



## **“Colombia, Costa Rica and Nicaragua – Reducing Pesticide Run-off into the Caribbean Sea” (GEF-REPCar)**

### **Report of the Second Meeting of the Coastal Monitoring Programme**

Kingston, March 27 - 28, 2008

#### **Summary and agreements of the Meeting**

The objective of the meeting was to discuss the progress made in developing the Pesticides Coastal Monitoring Programme of, review the capacity of participating institutions, define the most appropriate sampling techniques, select the matrices, compounds and methods of analysis to be used as well as the quality control standards to be developed, assess monitoring alternatives in the marine environment, and complete the general framework for the Programme.

Representatives from the research institutes involved in the programme (INVEMAR, CIMAR-CICA and CIRA/UNAN), as well as four external experts (Dr. Sericano, University of Texas A&M United States; Dr. Gerardo Gold, CINVESTAV Mexico; Dr. Carlos Alonso, CEAC Cuba; Dr. Fernando Ruiz, CIMAB Cuba) participated at the meeting. The external experts, together with the experts from participating institutions, make up the advisory panel on the coastal monitoring of pesticides. Also participating in the meeting were persons linked to the REPCar Project, through UNEP -RCU/CAR.

Dr. Nelson Andrade of UNEP CAR/RCU opened the session on the first day. The Project Coordinator, Dr. Alexandre Cooman, then reported on the state of implementation of the REPCar project. Dr. Sericano made a presentation on different sampling techniques, matrices and methods of analyzing pesticides. Dr. Gold presented a case study on the pollution of the Mesoamerican coral reef system. Finally, delegates from INVEMAR (Colombia), CIMAR/CICA (Costa Rica) and CIRA/UNAN (Nicaragua) reported on their respective institutions; their existing capacities for pesticide monitoring; and pesticide use in their respective countries. They also submitted their proposals for monitoring. Each participant received a CD with copies of the presentations made.

The second day was devoted to developing the technical aspect of the monitoring programme with a discussion of aspects related to the design of the programme (objectives, marine and coastal zone monitoring, sampling techniques, components to be monitored, quality control, training and information management).

The following is a summary of the most salient issues discussed and the agreements reached:

## **1. Objective of the Coastal Monitoring Programme**

In order to design a monitoring programme so that the information generated from it could contribute to the objectives of the REPCar Project, it was necessary to clarify the objectives of the programme.

The objective of the coastal monitoring programme is to monitor and evaluate pesticide run-off into the Caribbean Sea. Through this programme, baseline information on pesticide pollution in marine and coastal areas would be provided. It seeks, as far as possible, to complement this information with the monitoring of pesticide run-off in specific zones (watersheds), to provide agricultural users with this information and thus promote best practices in the use of pesticides. The information generated will serve as a baseline and will, in the long run, become an indicator of the environmental benefits generated by this project, among others.

## **2. Needs and Existing Capacities**

It was decided to hold a training course on sampling and pesticide analysis techniques of to cater to the needs of the three countries. This course will be conducted at the Center for Research on Environmental Pollution (CICA), in San José, Costa Rica. The course director will be Dr. Elizabeth Carazo of the University of Costa Rica (UCR) and the instructor will be Dr. José Sericano of the University of Texas A&M. Essentially, the training course will consist of two parts; the first part will be devoted to sampling, quality control and analysis of non-persistent pesticides. This first part of the course, which will take place from July 1–7, 2008, will be funded by the REPCar project. The second part will be organized by the IAEA and will run from July 9-18, 2008. The main focus of this second part will be the taking of samples of sediments, the analysis of non-persistent organochloride pesticides and data management.

Colombia and Costa Rica will appoint two technicians to participate in the training, while Nicaragua, following a request from the CIRA/UNAN to the Regional Project Coordinator, was allotted three spaces.

A preparatory logistical visit to the CICA by Dr. Sericano to discuss with the CICA Director the activities to be carried out as well as laboratory requirements is under consideration. UNEP-RCU/CAR will also contact IAEA and CICA officials to agree on the various thematic issues and the logistics for carrying out the relevant training sessions. The administrative part of the course will be covered by an MOU with the CICA and a special services contract (SSA) with the instructor.

The following table provides a summary of the needs and capacities of the various entities to implement coastal monitoring.

Table 1. Entities and their existing capacities and needs.

Entity	Existing Capacities	Needs
INVEMAR (Colombia)	<p>Technical staff: Two chemists, one chemical engineer, two laboratory assistants</p> <p>Ground transportation, four boats, one research vessel, multi-corer sampling equipment, sample-collection bottles and dredges.</p> <p>Gas-liquid chromatograph with electron-capture detector, gas chromatography-mass spectrometry, fluorescence.</p>	<p>High Performance liquid chromatography HPLC (50%).</p> <p>Staff: One chemist, one laboratory assistant.</p> <p>Pesticide standards Glass instruments Chemical reagents</p> <p>Soxhlet equipment Ultrasound equipment</p>
CIMAR / CICA (Costa Rica)	<p>Technical staff: Two Ph.Ds., one MSc, laboratory staff: chemists and laboratory assistants.</p> <p>Ground transportation, three hard-hull vessels, multi-corer sampling equipment, sample-collection bottles, chemical laboratory, Renewed laboratory accreditation in accordance with ISO Standard IEC 17025 with numerous tests on pesticide residues and parameters on water quality.</p> <p>Analytical techniques with the use of instruments: GC-ECD, GC-FPD, GC-NPD, GC-MS, CLAR-diode array detection, fluorescence, UV, Radiometric techniques and others..</p>	<p>Gas generators and complementary equipment, dredge</p> <p>Staff: One chemist and one laboratory assistant.</p> <p>Reagents and other laboratory tools</p> <p>Pesticide standards.</p>
CIRA / UNAN (Nicaragua)	<p>Technical staff: One Ph.D., one MSc, three chemists and one laboratory assistant.</p> <p>Ground transportation, 23-foot boat with outboard motor, tow vessel, multi-corer sampling equipment, sample-collection bottles, dredges and 12 V submersible pump.</p> <p>Gas chromatograph with ECD, FID and FPD detectors, Liquid chromatograph with DAD detectors and Fluorescence.</p>	<p>Gas chromatograph with mass spectrometer (100%).</p> <p>Flow centrifuge</p> <p>Pesticide standards, Glass instruments and inputs for new methodologies.</p> <p>If possible, data system, provided that UNEP's programmes are granted special prices, - Degree programmes.</p>

### 3. Compounds to be monitored

In order to select the compounds to be monitored, a matrix was first drawn up with the help of the advisory panel, representing the pesticides most frequently used in the main agricultural crops of the three countries (table 2). This was further complemented with information on the physical and chemical properties of these compounds, such as: soil dissociation coefficient (Kd), average life span ( $t_{1/2}$ ), dissociation constant Octanol – Water dissociation constant (Kow), Organic Carbon dissociation constant (Koc) and techniques used in their analysis: High performance liquid chromatography (HPLC), gas chromatography with Nitrogen-Phosphorous detector (NPD), electron capture detector (ECD), High Performance liquid chromatography with ultraviolet detector (HPLC –UV), High Performance Liquid Chromatography with fluorescent detector (HPLC - F),

photometric detector (FPD), Gas chromatography connected to a selective mass detector (CG – MS).

Table 2. Most widely used pesticides in Nicaragua, Costa Rica and Colombia, type of pesticide [Fungicide (F), Insecticide (I), Herbicide (H), Nematicide (N)], their characteristics and methods used to analyze them. Pesticides selected as tracers (highlighted in green). Pesticides removed from the list due to limited information (highlighted in yellow).

Molecules	NIC	COS	COL	Type	Methods								Kd	t <sub>1/2</sub>	Kow	Koc
					HPLC	NPD	ECD	HPLC-UV	HPLC-F	FPD	colorim.	GC-MS				
..Zoles	X	x	x	F			x							70	3,7	950
Azoxistrobina	X	x	x	F	x										2,5	
Bitertanol		x	x	F										10	4,1	
Bromacil		x		H	x		x							150	1,88	
Carbaryl	X	x	x	I					x					28	1,85	
Carbendazin	X	x		F				x						365	1,38	250
Carbofuran	X	x	x	I-N	x	x								60	1,5	22
Carbosulfan	X		x	I	x	x								30	5,4	
Chlorotalonil	X	x	x	F			x									
Chlorpirifos	X	x	x	I	x	x	x	x	x	x	x	x		120	4,7	12600
Diazinon	X	x	x	I		x				x				21	3,3	332
Dichlorvos	X			I		x	x			x		x		1	1,9	
Dimethoate	X	x		I		x				x		x		16	0,7	51
Diuron	X	x		H	x		x							240	2,8	
EBDs	X	x	x	F							x			1	0,26	1000
Endosulfan	X	x		I			x					x		240	4,7	20000
Etoprofos	X	x	x	I-N		x				x				28	3,6	
Fenamifos	X	x	x	N						x		x		50	3,3	
Fosetil-Al		x		F										1	0	
Glifosato	X	x	x	H					x					146	3,2	
Imazalil		x	x	F			x					x		68	3,82	
Imazapir		x		H										7	0,11	
Imazetapir	X	x		H										2	1,04	
Methylparation	X	x	x	I		x				x		x		30	3	
Oxamil	X	x		I-N					x					7	0,44	
Paraquat	X	x	x	H				x					100 00	7	4,5	
Piretroides	X	x	x	I			x	x					300 00	23	4,6	
Primetanil		x		F												
Spiroxamine	X	x		F								x			2,79	
Terbufos	X	x		I-N		x	x							27	2,77	
Tiabendazol		x	x	F			x					x		120	2,39	
Triadimefon	X	x		F		x	x							18	3,11	300
Triadimenol	X	x		F		x	x							375	3,08	
Triazines	X	x		H	x	x	x							120	2,63	300
Tridemorph	X	x	x	F										50	4,2	10000

Finally, due to their longer average life span (t<sub>1/2</sub>) and greater dissociation constant in Organic Carbon (Koc), the following compounds from table 2 were selected to be monitored by the

three countries: zoles (ciproconazole, propiconazole, among others), carbosulfan, chlorpirifos, diuron, endosulfan, ethoprosfos, fenamifos, glyfosate, imazalil, methylparation, triadimefon/triadimenol, triazines, tridemorf. Bromacil, carbendazim, carbofuran and tiabendazol were chosen to be monitored in water. Participants also considered using the pesticides chlorpirifos and endosulfan as tracers in coastal monitoring, as these molecules have a longer life cycle. It was further agreed to verify whether other organochlorate pesticides, such as DDT were detected and if so, to report their presence. However, once the countries have obtained all the information on the pesticides used, these will again be reviewed with the expert panel to determine the pesticides to be monitored in the future.

#### **4. Design of the monitoring programme: zone, stations, frequencies and matrices**

The specific proposals of the countries in the zones where coastal monitoring will be conducted are listed below:

##### **4.1 Colombia**

Monitoring will be carried out at 47 stations in the following zones: Ciénaga Grande de Santa Marta (6), the Magdalena River estuary (3), Bahía de Cartagena (3), Gulf of Morrosquillo (1), the Sinú River estuary (2), Gulf of Urabá (7) and the oceanic zone, including San Andrés and Providencia (25).

In the coastal stations, the water matrix will be monitored twice a year over a two-year period - once in the dry season and once in the rainy season. Only one ocean trip is planned for the oceanic stations during the rainy season of the first year. The matrix of surface sediment will be done in the different zones during the rainy seasons of the first and last years.

##### **4.2 Costa Rica**

Coastal monitoring will be carried out in the five zones located near the estuaries of the Matina, Estrella, Moín, and Tortuguero rivers, as well as in Puerto Vargas. At each of these sites, two samples of the water and sediment matrix will be taken. During the first two years of the Project, monitoring will be carried out twice a year, in the dry and rainy seasons.

Costa Rica will carry out preliminary monitoring, optimizing the IAEA Project (RLA/7/012) sampling to be conducted in the course of 2008, with the taking of samples of surface sediments at coastal points. These samples will be analyzed for granulometry, heavy metals and pesticides.

##### **4.3 Nicaragua**

Monitoring will focus on coastal lagoons, river estuaries and watersheds. The CIRA/UNAN will propose four watersheds to be considered for monitoring to the national coordination committee: (Río Grande de Matagalpa, Río Escondido, between Río Escondido and Punta Gorda and Río San Juan). The National Coordination Committee will be responsible for making a selection from among the proposals made, due consideration being given to agricultural crops present in the watersheds.

Other existing techniques for monitoring pesticides in coastal areas were revised. They are:

- Sediment traps: these should be left for a period of two to three months, as this is the time required for them to provide the necessary information. The dimensions of the traps were not specified, neither was it decided whether they would be made individually or acquired commercially. While these traps are a very good option, they were ruled out due to their lack of security and the time required for them to remain in the sampling area.
- Passive sampling: equipment with semi-permeable membranes or with a combination of polymeric resins, which allow for the accumulation of pollutants. They should be installed with due attention to the water current, and care should also be taken to avoid them being stolen. These were also ruled out due to lack of security. Furthermore, according to the hydrophylic characteristics of the molecules to be analyzed, the correlation of the results between the samplers with the other matrices to be studied (sediments and biota) could be hampered.

The matrices to be monitored were reviewed with the advisory panel. It was noted that the analysis of pesticides in water may provide an indication of run-off at a given period, but that due to significant variations in time and space, this information is difficult to use in monitoring programmes. For this reason, it is more advisable to conduct an analysis of marine sediments and biota that are characteristic of the area, since those results indicate the process of accumulation of pesticides over a given period. It was agreed to carry out one general study as a means of establishing a baseline to determine the presence of pesticides in marine and coastal areas. The study should cover the following matrices:

- Surface sediment with a resolution of 0.5 cm in the flocculate layer, with sampling to be carried out using a corer or multi-corer. This layer probably represents some two or three years of sedimentation.
- Water
- Particles in suspension
- Biota (Ronco Blanco fish (*Haemulon plumieri*), bivalves or other organisms).

Analyses should be based on the quantification of the pesticides previously selected for sediments and water.

Samples of water and particles in suspension must be collected at a depth of one meter. The sediments to be analyzed should weigh approximately 30-50 grams, while the volume of water to be used for sampling should be between 5 and 10 liters.

**Finally, the following recommendations should be taken into account with regard to coastal monitoring by the countries:**

- Nicaragua will conduct monitoring only in coastal zones, coastal lagoons and watersheds but not in marine zones, as it does not have much experience in monitoring on the open seas.
- Colombia will consider reducing the number of stations in marine monitoring and will review its sampling objectives to focus on the statistics of sample selection. Monitoring will also be carried out in San Andrés in order to obtain first-hand information on the boundary between Colombia and Nicaragua.
- In Costa Rica, the CIMAR/CICA will work together with the IAEA project in Costa Rica, which is headed by JAPDEVA, for the taking of samples in marine zones.

After conducting the baseline monitoring, each country will, on the basis of the results obtained, conduct a new review of the zones and stations to be monitored. To do this, zones (test plots are also considered as zones), compounds (baseline results and products used in specific crops), matrices (consider also techniques that can help determine run-off over short periods, such as passive sampling and sediment traps). This monitoring scheme will be circulated among participants and members of the expert panel for their review, comments and suggested changes.

## **5. Other variables to be monitored**

Mr. Christopher Corbin of the AMEP subprogramme (Assessment and Management of Environmental Pollution) of UNEP-CAR/RCU spoke on the need for participating countries to monitor water quality indicators. This would allow for the classification of coastal waters, thus complying with the provisions of the LBS Protocol of the Cartagena Convention.

These variables include such parameters as salinity, temperature, suspended solids, nutrients, coliforms, among others. It should be noted that these are not essential for the coastal monitoring programmes of the REPCar Project, but given the low cost of these types of analyses, it was recommended that countries include them in this programme wherever possible. The AMEP officer will submit a list of variables to the Project Coordinator for distribution to the participants.

In the case of Colombia, the REDCAM programme has been conducting tests on these parameters at different stations on the Caribbean and Pacific coasts since 2001.

## **6. Quality Assurance**

The insistence of the productive sector (Croplife LA) on receiving quality assurance of the pesticide monitoring programme was cited, as this sector could be directly affected by its results. It is therefore crucial to guarantee the quality of the results obtained.

Training courses will be organized as part of the actions undertaken in the three participating countries to guarantee the quality of the results. A standardized methodology will be used in these course ranging from the taking of samples to reporting on the results of the analysis of the compounds to be studied.

Furthermore, Dr. Sericano will be responsible for compiling a manual on sampling, analysis and reporting to be used in the three countries and ensure that they are conducted in the same way, although this depends on the equipment available in the respective laboratories and the methodology already in place. A consultancy contract will be made with Dr. Sericano for the preparation of this manual, which will also cover his services as lecturer for the CICA course and a preparatory mission to CICA.

The CICA, through Dr. Elizabeth Carazo, will provide Dr. Sericano with an unrestricted copy of the manual on laboratory techniques to serve as a basis for the manual which he will develop for the REPCar Project.

Since there is no available reference material on the pesticides covered under this programme, information will be optimized with the aid of calibration tests and inter-laboratory controls. This aspect should be considered as part of the training course.

## **7. Information Management**

UNEP-CAR/RCU proposed combining different tools for the management and dissemination of information. The AMEP subprogramme is currently designing its information management system in relation to its projects and activities. It is important that information be presented in a coherent fashion and be easily accessible to different types of users.

It was pointed out that each entity will be responsible for managing its own information, using its own resources or the resources of the monitoring programme. At the same time, UNEP-CAR/RCU wishes to receive a copy of all information gathered for its records and to ensure the widest possible dissemination of the results. To do this, funding will come from the Project's resources, different from the resources of the coastal monitoring programme. The mechanism for providing information to a third party still remains to be determined, as well as the possible reserve time period to allow scientific publications by participating institutions.

It was proposed that two complementary mechanisms be used for disseminating information arising from the monitoring programme. The first would be to develop "clickable maps" (interactive maps) as a tool by which summarized information and metadata on the coastal monitoring programme could be made available on the project web page. These interactive maps will facilitate the establishment of links to the participants' internet pages, as well as the downloading of files and pictures. This tool will be developed so that institutions may upload and update information on their activities.

As a second mechanism, consideration is being given to the option of providing users with the results of monitoring by means of a GIS IMS application. This will allow users the possibility of interactively viewing the different variables, localities, times and other factors. A module will allow participants in the monitoring programme to upload files or information on line. UNEP-CAR/RCU does not have the capacity to develop, store and maintain a GIS IMS application, and is therefore currently considering offers from different providers of the service. INVEMAR has offered this service to the IAEA Project (RLA/7/012), which is why it is a preferred option for the REPCar project. The CIRA has also expressed a wish to be considered as a provider of this service, especially if the GIS IMS infrastructure is to be installed in an institution.

## **8. Administrative Issues**

The overall budget for the coastal monitoring programme is US\$660,000 for the three countries, to be divided into three equal parts. These resources should be used to cover the activities aimed at strengthening the laboratories of participating institutions, and cover the costs specifically relating to diagnosis in marine zones and monitoring activities in watersheds, coastal lagoons and estuaries. Project funds may not be used to cover administrative costs, which should be considered the responsibility of participating institutions.

Since monitoring is a complex activity, requiring a budget of more than US\$100,000 and lasting for over a year, a Sub-project Document (SpD) must be prepared. As some time is required for the internal processing of the SpD, it is proposed that memoranda of understanding (MOUs) be established with the entities for start-up activities.

Each country will prepare a Project document that will serve as a basis for the SpDs or MOUs, with the following contents:

- Background of the institution
- Background and justification of the subject
- Objectives
- Results expected
- Activities to be carried out
- Methodology
- Time table
- Budget
- Logical framework matrix with indicators that establish a link with the REPCar Project.

## **9. Conclusions**

The monitoring of non-persistent pesticides and organochlorates in the coastal and marine zones of Costa Rica, Nicaragua and Colombia is quite a new undertaking, the possible results of which are as yet unknown. For this reason, it is very risky to have a pre-established, detailed programme on the compounds to be monitored and the frequency of testing. It was therefore decided that in the first instance, a diagnostic study should be done of pesticides in coastal and marine zones, and that this should serve as a baseline monitoring study. On the basis of this diagnostic study, actions could be suggested for the monitoring of pesticide run-off in future years.

In order to guarantee the quality of sampling, ensure standardization of working methods and security of the results, a training course will be organized at CICA, conducted by Dr. Sericano in collaboration with the experts from each country. The names of the two delegates to participate in the training must therefore be submitted by May 2008. At the same time, Dr. Sericano will undertake a bibliographical review of techniques to be used to detect the selected pesticides in water and sediment matrices.

Costa Rica will do a preliminary sample for pesticides monitoring in the field study to be performed with the IAEA Project (RLA/7/012), in mid-2008. A number of these samples will be processed during the CICA training course.

The results to be derived from this Project have a local, national and global impact. It is therefore important to guarantee the quality of the results at each stage. One of the actions that REPCar will undertake will be to engage Dr. Sericano as a consultant to develop a manual of the techniques to be followed by each participating institution. It is expected that the manual will be ready for distribution around June 16, 2008.

Each participating institution will need to revise the coastal monitoring proposal presented at this meeting and complement it with the items to be submitted by 30 April 2008. This will then be reviewed by the expert panel before being submitted to the Regional Coordinator for the preparation of MOUs and SpDs at the end of May 2008.

The third meeting on coastal monitoring will be held in early 2009 to provide follow-up on the activities and assess the results obtained.

## 10. Participants

Present at this meeting were delegates from the Research Centers of Colombia, Costa Rica, Nicaragua; external experts and officers from UNEP-RCU/CAR.

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