# NEW SLOW RELEASE APPLICATION TECHNIQUES WITH HETEROCYCLIC HERBICIDES IN AQUATIC WEED CONTROL

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Dedicated to Professor G. Stork on the occasion of his 65th birthday.

Abstract - Slow release formulations of s-triazine derivatives were prepared by extrusion of EVA copolymers with 1 and 2. Diffusion coefficients of the compounds in the matrix were measured for 1 as $D_O=0.39\cdot10^{-9}$ $cm^2\cdot s^{-1}$ and for 2 as $D_o=0.81\cdot10^{-9}$ $cm^2\cdot s^{-1}$. Slow release formulation of 2 showed a strongly herbicidal activity with a long duration in controlling *Lemna minor* in a laboratory flow system as well as *Eichornia crassipes*, *Salvinia molesta* and *Pistia stratiotes* under outdoor conditions.

s-Triazine derivatives are strong herbicides inhibiting the photo synthesis of plants[1,2]. They are mainly used as selective herbicides in agriculture. Application of these compounds in running waters to control aquatic weeds like *Eichornia crassipes*, *Salvinia molesta* etc. are limited because of their rapid displacement from the area of application. Therefore we investigated the possibility of preparing slow release formulations of s-triazine derivatives. In the course of studying the physico-chemical behaviour of bioactive materials in polymer matrices[3,4] we found a remarkable stability of Desmetryn (1 : 2-isopropylamino-4-methylamino-6-methylthio-1,3,5-triazine) and Terbutryn (2 : 4-ethylamino-2-tert-butylamino-6-methylthio-1,3,5-triazine) under the conditions of screw extrusion of EVA (ethyleneviny1 acetate copolymers with 20% comonomer content) at high temperature and high pressure ($T \geq 150$ °C, $p = 15\text{-}25\cdot10^6$ Pa).

Neither substance alteration nor chemical interactions between macromolecules and s-triazine derivatives occurred. This can be shown by spectroscopical data. In comparison with IR-spectra in KBr pellets $\nu$NH absorption in polymer matrix was shifted approx. 100-200 $cm^{-1}$ to higher frequency (3460 w, 3435 w, 3360 w $\nu$NH, 1550 s $\nu$C=N; 1300, 1180, 810 $cm^{-1}$: fingerprint).

During migration experiments with 1 and 2 as wettable powder, EVA granules and calcium alginate gel formulations, of which the preparation and release kinetics are described elsewhere[5], the optimal retardation of active ingredients (a.i.) was found in monolithic EVA formulations. Migration from EVA was controlled by substance diffusion in the matrix, and diffusion coefficients obtained from equation (2), which is derived from Fick's 2nd Law of Diffusion, amounted to $D_o=0.39 \cdot 10^{-9}\ cm^2 \cdot s^{-1}$ for 1 and $D_o=0.81 \cdot 10^{-9}\ cm^2 \cdot s^{-1}$ for 2:

$$m_t/m_g = 4 \cdot (D_o \cdot t/\pi \cdot a^2)^{1/2} \qquad \text{for } 0 \leq m_t/m_g \leq 0.6 \qquad (1)$$

$$D_o = (\pi \cdot a^2/16 \cdot m_g^2) \cdot (\Delta m_t^2/\Delta t) = \text{const.} \cdot (\Delta m_t^2/\Delta t) \qquad (2)$$

where a (cm) is diameter of EVA granules, $m_t$ (mg) migrated a.i., $m_g$ (mg) incorporated a.i. and t (s) time[6,7]. Compared with several months for EVA formulations the release of a.i. lasted only a few hours for wettable powder (as commercial products) or less than 2 weeks for alginate formulations.

Applying in a laboratory flow system with Lemna minor (duckweed) as testplants in a running nutrient solution, EVA formulations of 2 showed a high effectiveness in controlling the test species for several weeks even in a very low concentration (approx. 20 ppb) occurred by slow release of a.i. from the polymer matrix continuously, which could not be achieved with conventional formulations because of the rapid release and displacement of a.i. in running waters. When applied under outdoor conditions in Indonesia, $LT_{90}$-values of 2 in EVA strips (6-1 kg a.i./ha) to control Eichornia crassipes (waterhyacinth), Salvinia molesta (floating fern) and Pistia stratiotes (water lettuce) was found 8-16 days and the formulations were still effective after 10 weeks. This type of preparations of bioactive heterocyclic compounds offer not only the chance to use s-triazine herbicides in running aquatic systems for reducing residues during aquatic resource management and food production (e.g. rice-fish system) but also in the agricultural[8] and pharmaceutical[9] applications.

ACKNOWLEDGEMENTS

The authors gratefully thank Dr. Mohammad Soerjani, University of Indonesia, for carrying out the outdoor applications.

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Received, 11th August, 1986