149	33150	33151	33152
Residue							
Paraquat	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Diquat	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0

* Due to a reduction in standard response, the lowest standard used for the calibration has been increased to a concentration above the expected final concentration for rec. 2. Hence the LOD has been increased to the lowest measurable recovery, i.e. rec. 3

APPENDIX 2 – CEHI ANALYSIS RESULTS

CARIBBEAN ENVIRONMENTAL HEALTH INSTITUTE

P.O. Box 1111, The Morne. Castries, St. Lucia W.I.

Tel: (758) 452-2501/452-1412 **Fax: (758) 453-2721**

CERTIFICATE OF ANALYSIS

Client: Marine Resources Assessment Group Ltd

Address: 47 Princess Gate, London, SW7, 2QA
UK.

Telephone: 011 44 20 7594 9872

Fax: 011 44 20 7823 7916

Contact Person: Nicole Esteban

Date samples collected: Nov. 26- Dec. 1, 2001

Sample type/size: see tables 1.0 and 1.1

Project: DFID Natural Resources Systems Programme, Land Water Interface Project R7668: Impact and Amelioration of Sediment and Agrochemical Pollution on Caribbean Coastal Waters

Date of report: May 27, 2002

No. of pages: 34

Report no: 01- 0563

List of Tables

Table 1.0: Study watersheds, monitoring station locations and description

Mamiku Watershed area: 16.0km²	Boundaries: forested ridges either side of Mamiku valley. Main towns/villages are Mamiku, Mon Repos, Patience and La Pointe
Station 1 (upper valley)	N 13°52.408' W 60°55.766' The river is fast flowing with some deep, still ponds. Water is sampled from centre of the river at the surface. Bottom sediment is sand. Crops on surrounding steep banks are coconut (immediately adjacent), banana, mango, tertiary forest, wild ferns and vines. Further away are cultivated dasheen and yams
Station 2 (mid valley)	N 13°51.912' W 60°54.520' The river becomes a series of mini waterfalls with some deeper, stagnant pools with sandy bottoms. There is a private water intake point near the sampling point and the pool here is turbid. The sampling point for water is mid stream, surface and for sediment is at the bottom of the stagnant pool near the intake point. The area is surrounded by uncultivated/minor cultivation slopes and is perhaps an abandoned plantation. There are cows and an empty pigsty. No crops adjacent to the river but coconut, mango, bananas, guavas and secondary bush further away on the slopes.
Station 3 (lower valley)	N 13°52.199' W 60°53.849' Banana plantations continue almost to the shoreline and along the river until it becomes a mangrove forest. The river has a very slow flow and is very turbid with muddy river banks. The sampling point is mid stream on the surface of the water. Station 3 tissues were 9 crabs caught in traps in the river.
Station 4 (shore)	N 13°52.616' W 60°53.443' Sampling was conducted close to the site of sea moss culture around the island in the middle of Praslin Bay. Bottom sediment in the bay is fine sand with some sea grass. Station 4 tissues were cultured species (sea moss) and wild molluscs (11 red topshells, 9 chiton, 3 nudibranchs, 55 whelks) which were collected from western (closest to river) side of the island (0-4m depth).

Roseau Watershed area: 49.1km²	Boundaries (main towns/villages are Millet, Dame de Traversay, Durandeau, Sarot, La Treille, Vanard, Jacmel, Jean Baptiste, Morne, Door, Blair, Peru, Fond Manger, Collie town, Massacre, Roseau Distillery, Derriere Lagoon, Bois dined, La Croix Main got): • Upper watershed - from the forest reserve to Mont Gamier • Southern boundary - down the Venus/Anise La Rayed ridge to Roseau • Northern boundary – down the Ladle Carrot ridge to Margot
Station 1 (upper valley)	N 13°54.686' W 60°59.835' One of the main tributaries of the Roseau river passes through the Park Estate and this station is just below the Estate. The river is shallow and mainly bedrock and pebbles either side. There are spates of rapids then slower sections with pebbles and sand at bottom. Cultivation: dasheen, breadfruit, bananas, cocoa, coconut, tertiary forest and tree crops.
Station 2 (mid valley)	**N 13°55.721'** W 60°59.485' This location is just below the confluence of tributaries to the main river below the village of Durandeau. The river is slow flowing with average 0.25m depth and deep silty pools. The LHS bank is a wide, low embankment with reeds whereas RHS is steep with banana and vines. Further from river, this is an area of cultivation of bananas, coconut palms, mango trees, pineapple, mixed vegetables (chilli peppers, tomatoes).
Station 3 (lower valley)	N 13°57.353' W 61°01.237' The lower valley is intensively farmed with large banana plantations along both banks of the river. Sampling site is by the main coastal road bridge next to the school. The banks have a gentle gradient.

Station 4 (shore)	N 13°57.776' W 61°01.950' At the outlet of Roseau River there is a narrow beach (with fishing boats) and no visible reef. The sampling point was adjacent to the sedimentation trap north of the river (direction of current) along the coastline which is rocky, descending steeply to 4.0m. Station 3 tissues were aquatic green macrophytes/algae (similar to Ulva lactuca) (1 sample) and fish (juvenile Tilapia) and crustacean (cray fish) (1 sample). Station 4 tissues were molluscs (5 whelks, 3 rough tops, 10 small conch), crustacea (1 hermit crab) and fish (3 goatfish, 1 parrotfish).
Soufriere Watershed area: 17.2km²	Boundaries: Forested ridges either side of Soufriere valley. Main towns/villages are Soufriere, Ruby, La Perle, Zenon, Cressland, Diamond, Esperance, Fond St Jacque, Toraille, Belvedere, Migny, St Phillip.
Station 1 (upper valley)	N 13°50.362' W 61°00.929' Sampling site on Jeremy/James River (main tributary of Soufriere River) just above Migny village. The river flow is rapid and there is sediment accumulation on both river banks (silt, sand). The river bottom is mostly composed of boulders. Around the river is an area of cultivation of mixed vegetables (dasheen, celery, parsley, cucumber, tomato, cabbage). We spoke to a farmer who uses Gramoxone after clearing field and before planting crop.
Station 2 (mid valley)	N 13°50.258' W 61°01.678' Site below confluence of main tributaries to Soufriere river. The river flow is rapid with large boulders and silt/sand accumulated along the banks. Very steep banks adjacent to river with farming of breadfruit, citrus, pawpaw, coconut, pumpkin, banana, root crops and secondary forest (bush, vines, ferns). Lots of pools with sediment in the river. Access to river just below main road junction.
Station 3 (lower valley)	N 13°51.405' W 61°03.367' Sampling station along the straightened section of the river through Soufriere town adjacent to constructed channel/dam with riprap on one side (playing fields) and vegetated slope on the other. Lots of Tilapia fish in the dammed section of the river (sampled for Station 3 tissues).

Station 4 (shore)	N 13°51.485' W 61°03.815' Much of Soufriere Bay is protected by fringing reef with sediment below the reef crest. Sampling was conducted adjacent to sediment traps monitored by York to the north side of the main bay (direction of longshore current flow). Station 4 tissues are molluscs (9 slugs, 3 cowries, 68 rough tops

Table 1.1 Samples collected at each site

Stations	Matrices			
	Water	Sediment	Fish/invert	Algae
ROSEAU				
Farm	1	1	0	0
Mid course	1	1	0	0
Estuary	1	1	1 gastropods, crayfish, Tilapia	1 green algae
Reef	1	1	1 gastropods and reef fish	0
SOUFRIERE				
Farm	1	1	0	0
Mid course	1	1	0	0
Estuary	1	1	1 mullet	0
Reef	1	1	1 mollusca	0
MAMIKU				
Farm	1	1	0	0
Mid course	1	1	0	0
Estuary	1	1	1 crabs	0
Reef	1	1	1 gastropods	0
Aquaculture (Praslin Bay)	0	0	0	1 sea moss
OTHER				
Abstraction point: Vieux Fort Treatment Plant,Beausejour	1	0	0	0
CSL (1 replicate/station)	13	12	6	2
CEHI (2 replicates/station)	26	24	12	4

Overview of analyses

Water samples collected were stored in a refrigerator at 4^{o}C prior to extraction. The extracts were also kept refrigerated. Separatory funnel extraction using methylene chloride was the main extraction procedure used for water samples using 1L portions of the sample. Where necessary the extract was transferred to another solvent. Samples for Paraquat and Diquat were extracted by solid phase extraction using C8 cartidges.

Soil/sediment samples were extracted by Soxhlet extraction using 30g portions of the sample. All other samples were extracted by blending with the solvent.

The small quantity of fish/invertebrate samples made analysis for all parameters requested difficult. This significantly hampered our efforts to carry out the nutrient analysis on these samples.

Every effort was made to carry out the analyses within the specified holding times. As such samples were analyzed for phosphates and nitrates first, followed by carbamates, Paraquat and Diquat. Samples were then analyzed for organophosphates and Organochlorine compounds. Potassium was the final analysis carried out. Samples for potassium analysis were preserved with Nitric Acid soon after collection.

All samples analysed for pesticide residues were found to be negative.

Table 1.2 Characteristics of water sampling stations

Date	Watershed	Station	Width (Metres)	Depth (Metres)	Temperature (°C)	pH	Salinity (ppt)
26/11/01	Mamiku	1	5.0	0.15	25.1	6.73	0.00
26/11/01	Mamiku	2	9.1	2.1	25.5	7.66	0.00
26/11/01	Mamiku	3	6.0	2.3	26.2	7.15	0.7-4.0
26/11/01	Mamiku	4	N/a	4.0 sand 0.0-4.0 tissue	28.8	8.13	35.30
27/11/01	Roseau	1	4.9	0.3	25.8	7.98	0.00
27/11/01	Roseau	2	7.7	0.25	28.6	7.95	0.00
27/11/01	Roseau	3	14.4	0.8	27.6	7.25	0.10
29/11/01	Roseau	4	N/a	4.0 sand 0-4.0 tissue	28.9	8.25	35.6
27/11/01	Soufriere	1	1.5	0.4	23.2	7.25	0.00
27/11/01	Soufriere	2	1.4	0.8	24.3	7.49	0.00
27/11/01	Soufriere	3	5.1	1.4	27.1	7.21	0.10
29/11/01	Soufriere	4	N/a	4.0 sand 0-4.0 tissue	28.7	8.29	35.80

Table 1.3: List of analyses done by CEHI

Agro-chemical	Group	Priority	Lab tests	Sampling regime
Nutrients				
Nitrate	Nutrients	H	CEHI only	Water, sediment, fish/invert, algae
Potassium	Nutrients	H	CEHI only	Water, sediment, fish/invert, algae
Phosphorous	Nutrients	H	CEHI only	Water, sediment, fish/invert, algae
Group 1: organochlorine pesticides				
Endosulphan	Organochlorine	H	CEHI + CSL	Water, sediment, fish/invert, algae
Imazalil	Organochlorine	L/M	CEHI + CSL	Water, sediment, fish/invert, algae
Chlorpyrifos	Organochlorine	M	CEHI + CSL	Water, sediment, fish/invert, algae
Group 2: carbamate pesticides				
Oxamyl	Carbamate	H	CEHI + CSL	Water, sediment, fish/invert, algae
Carbaryl	Carbamate	L	CEHI + CSL	Water, sediment, fish/invert, algae
Carbofuran	Carbamate	L	CEHI + CSL	Water, sediment, fish/invert, algae
Group 3: organophosphate pesticides				
Ethoprophos	Organophosphate	H	CEHI + CSL	Water, sediment, fish/invert, algae
Diazinon	Organophosphate	L	CEHI + CSL	Water, sediment, fish/invert, algae
Malathion	Organophosphate	L	CEHI + CSL	Water, sediment, fish/invert, algae
Pirimiphos-methyl	Organophosphate	L	CEHI + CSL	Water, sediment, fish/invert, algae
Isazophos	Organophosphate	M	CEHI + CSL	Water, sediment, fish/invert, algae
Group 4: bipyridinium compounds				
Paraquat	Bipyridinium	H	CEHI + CSL	Water only (CEHI), Water, fish/invert, algae (CSL)
Diquat	Bipyridinium	M	CEHI + CSL	Water only*
Other groups of pesticides				
Diuron	Urea	L	CEHI + CSL	Water, sediment, fish/invert, algae

Table 1.4: Analytes not tested*

Agro-chemical	Group	Priority	Lab tests	Sampling regime
Metalaxyl	Acylalanine	L	CEHI + CSL	Water, sediment, fish/invert, algae
Cypermethrin	Pyrethroid	L/M	CEHI + CSL	Water, sediment, fish/invert, algae
Lambdacyhalothrin	Pyrethroid	L	CEHI + CSL	Water, sediment, fish/invert, algae
Cyromazine	Triazine	L	CEHI + CSL	Water, sediment, fish/invert, algae
Propiconazole	Triazole	M/H	CEHI + CSL	Water, sediment, fish/invert, algae
Cadusafos	Organophosphate	L/M	CEHI + CSL	Water, sediment, fish/invert, algae
Profenofos	Organophosphate	M	CEHI + CSL	Water, sediment, fish/invert, algae

* The above listed analytes were not tested for due to unavailability of appropriate standards and/or equipment

Table 2.0 Test Results for Nutrients – Water Samples

Sample station	*Nitrate mg/l	[1]Potassium mg/l	[2]Phosphorus mg/l PO_4^{3-}
Mamiku 1A	0.40	1.59	0.06
Mamiku 1B	0.42	1.41	0.06
Mamiku 2A	0.20	16.87	0.04
Mamiku 2B	0.21	16.51	0.04
Mamiku 3A	0.30	19.66	0.04
Mamiku 3b	0.30	19.79	0.04
Mamiku 4A	0.90	1878.7	0.02
Mamiku 4B	0.91	1850.5	0.02
Roseau 1A	0.10	14.54	0.16
Roseau 1B	0.10	14.86	0.17
Roseau 2A	0.30	1.76	0.07
Roseau 2B	0.30	1.86	0.07
Roseau 3A	0.27	5.73	0.04
Roseau 3B	0.26	5.81	0,04
Roseau 4A	0.05	1221.5	0.03
Roseau 4B	0.05	1232.7	0.03
Soufriere 1A	0.40	1.71	0.12
Soufriere 1B	0.41	1.65	0.11
Soufriere 2A	0.10	15.43	0.30
Soufriere 2B	0.10	15.26	0.30
Soufriere 3A	0.30	10.83	0.27
Soufriere 3B	0.30	11.01	0.28
Soufriere 4A	0.50	572.9	0.05
Soufriere 4B	0.52	591.2	0.05
Beausejour	0.41	5.36	0.05

A and B indicate duplicate samples, nos. indicate sampling stations
*Detection limits for nitrates = 0.01 mg/l
[1]Detection limit for Potassium = 0.01 mg/l
[2]Estimated detection limit PO_4 = 0.01mg/l

Table 2.1 Test Results for Organochlorine pesticides - Water

Results expressed as <MDL in μg/l					
Sample station	**Endosulfan I**	**Endosulfan II**	**Endosulfan Sulphate**	**Imazalil**	**Chlorpyrifos**
Mamiku 1A	<1.1	<1.0	<7.5	<5.0	<5.0
Mamiku 1B	<1.1	<1.0	<7.5	<5.0	<5.0
Mamiku 2A	<1.1	<1.0	<7.5	<5.0	<5.0
Mamiku 2B	<1.1	<1.0	<7.5	<5.0	<5.0
Mamiku 3A	<1.1	<1.0	<7.5	<5.0	<5.0
Mamiku 3B	<1.1	<1.0	<7.5	<5.0	<5.0
Mamiku 4A	<1.1	<1.0	<7.5	<5.0	<5.0
Mamiku 4B	<1.1	<1.0	<7.5	<5.0	<5.0
Roseau 1A	<1.1	<1.0	<7.5	<5.0	<5.0
Roseau 1B	<1.1	<1.0	<7.5	<5.0	<5.0
Roseau 2A	<1.1	<1.0	<7.5	<5.0	<5.0
Roseau 2B	<1.1	<1.0	<7.5	<5.0	<5.0
Roseau 3A	<1.1	<1.0	<7.5	<5.0	<5.0
Roseau 3B	<1.1	<1.0	<7.5	<5.0	<5.0
Roseau 4A	<1.1	<1.0	<7.5	<5.0	<5.0
Roseau 4B	<1.1	<1.0	<7.5	<5.0	<5.0
Soufriere 1A	<1.1	<1.0	<7.5	<5.0	<5.0
Soufriere 1B	<1.1	<1.0	<7.5	<5.0	<5.0
Soufriere 2A	<1.1	<1.0	<7.5	<5.0	<5.0
Soufriere 2B	<1.1	<1.0	<7.5	<5.0	<5.0
Soufriere 3A	<1.1	<1.0	<7.5	<5.0	<5.0
Soufriere 3B	<1.1	<1.0	<7.5	<5.0	<5.0
Soufriere 4A	<1.1	<1.0	<7.5	<5.0	<5.0
Soufriere 4b	<1.1	<1.0	<7.5	<5.0	<5.0
Beausejour Vieux Fort	<1.1	<1.0	<7.5	<5.0	<5.0

A and B indicate duplicate samples

Table 2.2 Test Results for Carbamate pesticides - Water

Results expressed as <MDL in μg/l			
Sample station	**Oxamyl**	**Carbaryl**	**Carbofuran**
Mamiku 1A	<2.0	<0.80	<0.50
Mamiku 1B	<2.0	<0.80	<0.50
Mamiku 2A	<2.0	<0.80	<0.50
Mamiku 2B	<2.0	<0.80	<0.50
Mamiku 3A	<2.0	<0.80	<0.50
Mamiku 3b	<2.0	<0.80	<0.50
Mamiku 4A	<2.0	<0.80	<0.50
Mamiku 4B	<2.0	<0.80	<0.50
Roseau 1B	<2.0	<0.80	<0.50
Roseau 2A	<2.0	<0.80	<0.50
Roseau 2B	<2.0	<0.80	<0.50
Roseau 3A	<2.0	<0.80	<0.50
Roseau 3B	<2.0	<0.80	<0.50
Roseau 4A	<2.0	<0.80	<0.50
Roseau 4B	<2.0	<0.80	<0.50
Soufriere 1A	<2.0	<0.80	<0.50
Soufriere 1B	<2.0	<0.80	<0.50
Soufriere 2A	<2.0	<0.80	<0.50
Soufriere 2B	<2.0	<0.80	<0.50
Soufriere 3A	<2.0	<0.80	<0.50
Soufriere 3B	<2.0	<0.80	<0.50
Soufriere 4A	<2.0	<0.80	<0.50
Soufriere 4B	<2.0	<0.80	<0.50
Beausejour, Vieux Fort	<2.0	<0.80	<0.50

A and B indicate duplicate samples

Table 2.3 Test Results for Organophosphate pesticides – Water

Results expressed as <MDL in μg/l					
Sample station	**Ethoprophos**	**Pirimiphos-Methyl**	**Diazinon**	**Isazaphos**	**Malathion**
Mamiku 1A	<1.0	<2.0	<5.0	<1.0	<1.5
Mamiku 1B	<1.0	<2.0	<5.0	<1.0	<1.5
Mamiku 2A	<1.0	<2.0	<5.0	<1.0	<1.5
Mamiku 2B	<1.0	<2.0	<5.0	<1.0	<1.5
Mamiku 3A	<1.0	<2.0	<5.0	<1.0	<1.5
Mamiku 3b	<1.0	<2.0	<5.0	<1.0	<1.5
Mamiku 4A	<1.0	<2.0	<5.0	<1.0	<1.5
Mamiku 4B	<1.0	<2.0	<5.0	<1.0	<1.5
Roseau 1A	<1.0	<2.0	<5.0	<1.0	<1.5
Roseau 1B	<1.0	<2.0	<5.0	<1.0	<1.5
Roseau 2A	<1.0	<2.0	<5.0	<1.0	<1.5
Roseau 2B	<1.0	<2.0	<5.0	<1.0	<1.5
Roseau 3A	<1.0	<2.0	<5.0	<1.0	<1.5
Roseau 3B	<1.0	<2.0	<5.0	<1.0	<1.5
Roseau 4A	<1.0	<2.0	<5.0	<1.0	<1.5
Roseau 4B	<1.0	<2.0	<5.0	<1.0	<1.5
Soufriere 1A	<1.0	<2.0	<5.0	<1.0	<1.5
Soufriere 1B	<1.0	<2.0	<5.0	<1.0	<1.5
Soufriere 2A	<1.0	<2.0	<5.0	<1.0	<1.5
Soufriere 2B	<1.0	<2.0	<5.0	<1.0	<1.5
Soufriere 3A	<1.0	<2.0	<5.0	<1.0	<1.5
Soufriere 3B	<1.0	<2.0	<5.0	<1.0	<1.5
Soufriere 4A	<1.0	<2.0	<5.0	<1.0	<1.5
Soufriere 4B	<1.0	<2.0	<5.0	<1.0	<1.5
Beausejour	<1.0	<2.0	<5.0	<1.0	<1.5

Table 2.4 Test Results for Paraquat, Diquat, Diuron - Water

Results expressed as <MDL in μg/l			
Sample station	**Paraquat**	**Diquat**	**Diuron**
Mamiku 1A	<0.80	<0.50	<0.54
Mamiku 1B	<0.80	<0.50	<0.54
Mamiku 2A	<0.80	<0.50	<0.54
Mamiku 2B	<0.80	<0.50	<0.54
Mamiku 3A	<0.80	<0.50	<0.54
Mamiku 3b	<0.80	<0.50	<0.54
Mamiku 4A	<0.80	<0.50	<0.54
Mamiku 4B	<0.80	<0.50	<0.54
Roseau 1A	<0.80	<0.50	<0.54
Roseau 1B	<0.80	<0.50	<0.54
Roseau 2A	<0.80	<0.50	<0.54
Roseau 2B	<0.80	<0.50	<0.54
Roseau 3A	<0.80	<0.50	<0.54
Roseau 3B	<0.80	<0.50	<0.54
Roseau 4A	<0.80	<0.50	<0.54
Roseau 4B	<0.80	<0.50	<0.54
Soufriere 1A	<0.80	<0.50	<0.54
Soufriere 1B	<0.80	<0.50	<0.54
Soufriere 2A	<0.80	<0.50	<0.54
Soufriere 2B	<0.80	<0.50	<0.54
Soufriere 3A	<0.80	<0.50	<0.54
Soufriere 3B	<0.80	<0.50	<0.54
Soufriere 4A	<0.80	<0.50	<0.54
Soufriere 4B	<0.80	<0.50	<0.54
Beausejour, Vieux Fort	<0.80	<0.50	<0.54

A and B indicate duplicate samples

Table 3.0 Test Results for Nutrients – Soil/Sediment/Sea moss

Sample station	Nitrate mg/kg	Potassium mg/Kg	Phosphorus mg/kg PO_4^{3-}
Mamiku 1A	Not detected	278.7	0.08
Mamiku 1B	Not detected	255.6	0.06
Mamiku 2A	Not detected	200.6	0.28
Mamiku 2B	Not detected	210.6	0.35
Mamiku 3A	Not detected	660	0.36
Mamiku 3b	Not detected	680.4	0.41
Mamiku 4A	2.0	345.5	Not detected
Mamiku 4B	2.17	361.2	Not detected
Roseau 1A	Not detected	5660.1	0.44
Roseau 1B	Not detected	5710.4	0.50
Roseau 2A	Not detected	1473.1	0.16
Roseau 2B	Not detected	1449.8	0.18
Roseau 3A	Not detected	755.4	0.20
Roseau 3B	Not detected	732.4	0.17
Roseau 4A	2.0	883.1	0.12
Roseau 4B	1.83	901.3	0.13
Soufriere 1A	Not detected	734.3	0.84
Soufriere 1B	Not detected	761.9	1.05
Soufriere 2A	Not detected	1558.3	1.96
Soufriere 2B	Not detected	1532.8	2.11.
Soufriere 3A	2.0	873.3`	0.12
Soufriere 3B	2.15	889.1	0.11
Soufriere 4A	3.2	3932.2	0.24
Soufriere 4B	2.88	3897.7	0.19
Sea moss A	2.95	1.567×10^5	Not detected
Sea moss B	3.10	1.397×10^5	Not detected

A and B indicate duplicate samples

Table 3.1 Test Results for Organochlorine pesticides – Soil/Sediment

Results Expressed as <MDL in mg/kg					
Sample station	**Endosulfan I**	**Endosulfan II**	**Endosulfan Sulphate**	**Imazalil**	**Chlorpyrifos**
Mamiku 1A	<0.020	<0.030	<0.040	<0.013	<0.080
Mamiku 1B	<0.020	<0.030	<0.040	<0.013	<0.080
Mamiku 2A	<0.020	<0.030	<0.040	<0.013	<0.080
Mamiku 2B	<0.020	<0.030	<0.040	<0.013	<0.080
Mamiku 3A	<0.020	<0.030	<0.040	<0.013	<0.080
Mamiku 3B	<0.020	<0.030	<0.040	<0.013	<0.080
Mamiku 4A	<0.020	<0.030	<0.040	<0.013	<0.080
Mamiku 4B	<0.020	<0.030	<0.040	<0.013	<0.080
Roseau 1A	<0.020	<0.030	<0.040	<0.013	<0.080
Roseau 1B	<0.020	<0.030	<0.040	<0.013	<0.080
Roseau 2A	<0.020	<0.030	<0.040	<0.013	<0.080
Roseau 2B	<0.020	<0.030	<0.040	<0.013	<0.080
Roseau 3A	<0.020	<0.030	<0.040	<0.013	<0.080
Roseau 3B	<0.020	<0.030	<0.040	<0.013	<0.080
Roseau 4A	<0.020	<0.030	<0.040	<0.013	<0.080
Roseau 4B	<0.020	<0.030	<0.040	<0.013	<0.080
Soufriere 1A	<0.020	<0.030	<0.040	<0.013	<0.080
Soufriere 1B	<0.020	<0.030	<0.040	<0.013	<0.080
Soufriere 2A	<0.020	<0.030	<0.040	<0.013	<0.080
Soufriere 2B	<0.020	<0.030	<0.040	<0.013	<0.080
Soufriere 3A	<0.020	<0.030	<0.040	<0.013	<0.080
Soufriere 3B	<0.020	<0.030	<0.040	<0.013	<0.080
Soufriere 4A	<0.020	<0.030	<0.040	<0.013	<0.080
Soufriere 4b	<0.020	<0.030	<0.040	<0.013	<0.080
Beausejour Vieux Fort	<0.020	<0.030	<0.040	<0.013	<0.080

A and B indicate duplicate samples

Table 3.2 Test Results for Carbamate pesticides – Soil/Sediment

Results expressed as <MDL in mg/kg			
Sample station	**Oxamyl**	**Carbaryl**	**Carbofuran**
Mamiku 1A	<0.028	<0.022	<0.024
Mamiku 1B	<0.028	<0.022	<0.024
Mamiku 2A	<0.028	<0.022	<0.024
Mamiku 2B	<0.028	<0.022	<0.024
Mamiku 3A	<0.028	<0.022	<0.024
Mamiku 3b	<0.028	<0.022	<0.024
Mamiku 4A	<0.028	<0.022	<0.024
Mamiku 4B	<0.028	<0.022	<0.024
Roseau 1A	<0.028	<0.022	<0.024
Roseau 1B	<0.028	<0.022	<0.024
Roseau 2A	<0.028	<0.022	<0.024
Roseau 2B	<0.028	<0.022	<0.024
Roseau 3A	<0.028	<0.022	<0.024
Roseau 3B	<0.028	<0.022	<0.024
Roseau 4A	<0.028	<0.022	<0.024
Roseau 4B	<0.028	<0.022	<0.024
Soufriere 1A	<0.028	<0.022	<0.024
Soufriere 1B	<0.028	<0.022	<0.024
Soufriere 2A	<0.028	<0.022	<0.024
Soufriere 2B	<0.028	<0.022	<0.024
Soufriere 3A	<0.028	<0.022	<0.024
Soufriere 3B	<0.028	<0.022	<0.024
Soufriere 4A	<0.028	<0.022	<0.024
Soufriere 4B	<0.028	<0.022	<0.024
Beausejour, Vieux Fort	<0.028	<0.022	<0.024

A and B indicate duplicate samples

Table 3.3 Test Results for Organophosphate pesticides – Soil/Sediment

Results expressed as <MDL in mg/kg					
Sample station	Ethoprophos	Pirimiphos-Methyl	Diazinon	Isazaphos	Malathion
Mamiku 1A	<0.048	<0.050	<0.044	<0.040	<0.050
Mamiku 1B	<0.048	<0.050	<0.044	<0.040	<0.050
Mamiku 2A	<0.048	<0.050	<0.044	<0.040	<0.050
Mamiku 2B	<0.048	<0.050	<0.044	<0.040	<0.050
Mamiku 3A	<0.048	<0.050	<0.044	<0.040	<0.050
Mamiku 3b	<0.048	<0.050	<0.044	<0.040	<0.050
Mamiku 4A	<0.048	<0.050	<0.044	<0.040	<0.050
Mamiku 4B	<0.048	<0.050	<0.044	<0.040	<0.050
Roseau 1B	<0.048	<0.050	<0.044	<0.040	<0.050
Roseau 2A	<0.048	<0.050	<0.044	<0.040	<0.050
Roseau 2B	<0.048	<0.050	<0.044	<0.040	<0.050
Roseau 3A	<0.048	<0.050	<0.044	<0.040	<0.050
Roseau 3B	<0.048	<0.050	<0.044	<0.040	<0.050
Roseau 4A	<0.048	<0.050	<0.044	<0.040	<0.050
Roseau 4B	<0.048	<0.050	<0.044	<0.040	<0.050
Soufriere 1A	<0.048	<0.050	<0.044	<0.040	<0.050
Soufriere 1B	<0.048	<0.050	<0.044	<0.040	<0.050
Soufriere 2A	<0.048	<0.050	<0.044	<0.040	<0.050
Soufriere 2B	<0.048	<0.050	<0.044	<0.040	<0.050
Soufriere 3A	<0.048	<0.050	<0.044	<0.040	<0.050
Soufriere 3B	<0.048	<0.050	<0.044	<0.040	<0.050
Soufriere 4A	<0.048	<0.050	<0.044	<0.040	<0.050
Soufriere 4B	<0.048	<0.050	<0.044	<0.040	<0.050
Beausejour Vieux Fort	<0.048	<0.050	<0.044	<0.040	<0.050

Table 4.0 Test Results for Organochlorine pesticides in Fish/Invert samples and Sea moss

Results expressed as <MDL in mg/kg					
Sample station	**Endosulfan I**	**Endosulfan II**	**Endosulfan Sulphate**	**Imazalil**	**Chlorpyrifos**
Mamiku 3A	<0.050	<0.050	<0.050	<0.070	<0.060
Mamiku 3b	<0.050	<0.050	<0.050	<0.070	<0.060
Mamiku 4A	<0.050	<0.050	<0.050	<0.070	<0.060
Mamiku 4B	<0.050	<0.050	<0.050	<0.070	<0.060
Roseau 3A	<0.050	<0.050	<0.050	<0.070	<0.060
Roseau 3B	<0.050	<0.050	<0.050	<0.070	<0.060
Roseau 4A	<0.050	<0.050	<0.050	<0.070	<0.060
Roseau 4B	<0.050	<0.050	<0.050	<0.070	<0.060
Soufriere 3A	<0.050	<0.050	<0.050	<0.070	<0.060
Soufriere 3B	<0.050	<0.050	<0.050	<0.070	<0.060
Soufriere 4A	<0.050	<0.050	<0.050	<0.070	<0.060
Soufriere 4B	<0.050	<0.050	<0.050	<0.070	<0.060
Sea moss*	<0.050	<0.050	<0.050	<0.070	<0.060

*Sea moss collected at Mamiku Station 4

Table 4.1 Test Results for Carbamate pesticides in Fish/Invert samples and Sea moss

Results expressed as <MDL in mg/kg			
Sample station	**Oxamyl**	**Carbaryl**	**Carbofuran**
Mamiku 3A	<0.030	<0.050	<0.050
Mamiku 3b	<0.030	<0.050	<0.050
Mamiku 4A	<0.030	<0.050	<0.050
Mamiku 4B	<0.030	<0.050	<0.050
Roseau 3A	<0.030	<0.050	<0.050
Roseau 3B	<0.030	<0.050	<0.050
Roseau 4A	<0.030	<0.050	<0.050
Roseau 4B	<0.030	<0.050	<0.050
Soufriere 3A	<0.030	<0.050	<0.050
Soufriere 3B	<0.030	<0.050	<0.050
Soufriere 4A	<0.030	<0.050	<0.050
Soufriere 4B	<0.030	<0.050	<0.050
Sea moss*	<0.030	<0.050	<0.050

*Sea moss collected at Mamiku Station 4

Table 4.2 Test Results for Organophosphate pesticides in Fish/Invert samples and Sea moss

Results expressed as <MDL in mg/kg					
Sample station	**Ethoprophos**	**Pirimiphos-Methyl**	**Diazinon**	**Isazaphos**	**Malathion**
Mamiku 3A	<0.050	<0.050	<0.060	<0.040	<0.050
Mamiku 3b	<0.050	<0.050	<0.060	<0.040	<0.050
Mamiku 4A	<0.050	<0.050	<0.060	<0.040	<0.050
Mamiku 4B	<0.050	<0.050	<0.060	<0.040	<0.050
Roseau 3A	<0.050	<0.050	<0.060	<0.040	<0.050
Roseau 3B	<0.050	<0.050	<0.060	<0.040	<0.050
Roseau 4A	<0.050	<0.050	<0.060	<0.040	<0.050
Roseau 4B	<0.050	<0.050	<0.060	<0.040	<0.050
Soufriere 3A	<0.050	<0.050	<0.060	<0.040	<0.050
Soufriere 3B	<0.050	<0.050	<0.060	<0.040	<0.050
Soufriere 4A	<0.050	<0.050	<0.060	<0.040	<0.050
Soufriere 4B	<0.050	<0.050	<0.060	<0.040	<0.050
Sea moss	<0.050	<0.050	<0.060	<0.04	<0.050

APPENDIX 1

Quality Control /Detection Limits

Quality control methods used in this analysis include, analysis of reagent blanks, laboratory fortified blanks and laboratory fortified matrices. Where possible, the method detection limit for each analyte in each matrix was determined

Table 5.0: Recovery and detection limits for carbamate pesticides in water

Analyte	Fortified conc. µg/l	N[a]	Recovery %	SD %	[b]MDL µg/l
Carbaryl	5.0	8	84	0.03	0.8
Carbofuran	5.0	8	86	0.02	0.5
Oxamyl	5.0	8	111	0.07	2.0

[a]N = Number of replicates
[b]MDL = S x t
where S = Standard deviation of replicate analyses
t = Student's t value for 99% confidence level with
n -1 degrees of freedom = 2.998

For N = 7, t = 3.143

Table 5.1: Recovery and detection limits for carbamate pesticides in soil/sediments

Analyte	Fortified conc. mg/kg	N[a]	Recovery %	SD %	[b]MDL mg/kg
Carbaryl	2.0	8	75	0.74	0.022
Carbofuran	2.0	8	74	0.81	0.024
Oxamyl	2.0	8	76	0.92	0.028

Table 5.2 Recovery and detection limits for Organophosphate pesticides in water

Analyte	Fortified conc. µg/l	N[a]	Recovery %	SD %	[b]MDL µg/l
Chlorpyrifos	25	7	89	0.16	5.0
Diazinon	50	7	86	0.16	5.0
Ethoprophos	25	7	84	0.032	1.0
Malathion	25	7	89	0.049	1.5
Pirimiphos-methyl	50	7	96	0.07	2.0
Isazophos	25	7	82	0.32	1.0
Diuron	10	7	95	0.018	0.54

Table 5.3 Recovery and detection limits for Organophosphate pesticides in soil

Analyte	Fortified conc. mg/kg	N[a]	Recovery %	SD %	[b]MDL mg/kg
Chlorpyrifos	0.5	7	72	2.54	0.080
Diazinon	0.5	7	86	1.4	0.044
Ethoprophos	0.5	7	70	1.53	0.048
Malathion	0.5	7	81	1.62	0.050
Pirimiphos-methyl	0.5	7	88	1.64	0.050
Isazophos	0.5	7	75	1.28	0.040
Diuron	0.5	7	73	3.1	0.097

Table 5.4 Recovery and detection limits for Paraquat and Diquat in water

Analyte	Fortified conc. µg/l	N[a]	Recovery %	SD %	[b]MDL µg/l
Paraquat	10	8	93	0.03	0.80
Diquat	10	8	87	0.02	0.50

Table 5.5 Recovery and detection limits for Organochlorine pesticides in water

Analyte	Fortified conc. µg/l	N[a]	Recovery %	SD %	[b]MDL µg/l
Endosulphan I	50	7	92	0.036	1.1
Endosulphan II	50	7	94	0.032	1.0
Endosulphan sulphate	50	7	91	0.25	7.5
Imazalil	50	7	89	0.26	8

Table 5.6 Recovery and detection limits for Organochlorine pesticides in soil/sediment

Analyte	Fortified conc. mg/kg	N[a]	Recovery %	SD %	[b]MDL mg/kg
Endosulphan I	0.050	7	89	0.51	0.016
Endosulphan II	0.050	7	91	0.83	0.026
Endosulphan Sulphate	0.050	7	86	1.4	0.044
Imazalil	0.050	7	76	0.43	0.013

Analytical Procedures

1. EPA Method 549.1, Determination of Paraquat and Diquat in drinking water by liquid-solid extraction and High Performance Liquid Chromatography High Performance Liquid Chromatography (HPLC) with UV detection, Revision 1.0, August 1992.

2. EPA Method 531, Measurement of N-Methylcarbomyloximes and N-Methylcarbamates in water by direct aqueous injection HPLC with Post column derivatization, Revision 3.1, 1995

3. EPA Method 1657, Determination of Organophosphorus pesticides in municipal and industrial wastewater

4. EPA SW-846 Method 8081A, Organochlorines by Gas Chromatography, December 1996

5. EPA SW-846 Method 8141A, Organophosphorus Compounds by Gas Chromatography: Capillary Column Technique, September 1994.

6. EPA SW-846 Method 8318, N-Methylcarbamates by High Performance Liquid Chromatography, September 1994.

7. EPA SW-846 Method 3050B, Acid Digestion of Sediments, Sludges and Soils.

8. SM[a] 3030E, Nitric Acid Digestion

9. SM 3111B, Direct Air/Acetylene Flame Atomic Absorption Spectroscopy

[a]**SM** – Standard Methods for the Examination of Water and Wastewater, AWWA/WEF/APHA, 19th Edition, 1996

Gas Chromatographic Operating Conditions for Organochlorine Pesticides

Instrument: Hewlett Packard 5890 series II
Columns: HP-1, 100% polysiloxane, 30m x 0.53mm x 1.5µm
(SPB-1701, 30m x 0.25mm x 0.25µm)
Carrier Gas: Nitrogen
Carrier Gas flow rate: 15 ml/min (1.0ml/min)
Make-up gas: Nitrogen, 60 ml/min
Detector: ECD
Detector temperature: 300^{o}C
Injector temperature: 250^{o}C
Initial temperature: 120^{o}C, hold 2 minutes
Temperature program: 120^{o}C to 180^{o}C at 10^{o}C/min, hold 10 mins.
180^{o}C to 260^{o}C at 8^{o}C/min, hold 5 mins.
Injection volume: 3µl, splitless injection

HPLC conditions for Carbamate Analysis

Carbamate Analysis with HPLC-Post Column Derivatizer

HPLC: HP series 1100 (Hewlett Packard)
Column: Carbamate Analysis Column C18, 150 mm (L) x 4.6 mm (ID), 5mm
Mobile Phase: A = Methanol, B = Water
Column Temperature: 42 ^{o}C
Flow: 1.0 mL/min
Gradient Table

Time (min)	Interval	% Water	% Methanol	Comment
0	0	100	0	Injection
1	1	100	0	Concentrate sample on column
1.01	0.01	82	18	Step change
36	35	30	70	Linear gradient
36.01	0.01	0	100	Step change
38	2	0	100	Clean out
38 -	10	100	0	Re-equilibration

Post-Column Derivatizer: PCX 5200 (Pickering Laboratories)
Reagent 1: 0.05 M NaOH, hydrolysis reagent (CB130)
Pump 1: 0.30 mL/min
Reactor 1: 500 mL at 100 ^{o}C
Reagent 2: OPA & Thiofluor in pH 9.1 borate buffer
Pump 2: 0.30 mL/min
Reactor 2: 100 mL at ambient temperature

Detector: Fluorescence Detector G1321A FLD (Hewlett Packard)
Excitation: 330 nm
Emission: 465 nm

Gas Chromatographic Operating Conditions for Organophosphorus Pesticides

Instrument: Hewlett Packard 5890 series II
Column: HP-1, 100% polysiloxane, 30m x 0.53mm x 1.5□m
Carrier Gas: Nitrogen
Detector gases: H_2 – 75ml/min, Air - 100ml/min
Carrier Gas flow rate: 15 ml/min
Detector: FPD
Detector temperature: 270^{o}C
Injector temperature: 250^{o}C
Initial temperature: 120^{o}C, hold 2 minutes
Temperature program: 120^{o}C to 260^{o}C at 6^{o}C/min, hold 5 mins.
.

Injection volume: 3µl, splitless injection

HPLC conditions for Paraquat and Diquat

Instrument: Hewlett Packard HP1100, Diode Array Detection
Column: Zorbax SB C18, 4.6mm x 250mm x 5µm
Column temperature: 35^{o}C
Flow rate: 2.0 mL/min Ion pair reagent
Ion pair reagent – 13.5 ml orthophosphoric acid, 10.3 mL diethylamine, 3.0 g of 1-hexanesulphonic acid, sodium salt diluted to 1L with deionized water.
Injection Volume: 100µl
Wavelengths: Diquat – 308 nm
Paraquat – 257 nm
Run time: 5.0 minutes

HPLC conditions for Diuron

Instrument: Hewlett Packard HP1100, Diode Array Detection
Mobile phase – Methanol/1% acetic acid, programmed linearly from 5 to 95% methanol at a flow rate of 2ml/min at ambient temperature.
Column: HP Zorbax SB C-18, 4.6mm x 250 mm x 5µm
Wavelength: 254nm

References

Standard Methods for the Examination of Water and Wastewater, 19th Edition, APHA/AWWA/WEF, 1996.

Methods and Guidance for Analysis of Water, EPA 821-C-97-001, USEPA, April 1997

The Pesticide Manual, 10th Edition, Clive Tomlin – Editor, RSC/BCPC, 1994

Literature Review on fate of Agrochemicals in the St. Lucian Environment, N. Boodram, CEHI, 2002.

Compilation of EPA's Sampling and Analysis Methods, Lawrence H. Keith, Editor, Lewis Publishers, 1992.

Signed:_____ ***Date: 26/4/02***

Andrew Lewis

Laboratory Supervisor

For Executive Director

5 APPENDIX 3 - PROPOSAL FOR THE CONTINUATION OF ENVIRONMENTAL MONITORING ACTIVITIES IN ST LUCIA BY CEHI OVER A PERIOD OF ONE YEAR, JANUARY –DECEMBER 2003

5.1 Background

This sampling programme forms part of the environmental monitoring activities of a three-year research project *Impact and amelioration of sedimentation and agro-chemicals in Caribbean coastal waters.* The project is funded by DFID's NRSP LWI programme (R7668) and is managed and conducted by two organisations: the University of York, responsible for the sedimentation aspects of the project (activities commenced in June 2000 and are concentrated in the SMMA in St Lucia); and MRAG Ltd, responsible for agro-chemical components of the project (activities are undertaken in St Lucia and Jamaica). Under the agro-chemical components of the project, MRAG Ltd is collaborating with a number of partners in St Lucia and Jamaica:

- Ministry of Agriculture, Forestry and Fisheries (MAFF), Depart of Agriculture, St Lucia
- Caribbean Environmental Health Institute (CEHI), St Lucia
- Caribbean Agricultural Research and Development Institute (CARDI), Jamaican Unit
- University of the West Indies (UWI), Mona Campus, Jamaica
- Caribbean Coastal Area Management Foundation (C-CAM), Jamaica

One of the project outputs is the estimation of the fate of agro-chemicals[9] in the environment, with particular emphasis on the land-water interface and impacts in the marine environment. Under this output, an important activity is a baseline snapshot survey of defined agro-chemicals in water, sediment and tissues in St Lucia. This survey was carried out towards the end of the wet season in November 2001. Based on the results obtained from the initial survey and discussions with collaborating partners, it was decided to extend monitoring activities over a one-year period taking into account seasonal fluctuations. It is proposed that sampling and analysis is conducted quarterly over a period of one year. This document outlines the sampling and analytical activities and associated costs for quarterly sampling at the selected points by CEHI's laboratory

5.2 Selection of Pesticides for Analysis

The list of imported pesticides imported into St. Lucia has been used to determine pesticides for analysis (as detailed in Table 5.1). The pesticides will be analysed by CEHI. Table 1.1 also indicates nutrients that will be analysed to estimate fate of fertilisers in the environment (nitrate, nitrite, potassium, phosphorus). Fertiliser constituents have been ascertained with information collated from the Extension Services of MAFF, St. Lucia.

Table 5.1 List of agro-chemicals for analysis

Agro-chemical	Group	Priority[10]	Lab tests	Sampling regime
Nutrients				
Nitrate	Nutrients	H	CEHI	Water, sediment, fish/invert
Nitrite	Nutrients	H	CEHI	Water, sediment, fish/invert

[9] For the purpose of this project, agro-chemicals will include fertilisers and all classes of pesticides (herbicides, insecticides, nematicides and fungicides).
[10] See Dasgupta and Perue, 2002.

Agro-chemical	Group	Priority [10]	Lab tests	Sampling regime
Potassium	Nutrients	H	CEHI	Water, sediment, fish/invert
Phosphorus	Nutrients	H	CEHI	Water, sediment, fish/invert
Group 1: organo-chlorine pesticides				
Endosulfan	Organo-chlorine	H	CEHI	Water, sediment, fish/invert
Imazalil	Organo-chlorine	L/M	CEHI	Water, sediment, fish/invert
Chlorpyrifos	Organo-chlorine	M	CEHI	Water, sediment, fish/invert
Group 2: carbamate pesticides				
Oxamyl	Carbamate	H	CEHI	Water, sediment, fish/invert
Carbaryl	Carbamate	L	CEHI	Water, sediment, fish/invert
Carbofuran	Carbamate	L	CEHI	Water, sediment, fish/invert
Group 3: organo-phosphate pesticides				
Ethoprophos	Organo-phosphate	H	CEHI	Water, sediment, fish/invert
Diazinon	Organo-phosphate	L	CEHI	Water, sediment, fish/invert
Malathion	Organo-phosphate	L	CEHI	Water, sediment, fish/invert
Pirimiphos-methyl	Organo-phosphate	L	CEHI	Water, sediment, fish/invert
Cadusafos	Organo-phosphate	L/M	CEHI	Water, sediment, fish/invert
Isazaphos	Organo-phosphate	M	CEHI	Water, sediment, fish/invert
Profenofos	Organo-phosphate	M	CEHI	Water, sediment, fish/invert
Group 4: bipyridinium compounds				
Paraquat	Bipyridinium	H	CEHI	Water
Diquat	Bipyridinium	M	CEHI	Water
Other groups of pesticides				
Diuron	Urea	L	CEHI	Water, sediment, fish/invert,

5.3 Location of watersheds

5.3.1 Selection of watersheds

The selection of watersheds was discussed at a number of meetings held with various institutions and governmental bodies during November 2000 (Kenward and Mees, 2000). Most people agreed that banana production had the highest impact on watersheds in terms of agro-chemicals and land-use. Three watersheds have been chosen with a variety of agricultural uses and pressures, as described below:

5.3.2 Watershed 1: Soufriere (17.2 km²)

This is a low impact watershed situated on the windward side of the island with high levels of precipitation. There is limited commercial farming and low banana production (MB); the main agricultural crops are root vegetables (dasheen, yams), which use a high amount of fertilisers (NPK). This watershed is critical due to the fringing reef along this coastline. This is the sedimentation research site of York University and thus important to include in the agro-chemical component of the project.

5.3.3 Watershed 2: Roseau (49.1 km²)

This river basin is located in the banana belt of St Lucia and is well known to be heavily impacted by agriculture, principally by banana production. The construction of a high dam has considerably reduced water flow in the river. Banana cultivation is year-round using aerial- and ground spraying. The Forestry Department has produced a report detailing a significant decrease in birds (St Lucia aurial hedgefeeder) due to aerial spraying.

5.3.4 Watershed 3: Praslin/Mamiku/Patience (16 km²)

This site has been selected to contrast with the other study locations; it has different coastal and climatic characteristics from Watersheds 2 and 3 as it is on the Atlantic side of the island with much lower levels of rainfall. Two watersheds drain into Praslin Bay, which has no coral reef, however there is a mangrove stand with sea moss cultivation. There is a virtual absence of banana cultivation (except at Mamiku Estate) and the presence of diverse fruit, vegetable and flower cultivation. It is believed that the impacts of these crops are an important area of study since banana production is on the decline in St Lucia and they represent expected future trends in agriculture. Sampling of this watershed will include seamoss, which is farmed in Praslin Bay.

5.4 Sampling procedures

The Caribbean Environmental Health Institute (CEHI) is the regional institution with pesticide analytical capabilities and will be conducting sampling and analyses. Collaboration has been organised so that all samples are collected by the project research assistant (Nicole Esteban) and CEHI. As detailed above (see Table 5.1), CEHI will analyse two of the replicate samples. A third replicate will be sent to a UK ISO-certified laboratory (Central Science Laboratory, MAFF) for analysis. This verification will aid CEHI in their quality control.

5.5 Sampling design

Sampling at all three watersheds will take place in four locations: the upper catchment, mid catchment, estuarine outlet and coastal reef/lagoon. At each monitoring station, three matrices will be sampled: water, sediment and tissue (fish/invertebrate). The possibility of contaminated drinking water was also highlighted by several institutions (Water Resources Management Unit, WASCO) and it has been decided to include drinking water extraction points when sampling. Sampling of drinking water extraction points will be conducted in collaboration with WASCO. Sampling of species farmed by aquaculture (Soufriere: Tilapia at Still Plantation, Praslin/Mamiku: seamoss in Praslin Bay) has also been included in monitoring programme. The sampling design matrix is shown in Table 5.2. Wherever possible, all matrices will be analysed for individual chemicals.

Table 5.2 Sampling design for three watersheds in St Lucia (Soufriere, Roseau, Praslin/Mamiku)

Stations	Matrices			
	Water	Sediment	Fish/invert	Algae
Farm	3	3	0	0
Mid course	3	3	0	0
Estuary	3	3	3	0
Reef	3	3	3	0
Drinking water abstraction point	3	0	0	0
Aquaculture	0	0	1	1

CEHI (1 replicate/station)	15	12	7	1
Total	**15**	**12**	**7**	**1**

5.5.1 Sampling methodology

It is planned that sampling will take place on a quarterly basis with the first sampling event taking place in December 2002/January 2003. Sampling will be carried out by the project researcher, Nicole Kenward in association with CEHI and WASCO (drinking water abstraction point only). Samples will be transported to the CEHI laboratory for analysis.

5.5.2 Water

The vertical profile of sampling is important, as some pesticides are non-soluble in water and so form a film on the surface. Water will thus be sampled from the surface of the water column. A total of 2 litres will be collected at each monitoring station. 1 litre will be collected into glass bottles (some pesticides diffuse into plastic, e.g., cypermethrin) and 1 litre will be collected into plastic bottles (other pesticides plate out or adsorb onto glass, e.g., paraquat). Stations 1-2 will be freshwater, station 3 may be freshwater/brackish and station 4 will be seawater. Solvent (Hexane HPLC or glass-distilled grade) will be added into glass bottles to prevent water insoluble compounds from plating onto glass (e.g. cypermethrin).

5.5.3 Sediment

It is preferable to sample sediment with small grain sizes (e.g., organic-rich mud, clay) as pesticides diffuse to the organic portion of sediments. Approximately 200 grams of sediment will be sampled from the surface at the side of the rivers. Sediment will be collected from station 4 (reef) by snorkel. In the case of Soufriere and Roseau, sediment will be collected from a location close to sediment traps laid by the University of York.

5.5.4 Tissues

Sessile invertebrates (e.g., mussels, clams) will be collected in preference to fish as they can be taken from a fixed location. Invertebrates also have lower fat content and fat-soluble pesticides are therefore more easily detectable in their tissues. Where it is not possible to find invertebrates, it will be necessary to collect fish. In this case, reef-resident species (surgeonfish) will be purchased from local fishermen. Approximately 200 grams of tissues are required for analytical purposes.

5.6 Financial Details

CEHI will provide MRAG with details of expenditure in accordance with the budget. On submission of invoices in accordance with the costs listed below MRAG will pay CEHI the amount prescribed.

Table 5.3 Cost of analyses by analyte and sample matrix

Sample matrix	**Water**	**Soil/sediment**	**Tissue**	**TOTAL**	**Cost US$**
Analyte	**Number of samples**				
Nitrate	15	12	7	34	1055.00
Nitrite	15	12	7	34	1055.00
Potassium	15	12	7	34	870.00
Phosphates	15	12	7	34	1020.00
Organochlorines	15	12	7	34	6140.00
Endosulphan					
Imazalil					

Sample matrix	Water	Soil/sediment	Tissue	TOTAL	Cost US$
Analyte	**Number of samples**				
Chlorpyrifos					
Carbamates	15	12	7	34	6140.00
Oxamyl					
Carbaryl					
Carbofuran					
Diuron					
Organophosphates	15	12	7	34	6140.00
Ethoprophos					
Diazinon					
Malathion					
Isazaphos					
Pirimiphos					
Bipyridinium compounds	15	12	7	34	6800.00
Paraquat					
Diquat					
TOTAL (US$)*					**29220.00**
TOTAL (US$) all samples duplicate					**36525.00**

* If ALL samples are to be done in duplicate an additional 25% will be added to the total above.

Table 5.4 Financial details per sampling period

Cost details per sampling period	Dec. 2002 - March 2003	April 2003 - June 2003	July 2003 - Sept. 2003	Oct. 2003 - Dec 2003	Total
	US$	US$	US$	US$	US$
Analytical work	29,220.00	29,220.00	29,220.00	29,220.00	116,880.00
Sampling	400.00	400.00	400.00	400.00	1,600.00
TOTAL	29,620.00	29,620.00	29,620.00	29,620.00	**118,480.00**
TOTAL[a]	36,925.00	369,25.00	36,925.00	36,925.00	**147,700.00**

[a]**Total if ALL samples are analysed in duplicate**

5.7 Contact Information:

Vincent Sweeney
Caribbean Environmental Health Institute
P.O. Box 1111
The Morne, Castries
St. Lucia
Tel: 758-452-2501
Fax: 758-453-2721
E-mail: cehi@candw.lc

Patricia Aquing

Caribbean Environmental Health Institute
P.O. Box 1111
The Morne, Castries
St. Lucia
Tel: 758-452-2501
Fax: 758-453-2721
E-mail: cehi@candw.lc