RESULTS OF AN INTERNATIONAL RESEARCH PROJECT

TRACKING PESTICIDES IN THE TROPICS

BY F.P. CARVALHO, D.D. NHAN, C. ZHONG, T. TAVARES, AND S. KLAINE

Since the 1940s, the use of pesticides has grown steadily at about 11% a year, reaching five million tonnes in 1995. Pesticides and fertilizers play a central role in agriculture and contribute to an enhanced production of food.

Modern trends are gradually influencing this picture. Agrochemical use, mainly in developed countries, is being reduced while biological farming methods are being developed. But in most countries agrochemicals will remain an essential component of agriculture practices for the foreseeable future.

Pesticides, especially insecticides and fungicides, are more heavily applied for tropical cash crops — such as banana, coffee, cotton and vegetables — than for crops in temperate regions. For example, the application of pesticides in banana plantations in Costa Rica attained 45kg (active ingredient) per hectare, whereas the comparable average application of pesticides in Japan for crops is 10.8 kg.

Experts have estimated that only a minor fraction of applied pesticide — less than 0.1% — reaches the target pest species; excess pesticide moves throughout the environment potentially contaminating soil, water, and biota. It is critical to characterize the fate and non-target toxicity of these pesticides to confidently assess the risk associated with their use.

Agricultural fields generally are located in coastal plains and river valleys, so it is not surprising that these rivers receive agriculture runoff and carry residues into estuaries and coastal seas. For example, the USA's Mississippi river may have transported an estimated 430 tonnes of atrazine in 1989 from midwestern corn and soybean plantations to the Gulf of Mexico.

The environmental impacts of pesticide residues and their effect on human health are matters of much concern. Recent studies on the estrogen-like behaviour of DDTs and PCBs in humans suggest the implication of these compounds in breast cancer. Furthermore, the growing awareness of the environmental persistence of organic pollutants (pesticides and industrial organic chemicals) recently led governments to internationally agree on a Convention on Persistent Organic Pollutants, phasing out a number of noxious substances, including DDT, PCBs and other chlorinated hydrocarbons. Nevertheless, the use of hundreds of old and new compounds as crop protection chemicals will continue worldwide. It is urgent that we develop strategies to facilitate the coexistence of productive, healthy, and economically viable agriculture with the preservation of natural resources.

To accomplish this, more research is needed in ecosystems that are subject to significant pesticide burden. Most studies on environmental cycling, fate and effects of pesticides have been carried out in temperate climates (North America and Western Europe). Much less information has been available on the behaviour of these chemicals in tropical ecosystems.

To help fill this information gap, the IAEA set up a coordinated research programme (CRP) on the "Distribution, Fate and Effects of Pesticides on Biota in the Tropical Marine Environment", funded by the Swedish International Development Authority. This

Mr. Carvalho is Head of MEL's Marine Environmental Studies Laboratory, in Monaco; Mr. Nhan is a researcher at the Institute for Nuclear Science and Technique, Hanoi, Viet Nam; Mr. Zhong is Professor at the Zhongshan (Sun Yat-sen) University, Guangzhou, China; Ms. Tavares is Professor at the Federal University, Bahia, Brazil; and Mr. Klaine is Professor at Clemson University, South Carolina, USA.

RADIOISOTOPES FOR PROGRESS

Eighteen laboratories in seventeen countries — Bangladesh, Brazil, China, Colombia, Costa Rica, Cuba, Ecuador, India, Jamaica, Kenya, Malaysia, Mexico, Philippines, Spain, the Netherlands, United States, and Viet Nam — took part in the IAEA's coordinated research programme on the fate and effects of pesticides in tropical environments.

Among the least expensive and best research tools that the laboratories applied were radiotracer techniques. Pesticides labelled with radioisotopes are used in in model systems that help researchers investigating, for example, the persistence of pesticides, degradation pathways, and pesticide transfer in marine food chains. Large numbers of samples can be processed rapidly and measured with standard liquid scintillation equipment at low cost. Several participating laboratories are applying this technique to obtain previously unavailable data on pesticide behaviour in tropical marine environments.

Research using compounds labelled with carbon-14 was introduced in twelve laboratories, and gas chromatography analytical techniques now are used in fourteen participating laboratories. Most of the laboratories have adopted quality assurance procedures, including regular participation in intercomparison exercises and the use of certified reference materials to ensure the quality of data.

Research results have been presented at various scientific fora, including the International Symposium on the Environmental Behaviour of Crop Protection Chemicals, organized jointly by the IAEA and Food and Agriculture Organization in 1996.

In Monaco, at the upcoming International Symposium on Marine Pollution in October 1998, participating scientists will present fourteen scientific papers on their work. *(See box, pages 4 & 5 for information on the Symposium.)*

Photos: Analytical work in the chemical laboratory at the University of Malaya in the Philippines. The university hosted a CRP meeting of participants in June 1995.

article highlights results of this project, including those achieved through national case studies.

RESEARCH AIMS & PARTICIPATION

The CRP's technical objectives were to measure the current levels of pesticide residues in coastal environments; to characterize the cycling and fate of pesticides using radiolabelled compounds and nuclear techniques; to evaluate the effects of residues on marine biota; to assess the risk associated with pesticide residues in coastal tropical ecosystems; and to advise on measures to protect the tropical marine environment.

A large number of requests for participation and information were received at the IAEA, which attested to the project's relevance among countries and their interest to act on associated environmental problems. Eighteen laboratories in seventeen IAEA Member States agreed to participate in the project, which was led by the IAEA's Marine Environment Laboratory in Monaco. *(See box, page 25.)*

The first Research Coordination Meeting was held at MEL in June 1994. It reviewed pesticide usage and data on contamination by pesticide residues in the participating countries, and identified the compounds to be targeted in research and applicable methodologies for meeting project objectives. Furthermore, the equipment and training needs of the participating laboratories were defined to organize IAEA technical support to the laboratories. Since then, annual coordination meetings have been organized to present and discuss the project results achieved in every country. Between the meetings, ongoing liaison and data exchange among participants was maintained through periodic circular notes.

Major joint activities were implemented to meet common needs or objectives. These included courses (lectures) on pesticide chemistry, aquatic toxicology, and ecological risk assessment; training workshops on pesticide analyses (one organized in Costa Rica and another in Malaysia) for the analytical training of CRP participants; and intercomparison exercises to test the accuracy of laboratory results and encourage progress with data quality assurance in the analyses of organochlorine pesticides and radiolabelled compounds. In these exercises, homogenates of marine samples of adequate matrix (sediments, seaweed, and mussels) were used as test samples.

A WIDE REACH

Crop protection chemicals are used in agriculture worldwide. The largest amounts of herbicides are used in North America, Western Europe, and Asia, whereas insecticides are mostly used in East Asia, North America, and Latin America. About 50% of the world's use of insecticides is in developing countries, in particular in tropical regions, mainly to control pests feeding off cash crops and household insects. In coming years, a general increase in pesticide use is expected in Asia, whereas use is expected to keep declining in Western Europe.

Photo: Spraying herbicides in Viet Nam's rice paddy fields.
(Credit: Carvalho/MEL)

RESULTS OF CASE STUDIES

Each CRP participating institute planned to carry out field investigations to monitor pesticide residues in coastal ecosystems in their respective countries. Study areas covered diverse ecosystems, such as Manila Bay in Philippines, the delta of the Zhujiang (Pearl) River in China, the Bay of Cartagena in Colombia, several watersheds at Kingston Harbour in Jamaica, the All Saints Bay in Brazil, the Red River Valley and delta in north Viet Nam, and the Indian Coast of Kenya.

Pesticide residues identified in coastal environments in these regions follow, as expected, the trends in local pesticide usage. Nevertheless, volatile compounds that are transported by atmospheric processes and re-deposited worldwide could also be measured in regions far from their original application area. Examples of the results obtained are presented below:

■ ***Research in Brazil.*** Analyses of sediments and molluscs

collected in a number of stations of the All Saints Bay, Brazil, found DDT residues in mollusc tissues ranging from 0.24 to 44 nanograms per gram (wet weight). Regular consumption of these edible molluscs, as done in the fishing community, leads to an ingestion of DDTs of between 75 and 589 nanograms per day. These levels, although not alarming, were considered high. Furthermore, in comparison with measurements carried out ten years before in the same areas, these levels indicate an increase of DDT concentrations in the Bay, despite Brazil's 1976 ban on DDT. The increase suggests use of DDT by farmers in the region.

DDT was not the only organochlorine pesticide found. Analyses of HCB, aldrin, dieldrin and endrin in the same samples have shown that these compounds were present in several sites, although at levels generally below one nanogram per gram.

Through the CRP, the capacity of laboratories to measure pesticide residues in marine samples, such as DDT residues in mussels, was improved significantly.

■ ***Research in China.*** The environmental survey carried out on benzene hexachloride (BHC) and DDT in the Zhujiang (Pearl) river delta was considered of much interest. This is because China, a major world producer of rice and wheat, mainly used DDT, HCH, and BHC in the 1950s and 1960s to control insect pests. In 1990 the total consumption of pesticides in China reached 2×10^6 tonnes of active ingredient (about one-third of world use), and officially DDT and BHC were discontinued for use in agriculture.

The Zhujiang river drains a wide fertile area, potentially carrying these pesticide residues into the South China Sea. Research under this CRP found low current transport of residues by the Zhujiang river water, which is in agreement with the ban of these pesticides today.

Nevertheless, in the bottom sediments and marine food chains, from phytoplankton to mussels and seabirds, DDT concentrations were high, attaining 1.3 and 2.1 micrograms per gram (wet weight) in the tissues of mussels and seabirds respectively. These high concentrations are due to the past use of the compounds in the region and confirm the very long persistence of DDT in the environment.

■ ***Research in Viet Nam.*** Studies carried out on the Red River delta in Viet Nam concluded that cyclodien pesticide compounds such as aldrin, dieldrin and endrin are practically absent in the aquatic environment there. This suggests that these persistent compounds, once very popular in America and Europe and now totally forbidden, were probably never used in Viet Nam. On the other hand, DDT was measurable in all samples. Furthermore, in freshwater carp fish collected near rice fields, DDT concentration (13 micrograms per gram lipid weight) were much above the maximum permissible levels in food covered by European standards.

Since DDT's use is banned in Viet Nam, these findings may require the competent authorities to enhance controls on pesticide use. Furthermore, the dense population of the Red River Valley and multiple re-use of the water along the river endorses a careful assessment of pollution problems. They should be controlled through integrated watershed management to enhance water quality and conservation.

■ ***Research in Mexico.*** A field survey on pesticide residues on coastal lagoons of Mexico, state of Sinaloa, indicated the presence of residues of DDTs, aldrin, dieldrin, and the organophosphorus compounds chlorpyrifos and parathion. The finding of organophosphorus compounds in the lagoon system was somewhat surprising. They are generally believed to be rapidly degradable and thus non-persistent in the environment. The presence of these residues, originating from sugar cane and horticulture plantations in the Culiacan river valley, was considered a potential threat to the development of shrimp farming activities in Sinaloa. Caution with the agriculture runoff and waste-water discharges was recommended to the regional authorities and farmers.

■ ***Research in Jamaica.*** The investigation on pesticide residues in Jamaica focused on contamination of mountain streams receiving drainage from coffee plantations. Endosulfan, as well as several organophosphorus pesticides, are worrysome contaminants of drinking water resources and freshwater biota. The stream

discharges into the coastal environment causes contamination of the marine ecosystems, although at low level. Neverthless, strict control on pesticide use in the mountain slopes seems to be urgently required to protect aquifers from contamination.

■ ***Research in Costa Rica.*** In Costa Rica, a monitoring programme was carried out on contamination by pesticide residues from banana plantations in two watersheds, one on the Caribbean coast (Tortuguero-Parismina) and another on the Pacific Coast (Tempisque river estuary). Costa Rica imports about 5000 tonnes of pesticide (active ingredient) per year — of which 56% are fungicides, 30% herbicides, and 12% insecticides/nematicides — almost totally applied in banana plantations. The high rainfall and frequent application of agrochemicals causes the seepage of residues to the major rivers of the country, which flow through

conservation areas (natural reserves) in both coastal regions. Residues of edifenphos, chlorpyrifos, diazinon, ametryn, carbofuran and ethoprofos were detected either in the water or in clams collected on the coast. The effects of these residues on the ecosystems, however, have yet to be assessed.

■ ***Research in Nicaragua.*** In Nicaragua a collaborative study was carried out by the University of Nicaragua and MEL to monitor contamination by pesticides in the main coastal lagoons of the Pacific Coast. Most of the country's agriculture and pesticide use has been taking place for decades in this region.

Results for a wide range of persistent chlorinated pesticides showed levels that were low in several lagoons. But levels were extremely high, particularly for toxaphene and DDTs, in the coastal lagoons of the cotton districts Chinandega and Leon. There, concentrations of toxaphene attained 6.9 microgram per gram (dry weight) in sediments and 1.6 microgram per gram (dry weight) in soft tissues of clams.

Toxaphene and DDT were used in cotton growing for several decades in this region. Although their use was discontinued in the early 1990s, the cumulative reservoir of these compounds in the soils and in the lagoon sediments is very high and their environmental persistence is very long.

Results of this investigation were presented at a National Conference on Pesticides held in Managua, November 1997, which preceded the long-awaited approval of the Pesticide National Law. Sound integrated management and measures to reduce the contamination of the coastal area can now be implemented by the Nicaraguan authorities.

■ ***Other surveys.*** Similar surveys to assess the environmental contaminants by pesticide residues are being done of other tropical coastal areas in Kenya, India, Bangladesh, and Ecuador. From the results obtained so far, the persistent organochlorine pesticides are present everywhere, although in some areas only in trace amounts fortunately. When detected, organophosphorus pesticides generally seem to be present in concentrations lower than organochlorine compounds.

RADIOTRACER TECHNIQUES

Experimental work was done using carbon-14-labelled compounds and liquid scintillation detection to investigate the behaviour of pesticides in the aquatic environment. The research focused on a selection of compounds — namely DDT, endosulfan, lindane, chlorpyrifos and parathion — which have been found in tropical coastal environments.

Experiments were designed to obtain information on several aspects related to the fate, persistence, and

Photo: Above, a liquid scintillation counter is part of the laboratory equipment pesticide researchers are using in Viet Nam. Left, a banana harvest in Costa Rica.
(Credit: ISTN/VINATOM)

bioaccumulation of these pesticides in marine waters. Studies were carried out in laboratory microcosms and model ecosystems according to common methodologies adopted by the CRP participating institutes.

The transport, dispersion, and ultimately the biological effects of pesticides in lagoon systems depend upon the persistence of these chemicals under tropical conditions and their bioaccumulation and biodegradation. It is generally believed that sunlight and the elevated temperatures in the tropics would contribute to a rapid breakdown of these compounds. However, preliminary experimental results indicate that photolysis plays a minor role in the breakdown of these compounds in comparison with chemical hydrolysis.

Results of experimental studies indicate that persistence half-lives of dissolved pesticides at 32^{o} C are in the range of 1.4 to 10 days for chlorpyrifos, 9 to 46 days for parathion and 130 to 155 days for DDT, depending upon the water's salinity.

Experiments involving sediment-water systems have demonstrated that the persistence half-lives of pesticides sorbed onto lagoon sediments are 10 to 100 times longer than the half-lives for the same compounds in the overlying waters, despite the larger microbial biomass in the sediment compared to the water. Therefore, the rapid sorption of pesticides onto sediment particles may increase their persistence. It is likely that the largest reservoirs of these compounds will be found in the sediments of lagoons which receive runoff from adjacent fields.

Several CRP participating institutes in Bangladesh, China, India, Philippines,Viet Nam, Malaysia, Jamaica and Mexico carried out similar experiments. They examined the fate of DDT and chlorpyrifos in aquaria simulating the conditions of the tropical marine environment and using the local species of marine biota. Results show that the accumulation of those pesticides from water by mussels, clams, shrimp, and fish is very rapid and occurs on time scales of minutes to hours. Furthermore, the biological concentration factor of lipophilic compounds, such as DDT and DDT metabolites, generally are very high.

Considerable progress has been achieved by the laboratories using radiotracer techniques in pesticide research. *(See box, page 25.)* It includes the development of miniaturized experimental systems to investigate compound degradation and volatilization. It also includes the attainment of results showing that persistence and bioaccumulation of pesticides in the marine environment are related with molecule configuration and chlorine content.

On the basis of experimental results obtained with radiolabelled compounds, it seems clear that organochlorine compounds, such as DDT, will degrade very slowly in the environment. On the other hand, some of the organophosphorus compounds may survive long enough to disperse into estuarine and coastal environments and impact aquatic biota. Nevertheless, these compounds will generally degrade much faster than organochlorine compounds in the marine environment.

EFFECTS ON MARINE SPECIES

Toxicity assays on marine species under tropical conditions are being carried out by several institutes in the Philippines, Jamaica, Costa Rica, and Mexico. The aim is to assess the sensitivity of common tropical species likely to be exposed to residues (e.g., Tilapia and farmed shrimp) under the conditions of tropical ecosystems.

One common feature of tropical coastal lagoons which are surrounded by mangrove forests is the elevated concentration of humic substances. Humic substances are formed by the gradual decomposition of the leaf litter from mangrove trees. Due to the hydrophobicity of organochlorine and organophosphorus compounds, a possible association of these pesticides with particulate and dissolved humics may modify the overall fate of these pesticide residues and their bioavailability.

This hypothesis was tested using marine mussels exposed to pesticides dissolved in sea water either without humic substances or with particulate humics already containing bound pesticides. Results showed that the accumulation by the mussels of pesticides dissolved in the water increased rapidly in the first 12 hours

followed by a slower increase thereafter. Pesticides bound by the humic substances were also accumulated in the mussel tissues, although to a lesser extent than directly from water.

Therefore, it seems that previous binding of pesticides by humics may act to reduce the bioaccumulation of those compounds by lagoon fauna. However, further research is needed to elucidate the exact mechanisms that govern the distribution, fate and, thus, the effects of pesticide residues in tropical lagoons.

ASSESSING RISKS & STRATEGIES

One overall goal of the CRP is to characterize the existing risk to both humans and coastal marine ecosystems and suggest strategies to reduce that risk (if it is presently unacceptable) in the future.

Several case studies within the CRP have generated sufficient pesticide residue data and toxicity data to begin to assess ecological risk in particular ecosystems. In some ecosystems, particularly estuarine/coastal lagoon systems receiving agricultural drainage, pesticide residues in sediments and biota approach the acutely toxic level. More often, however, residues are below lethal values and represent potential food chain problems.

Coincidentally, these ecosystems are ideal habitat for fish, shrimp, and oyster farming. Hence, these residues may find their way into the general population through the aquaculture industry. In addition, these residues present a measureable risk to the stability of the ecosystem in these areas. This instability could arise through the loss of a critical species or trophic level or through the deterioration of general water quality (e.g. dissolved oxygen) caused by the microbial degradation of these contaminants. The preservation of these systems and associated resources would require the implementation of integrated management plans for coastal zones in order to harmonize the interests of agriculturalists, aquaculturalists, and the fishing community.

The CRP's development facilitated the assessment of pesticide contamination in key coastal areas. Furthermore, experimental data on the cycling of pesticides was obtained to provide a more complete understanding of the impact and fate of residues in tropical coastal environments and about the implementation of environmental management strategies.

Other immediate benefits of the CRP to participating countries include the improved capability to measure pesticide residues in environmental samples, and to conduct research on pesticide cycling in tropical regions. Overall, the project has enhanced awareness of the need to reduce environmental contamination traced to persistent organic compounds.

A more comprehensive watershed-based ecological risk assessment is planned. It would incorporate existing pesticide residue and toxicity data, along with land-use data in the watershed, to develop cause-and-effect relationships for various activities. The study would provide the foundation for developing land and water resource management strategies to ensure ecosystem stability, and provide resources for agriculture, aquaculture, industrial development, recreation, and domestic dwellings.

Practical solutions to treat contaminated waste waters and surface runoff from agriculture fields still must be investigated and tested. Tentative solutions have been suggested in a few cases, such as the use of natural or constructed wetlands around agriculture fields to remove residues from water. Eventually this and other suggestions could be tested on a pilot scale in the tropics, for example around banana plantations. This move forward would be a logical step stemming from the work already performed by the world's laboratories through this IAEA-sponsored research project. ❑

Photo: Fishing in the Philippines' Manila Bay.