State of California

Memorandum

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Date : November 22, 1995

Place :

From : **Department of Pesticide Regulation** - 1020 N Street, Room 161
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Subject : TOXICITY MONITORING IN RICE RECIRCULATING SYSTEMS

Scope of this Memorandum

The scope of this memorandum is to provide results from the Toxicity Monitoring in Rice Recirculating Systems Study. This memorandum does not include any interpretation of the data, which will be provided in the final report.

Background

In 1993 the Central Valley Regional Water Quality Control Board (CVRWQCB) monitored emergency water releases from rice fields (CVRWQCB 1993) 6 to 17 days after molinate and 14 to 41 days after carbofuran applications. Water samples from fields treated with both pesticides were all toxic to *Ceriodaphnia dubia* in toxicity tests. The results generated concern about toxicity in drainage canals of recirculating systems receiving such runoff.

Water releases from rice fields treated with carbofuran and molinate are allowed after a 28-day post-application hold. Prior to 1994, emergency releases were permitted 6 days after molinate and carbofuran applications. Beginning in 1994 emergency releases were permitted from molinate treated fields only when water was held for at least 11 days, and then only if the 28 day holding time following a carbofuran application had lapsed. In contrast, water from rice fields in recirculating irrigation systems may be released 8 days after application of both pesticides. Results from the CVRWQCB toxicity test infer that water in recirculating systems may be toxic to aquatic life. Therefore, this study was conducted to monitor water in recirculating systems for toxicity using *Ceriodaphnia dubia* as the test species.

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Site Selection

Six rice fields were selected in Reclamation District no.108 (RD108), a multi-farm recirculating irrigation system in Colusa and Yolo counties. The selected fields were located in Colusa county, in the northern half of RD108. All fields used a post-flood "Leathers" or "Pin Point" method of carbofuran application to the checks and borders. The Leathers method is a post-flood application where the rice field is flooded, seeded, then the water level is lowered and carbofuran applied. The field is then reflooded and the water held for a minimum of 8 days. However, molinate is usually applied during the required 8 day carbofuran hold, and thus water cannot be released until at least 8 days after the molinate application.

Sampling Methods

The grower-cooperators were asked to release water at the earliest date that permit conditions allowed. Two replicate samples were taken from each field at its discharge point within 4-hours of the initiation of water release, background samples were collected at field irrigation inlets during the reflooding after the carbofuran applications. Two of the six field's discharge was sampled as it traveled through the drainage canals of the recirculating system. Water samples were collected in the drainage canal below the confluence of all subsequent canal outflows.

The discharge and background inlet water was collected as a grab sample, this water was assumed well mixed. Canal samples were collected using a hand held water sampler and the equal-width increment, depth integration method (Guy and Norman 1970). Flow rates and velocities at each canal sampling site were measured to determine appropriate sampling intervals, ensuring that the same parcel of water is monitored throughout the system.

Each sample consisted of eleven liters of water. Samples were split using a Geotech® Dekaport splitter into ten 1-liter amber glass bottles with Teflon® lined caps and one 1-liter polypropylene bottle. All samples were split on the day of collection and shipped on wet ice or refrigerated at 4°C until analyzed.

Toxicity Testing and Chemical Analysis

Five 1-liter samples were delivered to the California Department of Fish and Game's Aquatic Toxicity Laboratory (ATL) for toxicity testing. ATL initiated 96-hr toxicity test using *Ceriodaphnia dubia* within 30 hours of sample collection. Toxicity Identification Evaluation (TIE) was performed on the most toxic samples. ATL also received a 1-liter (polypropylene bottle) sample for copper analysis.

Three 1-liter samples were analyzed by the California Department of Food and Agriculture Chemistry Laboratory. Chemical analysis included molinate, thiobencarb, carbofuran, methyl parathion, and malathion. Immediately after splitting samples analyzed for carbofuran, methyl parathion, and malathion were acidified with 3N HCl to pH3 to increase storage stability (Miller 1991). The quality control split samples were analyzed by Alta Analytical Laboratory for carbofuran, methyl parathion, and malathion, and APPL Laboratory for molinate and thiobencarb.

Field Measurements

Water pH and temperature were measured with a Sentron (model 1001) pH/temperature meter. EC was measured with an Orion salinity-conductivity-temperature meter (model 140), and DO with a YSI dissolved oxygen meter (model 57). Ammonia was measured using an ammonia-nitrogen test kit made by CHEMetes (model AN-10). A Price meter, type AA, was used for flow measurements in the drainage canals.

Results

Toxicity test on water from the outlets of fields B1 and D2 had survival rates for *Ceriodaphnia dubia* of 0 and 25%, respectively (Table 1). These fields had very low water levels at the time of sampling and normally would not have discharged water, however, water was released at our request. The low water level may have attributed to the higher pesticide concentrations in the outlet water which affected the mortality rate in these samples. The survival rates from the remaining outlet sites ranged from 65 to 100%.

The inlet and canal samples had survival rates of 70 to 100% with the exception of the canal sample at the outlet of field B1, which had a 25% survival of *Ceriodaphnia dubia* (Table 2).

The outlet concentrations for the six fields ranged from .87 to 10.1 ppb for carbofuran, no detectable amount to 194 and 252 ppb for thiobencarb and molinate respectively. Molinate was not applied to field D1, and fields A1, A2, A3, and B1 did not receive thiobencarb applications. Carbofuran was not detected in any inlet samples, while the concentrations of molinate and thiobencarb were below 8 ppb. The canal sample concentrations ranged from no detectable amount to 2.74 and 15.9 ppb for carbofuran and thiobencarb respectively, and 12.7 to 144 ppb for molinate.

Methyl parathion and malathion were not detected in any samples. Results from TIE and copper analysis have not been received from the laboratory, but will be included in the final report.

Table 1. Pesticide concentrations and toxicity results of field inlet and outlet water. Values in parenthesis are the number of days after pesticide application when water samples were collected.

	Toxicity, % Survival (control/sample)		Carbofuran ppb		Molinate ppb		Thiobencarb ppb	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Field A1	95/75	95/65	nd (2)	2.13(14)	0.1	107(10)	1	0.1(na)
Field A2	95/100	100/95	nd (2)	0.93(14)	2.18	166(9)	nd	nd(na)
Field A3	100/100	95/100	nd (0)	0.87(12)	nd	215(9)	nd	nd(na)
Field B1	100/100	95/0	nd (3)	10.1(18)	7.36	252(9)	6.97	0.3(na)
Field D1	100/95	100/80	nd (2)	1.5(15)	nd	nd (na)	nd	72.2(12)
Field D2	95/100	100/25	nd (3)	1.37(16)	nd	164(10)	4.12	194(12)

nd = Not Detected, see appendix for minimum detection limits.
na = Chemical not applied.

Table 2. Pesticide concentrations and toxicity results of canal water from two fields. Values in parenthesis are the number of days after pesticide application when water samples were collected.

		Toxicity, % Survival (control/sample)	Carbofuran ppb	Molinate ppb	Thiobencarb ppb
Field A3	Outlet	95 / 100	0.873 (12)	215 (9)	nd
Canal	0*	95 / 100	0.498 (12)	130 (9)	nd
	1	95 / 70	0.52 (12)	142 (9)	nd
	2	95 / 95	0.343 (12)	57 (9	nd
	3	95 / 90	0.452 (12)	144 (9)	nd
	4	95 / 100	0.269 (12)	32.8 (9)	1.64
	5	95 / 100	0.437 (12)	107 (9)	1.06
	6	95 / 100	0.114 (12)	34.6 (9)	15.9
Field B1	Outlet	95 / 0	10.1 (18)	252 (9)	0.3
Canal	Upstream	95 / 100	nd	0.72 (9)	nd
	0*	95 / 25	2.74 (18)	63.9 (9)	nd
	1	100 / 100	0.231 (18)	15.6 (9)	nd
	2	100 / 100	nd (18)	12.7 (9)	0.47
	3	100 / 80	0.359 (18)	22.1 (9)	5.72
	4	100 / 95	nd (18)	19.1 (9)	5.52
	5	100 / 85	0.15 (18)	54.7 (9)	7.15

nd = Not Detected. Refer to appendix for minimum detection limits.
* 0 = Canal sampled at field discharge, 1 thru 6 are subsequent downstream samples.

IX. References

California Regional Water Quality Control Board - Central Valley Region, 1993. Molinate Concentrations in Rice Field Discharges, 1993. Memorandum from Rudy Schnagl and Wendy Wyels to Marshall Lee. August 6, 1993.

Guy, H.P. and V.W. Norman. 1970. Field methods for measurement of fluvial sediment. In: Techniques of Water-Resources Investigations of the United States Geological Survey, Book 3, Chapter C2, 59p.

Miller, Nancy. 1991. Study X87 - Storage Stability Study for Carbofuran. California Department of Food and Agriculture Chemistry Laboratory - in house study.

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