

Monitoring of Glyphosate and AMPA in sediment samples from streams around the Itaipu Reservoir, Brazil-Paraguay transboundary region.

Emerging pollutants in aquatic ecosystems

INTRODUCTION

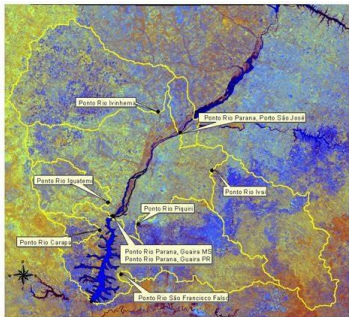
This work presents the determination of Glyphosate (GLY) and its biological degradation by-product, aminophosphonic acid (AMPA), in sediment samples collected in February (1^a campaign), in June (2^a) and November (3^a) of 2019. The samples come from rivers/streams around the Itaipu Reservoir, on the Brazilian (BR) and Paraguayan (PY) sides. According to **Table 1**, it is possible to see the average percentage of occupation and land use. The samples are indicated with (a), (b) and (c) where group a covers areas possibly little impacted, group b with scenarios impacted by agriculture, but without the high presence of pesticides and group c with impact by agriculture and large amounts of pesticides. (BECKER, 2021)

Table 1. Use and Occupancy (%)

USE AND OCCUPANCY (%)	Group a		Group b		Group c	
	BR	PY	BR	PY	BR	PY
Agriculture	13,36	46,81	70,43	79,62	63,89	75,17
Urban Area	0,60	46,81	0,13	0,02	5,74	0,76
Forests	7,00	0,00	3,29	1,46	5,53	5,36
Riparian	15,46	6,43	12,51	11,26	10,56	4,75
Forest Pasture	60,05	36,65	11,45	5,20	10,38	10,52

METHODOLOGY

Collect:



Itaipu watershed

Sample characterization:

Granulometry, pH, Quantification of metals (Fe, Al and P) by ICP OES;

Analysis of the analytes of interest:

Quantification by standard addition; Extraction with 0.2 mol L⁻¹ KOH solution and derivatization of samples in the presence of buffer solution, FMOC-Cl in acetonitrile; UHPLC analysis with fluorescence detection;

RESULTS AND DISCUSSION

Figures 1 and 2 show the group means found in each campaign analyzed with concentrations in $\mu\text{g Kg}^{-1}$. The highest concentration of herbicides was found in the 3rd sampling campaign, where there is a greater application of glyphosate between October and November (normally the beginning of soybean germination and growth) than in March, which is usually the final process and soybean harvest (CONAB, 2019). Analyzing the characteristics of the sediment, **Figures 3 and 4** present the analysis of principal components in relation to the concentrations of the analytes.

Analyzing the graphs, the amount of iron (Fe) and phosphorus (P) are inversely proportional to the presence of GLY and AMPA for the Brazilian samples, but the Paraguayan samples demonstrate an affinity between the amount of organic compounds and the presence of these minerals, which corroborates with the idea that P competes with the active sites present in the sediment (ACCINELLI, 2004). The increase of aluminum (Al) in the samples demonstrated a greater relation to the increase of GLY and AMPA in both sampling groups.

The presence of Fe and Al favor the connection with organic compounds and their accumulation in the medium, by making them unavailable for microbiological degradation (SØRENSEN et al., 2006). Regarding the analytes, in both PCA analyses, the increase in %MO is related to the increase in GLY and AMPA, it is known that a low pH value facilitates the interaction between deprotonated oxygenated groups of the compounds (MUSKUS et al., 2019) and in basic medium there is a disadvantage in the adsorption of these compounds.

CONCLUSION

The samples collected in this work do not present direct spraying of glyphosate because they are not exactly agricultural areas, but glyphosate particles can be carried to places close to the field of application and also the compounds can be leached into the soil and be transported by rain (greater rainfall rates between the spring/summer season – indicated as the main season for planting soybeans).

REFERENCES: BECKER, R. et al. Microchemical Journal 168 (2021) 206502; CONAB. Calendário de Plantio e Colheita de Grãos no Brasil, 2019. ISSN: 2318-6852; MUSKUS, A. M. et al. Science of the Total Environment, v. 658, p. 697–707, 2019; SØRENSEN, S. R., et al. Environ Pollut, 141, 184-194, 2006.

Figure 1. Concentration of GLY

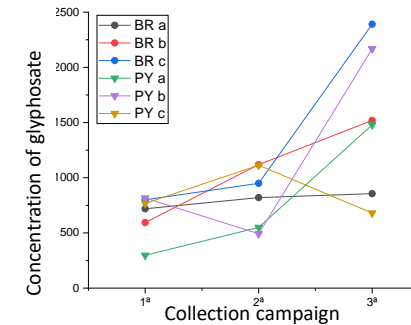


Figure 2. Concentration of AMPA

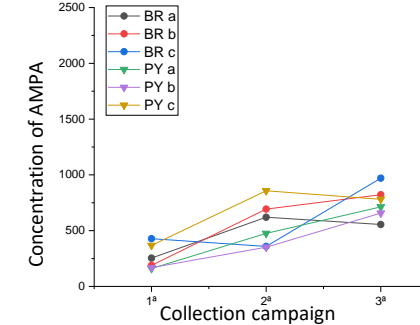


Figure 3. Analysis of Brazilian samples

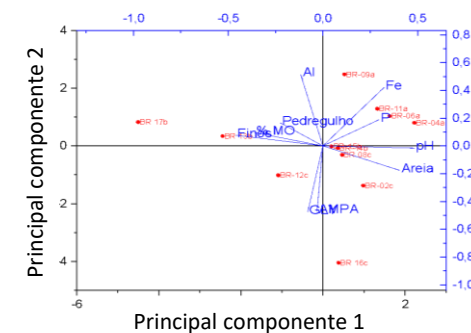
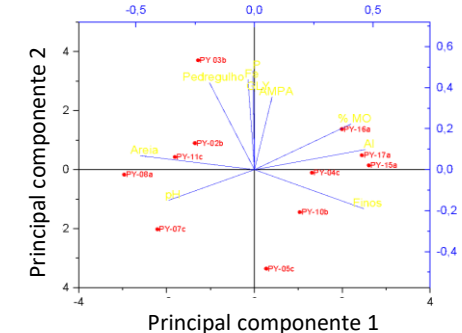


Figure 4. Analysis of Paraguayan samples



ACKNOWLEDGMENT:

