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# Cypermethrin and Chlorpyrifos Concentration Levels in Surface Water Bodies of the Pampa Ondulada, Argentina

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Runoff events in soybean growing areas of the Pampa´s plains cause the mobilization of pesticides from agricultural fields into water bodies, contributing to invertebrate, fish and anuran kills (Natale and Ronco 2003; Jergents et al. 2004a; Carriquiriborde et al., personal communication). Cypermethrin, Chlorpyrifos and Endosulfan are commonly used insecticides in soybean crops of the region, though their concentration levels in water and sediments of related surface water bodies has only recently been characterized (Peruzzo et al, 2003; Jergents et al. 2004a-b; Marino et al. 2004).

Taking into account that the extent of the crops in the region is about ten million hectares of the genetically modified soybean variety (RR), the aim of the present study is to determine concentration levels of cypermetrin and chlorpyrifos in water and sediments from a first order stream of the Pergamino- Arrecifes system, and in the lower basins of five main tributaries flowing into the Paraná river.

## MATERIALS AND METHODS

The study area took into consideration the assessment of cypermethrin and chlorpyrifos concentrations at two scale levels of the Pampa Ondulada region. For a detailed scale study, a first order stream of the Pergamino-Arrecifes system was chosen (Figure 1) with its source within crop fields. The sampling campaigns during two consecutive years took into account the time for spraying of pesticides and the rain events immediately following sprays (table 1). Three sampling sites were selected to assess a direct influence of agricultural activity: Site 1, adjacent to field crops; Site 2 at 200 meters down stream, following the first site, adjacent to pasture, and Site 3 down stream next to a marshy sector, 500 meters from the first site. For the extended work scale, the assessment covered the lower basins of five rivers traversing crop field production areas. The water courses flow from the west to the east within the province of Buenos Aires, reaching the Paraná river in its middle and low sectors (Manassero et al. 2005). Listed from north to south they are: del Medio stream, and Ramallo, Tala, Arrecifes and Areco rivers. All sampling sites and campaign details for the first order tributary are shown in figure 1 and table 1. Campaign sampling dates for the extended work scale are given in table 2.

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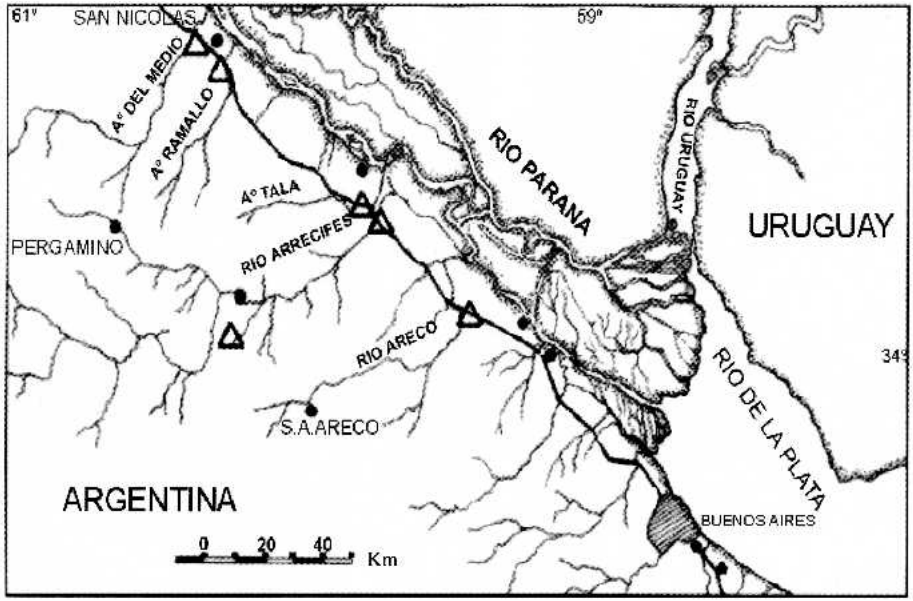


**Figure 1.** Study area. Open triangles indicate monitoring sampling points location.

**Table 1.** Arrecifes first order tributary sampling dates, rain events and agricultural activities in related area.

| Sampling site | Sampling date | Related rain events | Activities in crop fields |
|---|---|---|---|
| S1, S2 and S3 | 27-10-02 | | Before spraying |
| (see description | 27-11-02 | | Spray (gly+cyp) |
| in text) | 17-12-02 | 57 mm 15-12-02 | After rain |
| | 11-01-03 | 12 mm 08-01-03 | Spray 8 Jan. (gly+chlor) |
| | 03-09-03 | | Time between crops |
| | 07-01-04 | | Spray (glyp+cyp) |
| | 23-01-04 | 5 mm 10-01-04 | After rain |
| | 22-02-04 | | Spray (gly+cyp+chlor) |
| | 02-03-04 | 34 mm 01-03-04 | After rain |

gly= glyphosate; cyp= cypermethrin; chlor= chlorpyrifos

Pretreatment steps of water samples were: filtration of 300 mL through C18 disks (ENVI™-18 DSK Supelco, 47 mm diameter) to separate and concentrate the pesticides (associated to dissolved and suspended particle fractions); following extraction from disks with methanol; then roto-evaporation (vacuum: 600 mmHg; bath temperature: 40 °C); finally changing solvent to n-hexane to reach a final concentration factor of 1000 (Diaz-Baez et al. 2000). Eighty grams of wet sediments were extracted in a solid: liquid system (50g:50 ml n-hexane; 1 h stirring; followed by 2 steps of extraction by sonication with 25 ml of same solvent), filtration (paper filter with Na2SO4 anh.) and taken to a final volume of 0.5 ml with nitrogen flow (Method 3550, USEPA 1986). A clean-up procedure (Method 3620, USEPA 1986), using 10 g florisil for

100 mL of n-hexane: ethyl ether (94: 6) was performed for samples with a high absorbance in the UV wavelength used for detection (see cypermethrin analysis section). Method recovery was done by spiking environmental samples with known concentrations of the tested pesticides. Sample storage at –20 °C was also tested to assess holding time of the tested pesticides. Concentrations in sediments refer to dry weight.

Analysis of cypermethrin and chlorpyrifos was carried out using different methods according to sample characteristics (EHC82 1989; EHC142 1992; WHO 2002). Sample screening was done by HPLC, normal phase separation with n-hexane: isopropyl alcohol (95:5) in a 25 cm x 4.6 ID cyano column, and detection at 230 nm (method 1), conditions allowing the chromatographic separation of cypermethrin isomers in three peaks, yielding a detection limit of 0.2 mg/L (in injected extract). This method was also used for quantification of total cypermethrin or chlorpyrifos content for samples with a concentration range of 0.2-100 mg/L in injected extract. Confirmation of the presence of cypermethrin in dubious samples was done in the same conditions as before, changing the elution solvent to n-hexane: dichloromethane (90: 10) allowing the separation of four diastereomers. Alternatively, analysis of both insecticides in noisy samples was done via GC-ECD with an HP-1 30 m x 0.53 mm column, N2 carrier, with a temperature ramp between 180 and 220 °C, with a limit of detection of 0.01 mg/L (in injected sample extract).

Reagents: Solvents used were J.T Baker for pesticide analysis. Standards of cypermethrin and chlorpyrifos were from SENASA (Argentinean National Service for Sanitary and Quality of Agriculture and Food).

## RESULTS AND DISCUSSION

Results of analysis of cypermethrin and chlorpyrifos in water and sediments are shown in table 2. Spray events and related rains after spraying are associated with the detection of both pesticides in the first order tributary to the Arrecifes River, being the sediments the main immediate sink with detectable levels of cypermethrin in all campaigns. Thirty four percent of a total of 41 tested unfiltered water samples exhibited detectable concentrations of cypermethrin of less than 3.5 µg/L, and only one sample had a concentration of 194 µg/L. For the case of chlorpyrifos, 42% of the 26 tested samples exhibited detectable levels, being mainly the samples of the first order tributary adjacent to crop fields most frequently affected. All of the 27 tested sediment samples of the first order tributary had detectable concentrations of cypermethrin and most of them also had chlorpyrifos, with mean, maximum and minimum values of 160 (1075-1) µg/Kg and 4.8 (15-<1) µg/Kg, respectively. The lower basins of the Paraná River tributaries have mean, maximum and minimum concentration levels of 15 (174-<1) and 3.4 (19-<1) µg/Kg of cypermethrin and chlorpyriphos, respectively, detected in only 50% of the sediment samples tested. These lower basins only show detectable concentrations of the insecticides in the hot season, when the spray events are more likely to occur. The first order tributary

**Table 2.** Concentration levels of cypermethrin and chlorpyrifos in water and sediments of surface water bodies from the Pampa Ondulada. Concentration in sediments is referred to dry weight.

| Sampling site | | Sampling Date | Cypermethrin | | Chlorpyrifos | |
|---|---|---|---|---|---|---|
| | | | Water µg/L | Sediment µg/Kg | Water µg/L | Sediment µg/Kg |
| Arrecifes tributary | Site 1 | 27-10-02 | < 0.2 | Detectable | - | - |
| | | 27-11-02 | < 0.2 | 36.7 | - | - |
| | | 17-12-02 | < 0.2 | 1075.0 | - | - |
| | | 11-01-03 | < 0.2 | 90.0 | - | - |
| | | 03-09-03 | < 0.2 | 12.9 | - | - |
| | | 07-01-04 | 0.46 | 100.0 | 1.4 | 7.7 |
| | | 23-01-04 | < 0.2 | 7.5 | 0.4 | 10.0 |
| | | 22-02-04 | 2.01 | 399.0 | 5.0 | 15.0 |
| | | 02-03-04 | 3.55 | 4.6 | 10.8 | 3.3 |
| | Site 2 | 27-10-02 | < 0.2 | 20.0 | - | - |
| | | 27-11-02 | < 0.2 | 53.5 | - | - |
| | | 17-12-02 | < 0.2 | 595.0 | - | - |
| | | 11-01-03 | < 0.2 | 120.0 | - | - |
| | | 03-09-03 | < 0.2 | 10.0 | - | - |
| | | 07-01-04 | 0.29 | 42.1 | 0.5 | < 1.0 |
| | | 23-01-04 | < 0.2 | 4.0 | < 0.2 | 6.0 |
| | | 22-02-04 | 0.81 | 180.0 | 2.0 | 10.0 |
| | | 02-03-04 | 0.56 | 8.0 | < 0.2 | < 1.0 |
| | Site 3 | 27-10-02 | < 0.2 | 34.0 | - | - |
| | | 27-11-02 | < 0.2 | 600.0 | - | - |
| | | 17-12-02 | < 0.2 | 4.2 | - | - |
| | | 11-01-03 | < 0.2 | 150.0 | - | - |
| | | 03-09-03 | < 0.2 | Detected | - | - |
| | | 07-01-04 | Detected | 744.0 | < 0.2 | < 1.0 |
| | | 23-01-04 | < 0.2 | 14.0 | < 0.2 | 4.6 |
| | | 22-02-04 | 0.50 | 15.0 | < 0.2 | Detected |
| | | 02-03-04 | 0.12 | Detected | < 0.2 | < 1.0 |
| del Medio stream | | 15-12-03 | 194 | < 1.0 | 2 | Detected |
| | | 07-01-04 | < 0.2 | 10.1 | < 0.2 | - |
| | | 05-03-04 | 3.58 | 2.7 | 7 | 19.0 |
| Ramallo river | | 06-11-03 | < 0.2 | 13.7 | < 0.2 | < 1.0 |
| | | 07-01-04 | < 0.2 | < 1.0 | < 0.2 | < 1.0 |
| | | 05-03-04 | 0.2 | 1.91 | 10.4 | Detected |
| Del Tala stream | | 16-12-03 | < 0.2 | < 1.0 | < 0.2 | < 1.0 |
| | | 05-03-04 | < 0.2 | 1.3 | < 0.2 | < 1.0 |
| Arrecifes river | | 06-11-03 | < 0.2 | < 1.0 | < 0.2 | < 1.0 |
| | | 07-01-04 | < 0.2 | 7.0 | < 0.2 | 4.7 |
| | | 05-03-04 | 1 | 174 | Detected | 17 |
| Areco river | | 06-11-03 | < 0.2 | < 1.0 | < 0.2 | < 1.0 |
| | | 07-01-04 | < 0.2 | < 1.0 | < 0.2 | < 1.0 |
| | | 05-03-04 | Detected | < 1.0 | 1.0 | Detected |

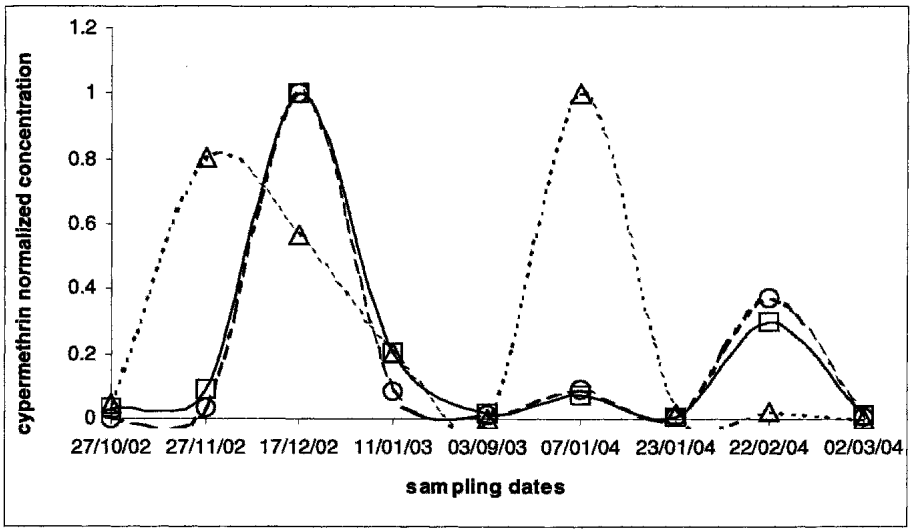


**Figure 2.** Relative concentration of cypermethrin with respect to maximum concentration levels (measured concentration: maximum concentration in the site during sampling periods) per site and time in the first order tributary of the Arrecifes river. Dashed line with circles corresponds to site 1; continuous line with squares to site 2; dotted line with triangles to site 3.

exhibits concentrations of cypermethrin in sediments ten times higher than in the lower course of the same basin, but are of the same order of magnitude in both basin sectors for the case of chlorpyrifos.

Concentration levels in the low basins of the Paraná River tributaries indicate that the del Medio stream and Arrecifes river are the most contaminated studied water courses with both insecticides, in accordance with a higher proportion of land being occupied by soy-bean crops. The screening also shows higher concentrations levels of cypermethrin in comparison to chlorpyrifos. Although the proportion of the insecticides favors higher loads of chlorpyrifos formulates when spraying (i.e.: the application of mixtures have at least a 1:10 ratio of cypermethrin: chlorpyrifos), cypermethrin is more frequently used and exhibits a longer persistence (EXTOXNET 1996).

Figure 2 analyzes the relative cypermethrin concentration in sediments from the three sites of the detailed study area. To compare the sites in different conditions of sprayings, rain events and sampling time, measured concentrations in each site were divided by the maximum detected concentration in the site in all sampling campaigns. This estimation allows the observation of a very similar pattern for sites 1 and 2 during the study. On the contrary, sediments of site 3 from the marshy sector, down stream, at a longer distance and with rooted aquatic vegetation acting as a sieve, show a different relative distribution with respect to time than the other up

stream sectors. Pesticides are rapidly mobilized during sprays and are transported and retained in sediments of the small marsh (see detected cypermethrin ratios in sampling dates and events of 27/11/02 and 07/01/04).

Although previous screenings in the region only detected measurable concentrations of endosulfan (Jergentz et al, 2004a-b), another one of the insecticides used in the region, the present study contributes with new data indicating the potential risk of agricultural activity associated with the use of cypermethrin and chlorpyrifos at local and regional scales. A major surface water course like the Paraná River is being threatened by detectable loads of cypermethrin and chlorpyrifos during the hot season, when an increased use of insecticides occurs.

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