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AGRICULTURAL CHEMICAL SCREENING AND DETECTION OF CHLORPYRIFOS IN FISHES FROM THE APURE DRAINAGE, VENEZUELA

Leo G. Nico*, David J. Schaeffer**, Donald C. Taphorn***, and Aniello Barbarino-Duque***

*National Biological Survey, U.S. Dept. Interior, 7920 NW 71st St., Gainesville, FL 32653 USA;
**University of Illinois, Veterinary Biosciences, 2001 S. Lincoln Ave., Urbana, IL 61801 USA;
***Museo de Ciencias Naturales, UNELLEZ, Guanare, Estado Portuguesa, Venezuela.

SUMMARY: To evaluate aquatic effects of large-scale agricultural operations, we determined agricultural chemical concentrations in muscle tissues from nine fish, representing important food species, taken in December 1993 from the Apure River drainage, Venezuela. In a series of screenings that included carbamates, herbicides, and other pesticides (organophosphates and chlorinated hydrocarbons), the only chemical detected was the organophosphate chlorpyrifos (=Dursban), in six of seven samples. Chlorpyrifos concentrations in fish flesh were generally 3 to 10 ppb wet weight. These preliminary results suggest that fishes from this area of the Apure River drainage are not heavily contaminated with persistent pesticides and do not appear at present to pose a serious food safety or human health hazard. However, future monitoring of a broad range of fish species for environmental contaminants is recommended.

KEY WORDS: chlorpyrifos, Dursban, insecticides, Neotropical fish, organophosphates, Orinoco River basin, pesticides, South America, tissue residues

INTRODUCTION

Aerial spraying of chemicals for controlling animal and weed pests is common and widespread in large agricultural areas of Venezuela. However, the long-term effects of these chemicals on complex tropical ecosystems is not well understood. The Apure River is a major tributary of the Orinoco River, and its drainage supports an extremely diverse and abundant fish fauna (1). Moreover, soils in the Apure drainage, especially those in its northwestern sections, are some of the most fertile in Venezuela. Unfortunately, the growing human population has made increasing demands for the agricultural land and water in the drainage. Consequently, many streams have become polluted to the point that we will never know much, if anything, about their original fish faunas (1).

The Apure River and its larger tributaries once supported a large commercial fishery and still provide a significant source of protein and extra income for many rural families. However, catches have declined in recent years, raising concerns about land-use practices. For instance, massive fish kills occur annually during the onset of the rainy season, and these kills are thought to be the result of flood waters flushing large amounts of agricultural chemicals into local streams (1). Surveys carried out in 1981-1983 in three sections of Portuguesa State indicate that aerial sprayers released from 20 to 40 metric tons (t) of insecticides per year in agricultural areas around the city of Guanare, 59 to 121 t per year in agricultural areas surrounding the city of Acarigua, and 57 to 167 t per year in the agricultural area of Turén (2,3,4). In this paper, we present preliminary results of agricultural-chemical analyses of muscle tissue samples from several commercially-important fishes from the Apure River drainage. As far as we are aware, these are the first published results on chemical contamination in food fishes from this area.

STUDY AREA

The Apure River drainage is located in western Venezuela and drains 167,000 km^2 or about 15% of the total area of the Orinoco basin. Average annual rainfall in Portuguesa is about 1200 mm, with most precipitation occurring in the 7- or 8-month wet season from April to November. Although very seasonal, average annual runoff from the Apure River drainage is about 361 mm, and the annual mean discharge is greater than 1750 m^3/sec (5). The Apure mainstem is a typical white-water river, having a relatively high sediment load (range 64-644 mg/L, median 233) and high conductance (range 88-225 μS/cm, median 123) (6). Its drainage area includes all of the territory in the Venezuelan states of Portuguesa, Cojedes, and Barinas, a large portion of Apure and Guárico, and parts of Táchira, Mérida, Trujillo, Lara, Yaracuy, Carabobo, and Aragua. Portuguesa State contains some of the largest and most extensive agricultural areas in the drainage, with major crops that include cotton, rice, sugar cane, corn, beans, sorghum, watermelon, tobacco, tomato, and sesame (2,3,4).

MATERIALS AND METHODS

Fish specimens used in this study were obtained during December 1993. Most of these fish were purchased partially frozen or fresh from the main fish market in Guanare, Portuguesa State; these market fish were caught by local commercial fisherman probably working the Apure River where it borders Portuguesa and Apure states, near the town of Bruzual. The remaining fish, three speckled pavon (*C. temensis*), were taken with hook and line from the Las Majaguas reservoir, an artificial lake in the Apure drainage that receives polluted water from upstream areas. In summary, samples representing seven fish species and six families were selected for pesticide analysis: *Goslinia platynema* and *Pseudoplatystoma fasciatus* (large carnivorous catfishes), *Ageneiosus brevifilis* (a medium-sized catfish), *Piaractus brachypomus* (a large, omnivorous relative of piranhas), *Prochilodus mariae* (a medium-sized detritivore), *Pellona flavipinnis* (a large carnivorous clupeid), and *Cichla temensis* (a large predatory cichlid). Voucher specimens are deposited in the Museo de Ciencias Naturales (MCNG) of the Universidad de Los Llanos Occidentales (UNELLEZ), in Guanare, Venezuela.

All fish were placed on ice immediately after procurement and transported to UNELLEZ. In the laboratory, frozen fish were identified and measured from tip of snout to base of caudal fin (i.e., standard length [SL]). We chose muscle tissue for our preliminary pesticide analyses because its importance as food for humans is a major concern. A 10-20 g sample of skeletal muscle was dissected from the right side of each fish, lateral and ventral to the dorsal fin, with clean stainless steel implements. Axial muscle samples were wrapped in clean (new) aluminum foil, sealed in plastic bags, and kept frozen while being transported to the United States. Frozen tissue samples were sent to the Animal Disease Laboratory, Illinois Department of Agriculture, Centralia, Illinois. The nine fish were analyzed as follows: six individually, and one as a composite sample of three fish (the composite sample consisting of similar-sized *C. temensis*).

Screenings included 90 different pesticides (detection lower limits, in parts per million, are in brackets). The carbamate screen included: Aldicarb [1], Aminocarb [0.8], Bendiocarb [1], Benomyl [0.8], Carbaryl [0.5], Carbofuran [0.5], Carbofuran phenol [0.8], 3-Hydroxy carbofuran [0.8], 3-Keto carbofuran [0.8], Lannate [0.5], Methiocarb [0.8], Methomyl oxime [0.8], Oxamyl [0.5], Oxamyl oxime [0.8], Thiobencarb [1]. The herbicide screen included: Alanap [0.8], Atrazine [0.5], Barban [0.8], Basalin [0.8], Bladex [0.8], Bromacil [0.8], Dacthal [0.8], Devrinol [0.8], Dinitramine [0.8], Dinoseb [0.8], Diuron [0.8], Dual [0.8], Eradicane [0.8], Furloe [0.8], Hoelon [0.8], Kerb [0.8], Lasso [0.8], Lorox [0.8], Modown [0.8], Monuron [0.8], Pebulate [0.8], Pramitol [0.8], Preforan [0.8], Prometryne [0.8], Propanil [0.8], Propazine [0.8], Prophan [0.8], Prowl [0.8], Ramrod [0.8], Sencor [0.8], Sesone [0.8], Simazine [0.5], Spergon [0.8], Sutan [0.8], Tolban [0.8], Treflan [0.8], Vegadex [0.8], Velpar [0.8], and Vernolate [0.8]. The pesticide screen included the organophosphates Amaze [0.01], Baytex [0.02], Counter [0.01], Cygon [0.05], DDVP [0.01], Diazinon [0.01], Disulfoton [0.01], Dursban [0.01], Dyfonate [0.01], Dylox [0.01], Ethyl Parathion (=Parathion) [0.01], Malathion [0.05], Methidathion [0.05], Methyl Parathion [0.05], Mevinphos [0.01], MoCap [0.01], Phosmet [0.05], Ronnel [0.01], and Thimet [0.01], and the chlorinated hydrocarbons Aldrin [0.01], BHC [0.01], Chlordane [0.05], DDD [0.01], DDE [0.01], DDT [0.02], Dieldrin [0.01], Endrin [0.05], Heptachlor [0.01], Heptachlor epoxide [0.01], Hexachlorobenzene [0.01], Lindane [0.01], Methoxychlor [0.06], Mirex [0.01], Thiodan [0.01], *cis*-permethrin [0.05], and *trans*-permethrin [0.04].

Muscle tissue homogenates of each sample were analyzed for contaminant residues and the results reported in ppb (parts per billion) (=ng/g) on a wet-weight basis. Methods generally followed Association of Official Analytic Chemists guidelines (7). Carbamates and herbicides were determined by using approximately 5 g of sample tissue placed in a large test tube, adding 10 mL of acetonitrile HPLC grade, allowing to sit for at least one hour while vortexing periodically, and filtering as necessary before proceeding to liquid chromatography (LC) analysis. In LC analyses, injections of 100 µL of the samples were compared against standards using a PRP-1 Hamilton 25 cm 10 µm column at a flow rate of 0.8 mL/min; UV detector was 220 nm. Spiked recoveries were in the 90% range.

RESULTS

None of the herbicides or carbamates were detected from the seven fish samples. The only pesticide detected was the organophosphate chlorpyrifos (commonly-used synonyms include Dursban and Lorsban) (formula: $C_9H_{11}Cl_3NO_3PS$) (Table 1).

Table 1: Chlorpyrifos concentration in muscle tissue from seven fish species. Numbers represent single samples of individual fish except for *Cichla temensis* (see text).

Family and species	Common name	Length (SL, mm)	Chlorpyrifos ppb ww
Pimelodidae			
Goslinia platynema	bagre garbanzo	557	4
Pseudoplatystoma fasciatus	bagre rayao	>500	nd
Ageneiosidae			
Ageneiosus brevifilis	chancleta	327	3
Characidae			
Piaractus brachypomus	morocoto	>400	4
Prochilodontidae			
Prochilodus mariae	coporo	280	8
Clupeidae			
Pellona flavipinnis	sardinata	380	10
Cichlidae			
Cichla temensis	pavón lapo	440-540	3

ppb ww= parts per billion (ng/g) wet weight; nd = none detected

DISCUSSION

There exist several possible explanations for nondetection or low levels of agricultural chemicals in our results. (i) The heavy rainfall, heavy flooding and resulting high water flows carry most agricultural chemicals downstream, and, thus, these chemicals may not remain long in local environments and may not enter the local aquatic food chain to any significant degree. (ii) The residence time of most of these chemicals in some fish tissues is short. (iii) Fish may be very sensitive to even low amounts of chemicals; thus, fish with moderate to high chemical loads may not survive (possibly dying early as eggs or larva, or in other early-life stages) and are therefore not included in samples. (iv) The use of chemicals in agriculture has decreased over the last 10 years, and this decreased use is reflected in the low amounts found in our study.

In 1983 and again in 1989, 1993, and 1994, Venezuelan currency decreased significantly in the international exchange rate. The loss of buying power reduced imports of materials needed for production of insecticides and, as a result, there has been marked reductions in agricultural pesticide use (8). Because of the increased costs associated with chemical controls, there has also been an increase in the use of biological control methods (8). Additional changes in pesticide use resulted from a Venezuelan law (Gaceta Oficial No. 32741, 6 June 1983), effective in August 1983, that prohibited the agricultural use of organochlorides, except in emergency situations and under federal authorization (3). As a result of the above changes, certain less-costly or unrestricted chemicals are used more extensively, or at least in greater proportion, than in the past. Agricultural chemicals that have seen greater use include three organophosphates: chlorpyrifos, Parathion (=Ethyl Parathion) and monocrotophos (Azodrin, Inisan, and Nuvacron); a carbamate, Carbaryl (=Sevin); and, especially, pyrethroids. For instance, the use of pyrethroids in the Guanare area has increased over the last 10 years from under 4% of total insecticides used to as much as 50% (8).

Developed in the 1960's to replace DDT, chlorpyrifos has been used widely to control agricultural insects and such pests as mosquitoes and cattle ticks (9, 10). Although degradation time is comparatively short in biological samples, adverse effects from chlorpyrifos have been documented for fish and other aquatic life (10). As such, the U.S. Environmental Protection Agency (EPA) established criteria for protecting aquatic organisms, including freshwater levels of 0.41 μg/L (4-day mean concentration) and 0.083 μg/L (1-h mean concentration) (9, 10). However, as of 1992 the EPA had not established criteria or standards for chlorpyrifos as related to human consumption of fish (9). Others have recommended 2.0 mg/kg (=μg/g) fresh weight as an acceptable tolerance level of chlorpyrifos in meat products used for human consumption (10).

In conclusion, these preliminary results suggest that, from food safety and human health perspectives, muscle tissues of fish from this particular area of the Apure River drainage do not appear at present to be heavily contaminated with persistent pesticides. However, it should be recognized that compounds not observed in fish muscle tissues can accumulate in the internal organs, skin, and fat of fish and may potentially be ingested by humans, depending on such factors as inappropriate food handling and preparation methods, and on dietary preferences. Furthermore, even low levels of agricultural chemicals may have other yet unknown impacts to aquatic ecosystems (10). Tropical ecosystems may be especially vulnerable. Given the increasing agricultural development of Portuguesa State and other regions in Venezuela, we recommend monitoring of selected fish species for possible chemical contaminates.

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