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Imazethapyr and imazapic, bispyribac-sodium and penoxsulam: Zooplankton and dissipation in subtropical rice paddy water

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HIGHLIGHTS

- Selective herbicides in paddy rice fields, do not affect water quality.
- Zooplankton communities show good response with herbicide dissipation.
- The use of commercial herbicide mixture has strong effects on freshwater Rotifers.

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ABSTRACT

Herbicides are very effective at eliminating weed and are largely used in rice paddy around the world, playing a fundamental role in maximizing yield. Therefore, considering the flooded environment of rice paddies, it is necessary to understand the side effects on non-target species. Field experiment studies were carried out during two rice growing seasons in order to address how the commonly-used herbicides imazethapyr and imazapic, bispyribac-sodium and penoxsulam, used at recommended dosage, affect water quality and the non-target zooplankton community using outdoor rice field microcosm set-up. The shortest (4.9 days) and longest (12.2 days) herbicide half-life mean, estimated of the dissipation rate (k) is shown for imazethapyr and bispyribac-sodium, respectively. Some water quality parameters (pH, conductivity, hardness, BOD_5, boron, potassium, magnesium, phosphorus and chlorides) achieved slightly higher values at the herbicide treatment. Zooplankton community usually quickly recovered from the tested herbicide impact. Generally, herbicides led to an increase of cladocera, copepods and nauplius population, while rotifer population decreased, with recovery at the end of the experiment (88 days after herbicide treatment).

1. Introduction

The current widespread use of a range of herbicides in agriculture as a means of controlling weed has been contributing to a growing concern with the contaminations of surface and groundwater bodies. Likewise, the use of herbicides must be considered as a potential risk for aquatic life as well as for the quality of drinking water.

Once releases into the environment, the behavior of the herbicide has great influence on its soil activity and weed control. Herbicides can be lost by volatilization, photolysis, microbial degradation, chemical degradation, or plant uptake (Goetz et al., 1990). The dissipation rates, persistence and environmental fate of the herbicide are subject to intrinsic herbicide physicochemical properties such as vapor pressure, water solubility, octanol–water (K_{ow}) and organic carbon (K_{oc}) partition coefficients. Furthermore, dissipation is affetcted by many abiotic factors such as water temperature, pH, organic contents like dissolved organic matter (Goetz et al., 1990), inorganic contents like the presence of reduced sulfur species (Zeng et al., 2011, 2012) and even human activities as agricultural practices (Damalas and Eleftherohorinos, 2011).

However, risk assessment of chemicals is still based on the effects on individuals and data are often generated only through single species toxicity tests (EU, 1997). Therefore, it is difficult to extrapolate the effects resulting from single species laboratory studies to the effects on natural ecosystems (Wendt-Rasch et al., 2003). Nevertheless, most laboratory experiments (and some mesocosm experiments) are 'renewed' experiments that keep up a constant pesticide concentration. We thus

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clearly need experiments to be better connected to reality of real-world applications (Relyea and Hoverman, 2006), increasing our knowledge about how the structure of aquatic organism communities may be affected by chemicals.

Studies involving environmental chemical stress that are carried out in natural experimental ecosystems (e.g. rice paddy) can be more profitable and increase our understanding of both direct and indirect processes here involved, thus providing support for more sustainable activities. Paddy fields provide habitat for several non-target organisms, such as zooplankton species, which play a key role in freshwater ecosystems as they occupy a central position in the food chain, transferring energy from primary producers to higher trophic organisms (Chang et al., 2005).

Imazethapyr {2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl]-5-ethyl-3-pyridinecarboxylic acid} and imazapic 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl]-5-methyl-3-pyridinecarboxylic acid are imidazolinone herbicides, widely used to control red rice and other weeds in commercial rice. These two chemical products present high water solubility, 1400 and 2200 mg L^{-1} (20 °C) respectively (Senseman, 2007). Bispyribac-sodium (sodium 2,6-bis[(4,6-dimethoxy-2-pyrimidinyl)oxy]benzoate) a pyrimidinyl thiobenzoate herbicide, and penoxsulam (2-(2,2-difluoroethoxy)-*N*-(5,8-dimethoxy[1,2,4]triazolo[1,5-*c*]pyrimidin-2-yl)-6-(trifluoromethyl)benzenesulfonamide), a sulfonamide; triazolopyrimidine herbicide widely provide a broad spectrum effect on grasses and broadleaf weeds in rice. These have high and low water solubility, 73,300 mg L^{-1} (20 °C) and 5.7 mg L^{-1} (19 °C), respectively (Senseman, 2007).

The effects on the zooplankton community, which usually coexists in rice paddy water, as well as the dissipation of herbicides used in the rice fields have been insufficiently studied. So, the purpose of the present study was to investigate the water dissipation and the effect of the herbicides imazethapyr + imazapic, bispyribac-sodium and penoxsulam on zooplankton communities, associated with a subtropical irrigated rice-crop field during the 2009 and 2010 crop years.

2. Material and methods

2.1. Experimental set-up

The experiment began in December 2009/2010 and ended in March 2010/2011 (first and second trial), using a completely randomized block design with two replications. The following were employed: eight rectangular 11.05 m^3 (length 9.7 m; width 7.6 m and water depth 0.15 m) outdoor experimental irrigated rice plots (here called mesocosms) set up in lowland, located in the municipality of Santa Maria, Southern Brazil. Two of the eight mesocosms served as controls. The others were treated with herbicides (dosage): imazethapyr (75 g ha^{-1}) and imazapic (25 g ha^{-1}) applied as a commercial mixed formulation, bispyribac-sodium (50 g ha^{-1}) and penoxsulam (48 g ha^{-1}), these herbicide doses were meant to mimic realistic agricultural scenarios. All mesocosms received no other herbicides or pesticides. One day after treatment, the plots were flooded and water depth was kept at 0.15 m throughout the experiment.

2.2. Application and analysis of the test herbicides

Herbicides were sprayed over the experimental plots on the 25th day after seeding using a CO_2-pressurized backpack sprayer with four nozzles Teejet XR 110015 in a boom calibrated to deliver 150 L ha^{-1} of spray solution and working at 275 kPa. Surface water samples were collected from each plot six times during the first week, twice during the second and, after that, on a weekly basis. Triplicate samples were taken from each plot, comprising a 1000 mL final sample after mixing, stored into amber glass bottles and transported to laboratory.

Samples were analyzed for imazethapyr according to Santos et al. (2008), imazapic by Reimche et al. (2008), bispyribac-sodium by Kurz (2009) and penoxsulam by Zanella et al. (2003), using High Performance Liquid Chromatography with Diode Array Detection (HPLC-DAD) with a Varian system (Palo Alto, CA, USA) composed of ProStar 210 pump and ProStar 335 DAD detector. The column configuration consisted of a Phenomenex (USA) C-18 reversed-phase column (250 × 4.6 mm; 5 μm) and a Phenomenex C-18 guard column (10 × 4.6 mm; 5 μm). The mobile phase consisted of purified water:methanol (35:65, v/v) acidified to pH 3 with phosphoric acid. A flow rate of 0.8 mL min^{-1} was used, with injection volume of 20 μL and detection wavelength set at 254, 254, 247 and 295 nm, respectively. Before the HPLC-DAD analysis, the analytes were preconcentrated from the water samples by solid phase extraction (SPE).

2.3. Water quality parameters

Dissolved oxygen (DO) and water temperature were measured on site by portable oxygen meter, pH (pH-meter), electric conductivity (EC) (conductivimeter), turbidity (T) (turbidimeter), and total hardness (TH) (titrimetric), and the elements boron (B), calcium (Ca), cobalt (Co), chromium (Cr), copper (Cu), sulfur (S), tin (Sn), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), and phosphorus (P) were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). The anions fluoride (F^-), chloride (Cl^-), sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), nitrite (NO_2^-) and nitrate (NO_3^-) were determined by ion chromatography (IC) all measured at the same zooplankton sampling days, to detect possible changes in water parameters.

2.4. Zooplankton communities

On the 3rd, 14th, 28th, 56th and 88th days after herbicide application, a 12 L water sample from each plot was collected by means of a submersible filter-pump apparatus and samples were concentrated by using a 25 μm mesh net. Gaseous water was added to samples in order to narcotize specimens and preserve with formaldehyde (final concentration: 4%, v/v). Subsamples of the zooplankton sample were counted with light microscope using the Sedgewick-Rafter Cell method (APHA, 1992). Rotifers were identified to genus and cladocerans to family levels. Copepods were separated into nauplii (immature stages), calanoids, and cyclopoids (mature stages). Ostracoda were not further identified. Zooplankton numbers were converted to individuals per liter.

2.5. Data analysis

The effects of the herbicide treatment on the zooplankton communities were analyzed by the principal response curve (PRC) method (van den Brink and ter Braak, 1999). The canonical coefficients calculated by PRC express the part of the variance in community structure between mesocosms, which can be attributed to treatment. By plotting the community-level multivariate response against time (x-axis), treatment effects are separated from temporal changes in community structure and therefore easy to interpret. Treatment effects are expressed as deviations from the control so that control becomes a straight line over time, at which all treatments contrast. With the PRC, calculated species weights can be interpreted as the affinity of the taxon to the principal response curve. Taxons with a positive weight increase in abundance and taxons with a negative weight react inversely if the overall PRC analysis has a positive sign. It is the contrary if the overall PRC analysis has a negative sign. We used two-way repeated-measures analysis of variance (RM-ANOVA) to test differences between treatments from sampling days 3 through 88. RM-ANOVA was followed by multiple comparison test (post hoc testing), using Tukey's test ($p < 0.05$) to examine differences between treatments. Before analyses were