



## **Controlled release formulations of Atrazine and Mesotrione: characterization and sorption on soils**

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Atrazine is a widely used herbicide on corn and sugar cane plantations, which, along with soybeans, are the most productive crops in Brazil and are responsible for 36.5% of the annual national consumption of herbicides. Mesotrione is a new herbicide registered in the last years used for controlling weeds in corn plantations as a tentative substitution for atrazine. After its application in the field, reactions between the herbicide and chemical groups from the soil matrix surface occur, and this complexed form remains in the soil, representing a potential source for environmental contamination and also affecting its agronomic efficiency. Therefore, the application of herbicides associated to carrier systems may represent an alternative to mitigate the environmental impact caused by their intense usage, considering that the interaction between the soil matrix and the xenobiotic is reduced, and thus, diminishes the recommended dosis and reduces the environmental pollution.

The objectives of this study are to evaluate the chemical and morphological characteristics of controlled release formulations of atrazine (ATZ) and of mesotrione (MES) and to investigate their sorptive behavior in three representative Brazilian soils. To assess the feasibility of using these associated systems, four formulations (SGATZ) containing different concentrations of atrazine and four formulations (SGMES) containing different levels of mesotrione (MES) were synthesized by the sol-gel method (SG), using tetraetil-ortho-silicate as precursor and NaF as catalyst. The formulations were characterized by elemental analysis, adsorption and desorption isotherms of nitrogen, thermal analysis (DSC), scanning electron microscopy (SEM) and infrared spectroscopy (FTIR). For comparison, samples of pure xerogel (SG), commercial MES (Callisto-Syngenta), pure ATZ (99% of active principle, Milênia), granulated ATZ (Gesaprim GrDA Syngenta) and dried commercial ATZ (Nortox 500 SC) were analyzed. The herbicides release from the formulations and from the commercial products in CaCl<sub>2</sub> 0,01 mol.L<sup>-1</sup> medium was quantified by UV/vis spectroscopy along 24 hours. Mathematical models were tested in order to establish the release kinetics. Sorption isotherms of the formulations SGATZ150 and of the SGMES150 and of the commercial products were determined in three types of soil. The ATZ yields in the formulations were around 60%, while for MES the values reached 80%. In all formulations, ATZ was physically dispersed on the Si-polymer, and the dispersion grade decreased with increasing amount of added herbicide. The same behaviour was shown by MES. Both dissolution and diffusion processes controlled the release kinetics of ATZ from the formulations, whose data was fitted to the Korsmeyer-Peppas model. With the decrease of ATZ dispersion, the mechanism of dissolution assumes a more important role. In the case of MES, the dissolution to the aqueous media was rapidly achieved and the herbicide was located mostly outside the carrier polymer. Nevertheless, both herbicides in the form of xerogel presented a lower affinity for soil than in the commercial form. However, in soils with high contents of organic matter, the retention of ATZ in high affinity sorptive sites occurs both with the herbicide in molecular form as well as bound to the sol-gel matrix.