

**Environmental Fate of Imidazolinone Herbicides and Their
Enantiomers in Soil and Water**

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Declaration

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Abstract

Imidazolinones represent a new class of herbicides with low mammalian toxicity that can be used at low application rates, either pre- or post-emergence for the control of a wide range of weeds in broadleaf and cereal crops, and non-crop situations. All imidazolinone herbicides are chiral, containing two enantiomers that derive from the chiral centre of the imidazolinone ring. The inhibitory activity of the R(+) enantiomer is nearly eight times greater than that of the S(-) enantiomer. The use of imidazolinone herbicides has increased in recent years in Australia owing to increased popularity of pulses and the introduction of imidazolinone-tolerant canola and wheat. Concerns have been raised about the potential carry over damage to the subsequent crops grown in rotation with legumes and herbicide tolerant crops. Furthermore, the presence of alkaline soils in some regions of Australia may lead to the repellence of imidazolinone herbicides, which are chiefly present in anionic form at high pH values. Thus leaching and potential contamination of ground water may occur when these herbicides are applied on alkaline soils in certain agroclimatic zones. There is some information in the literature on the degradation, sorption and leaching behaviour of these herbicides in the environment. However, there is little information about the behaviour of these herbicides in alkaline soils found in some areas of Australia. Until now there has been no investigation of enantioselectivity in the degradation of imidazolinone herbicides in soils. Therefore, this study was undertaken to determine the behaviour of three imidazolinone herbicides in solution and Australian soils including enantioselectivity in the degradation of these herbicides in Australian soils.

Analytical method for these herbicides needed to be developed/improved to cater for specific experimental conditions for this study, namely the matrices containing higher

levels of organic carbon and to analyse the two enantiomers of these herbicides. The extraction of imazapyr, imazethapyr and imazaquin was investigated using solid-phase extraction (SPE) procedure. The evaluation of different aqueous solutions (0.1 KCl, 0.5 M NaOH, 0.01M NaOH and 0.5M MeOH:NaOH, (80:20)) showed that the recovery of all three herbicides was greater than 70%. However, the highest level of herbicide recovery was obtained with 0.5M NaOH as the extraction solution. Evaluation of different solid phase extraction cartridges showed that PPL cartridge is most appropriate for the isolation and subsequent quantification of these herbicides in water and humic-amended solutions when used at pH 2. When used with soil extracts, SPE cartridges C₁₈ + SCX allowed removal of co-extracting substances, resulting in high levels of herbicide recovery and accurate quantification with HPLC. These improved protocols were used in subsequent studies.

The abiotic degradation of the imidazolinone herbicides imazapyr, imazethapyr and imazaquin was investigated under controlled laboratory conditions. Hydrolysis, where it occurred, and photodegradation both followed first order kinetics for all herbicides. There was no hydrolysis of any of the herbicides in buffer solutions at pH 3 or pH 7; however, slow hydrolysis occurred at pH 9. Degradation of the herbicides in the light was considerably more rapid than in the dark with half lives for the three herbicides of 1.8, 9.8 and 9.1 days for imazaquin, imazethapyr and imazapyr, respectively. The presence of humic acids in the solution reduced the rate of photodegradation for all three herbicides, with higher concentrations of humic acids generally having greater effect. The enantioselectivity of photodegradation was investigated using imazaquin, with photodegradation occurring at the same rate for both enantiomers. Abiotic degradation of imidazolinone herbicides on the soil surface only occurred in the presence of light. The

rate of degradation for all three herbicides on the soil surface was slower than in solution, with half-lives of 15.3, 24.6 and 30.9 days for imazaquin, imazethapyr and imazapyr, respectively.

Sterilizing the soil significantly ($p < 0.05$) decreased the degradation rate of both enantiomers of imidazolinone herbicides, with 81.5 to 89.5% of each enantiomer of the two herbicides remaining unchanged. However, in non-sterilized soils, the degradation of imazapyr and imazethapyr showed enantioselectivity with faster degradation of R(+) enantiomer compared with S(-) enantiomer. There were also some differences in enantioselectivity between different soils, which could be related to variation in microbial populations and enzymes present in different soils. Soil pH had a significant effect on enantioselectivity, which could be due to the effect of this soil property on herbicide sorption and ease of its availability for microbial degradation. This aspect however needs further investigations.

Results from studies on soils receiving organic amendment (lupin residue) showed that degradation of the S(-) and R(+) enantiomers of imazethapyr and imazaquin followed first-order reaction with half-life values of 45.9 to 105 days in non-sterilized soils for S(-) and R(+) enantiomers, respectively. Irrespective of the organic amendment, the degradation rate of the S(-) and R(+) enantiomers of the two herbicides was greater in the Roseworthy (pH 8.2) soil compared with the Clare soil (pH 5.2). Addition of lupin residue as organic amendment (2% w/w) increased degradation rates of both the S(-) and R(+) enantiomers of imazethapyr and imazaquin and significantly ($p < 0.05$) decreased their half-lives in the Clare soil. However, this amendment produced no significant change in degradation of

enantiomers of either of the two herbicides in Roseworthy soil. The enantiomer fraction (EF) values of both herbicides increased over time, which suggested selective degradation of one enantiomer in preference to the other depending on the type of soil and amendment treatment. In the Clare soil, organic amendment increased the EF value at the end of incubation period from 0.61 to 0.76 for imazethapyr and from 0.56 to 0.66 for imazaquin, indicating enantioselective degradation of these herbicides. There was no significant increase in EF values for both herbicides in Roseworthy soil as the result of organic amendment.

In conclusion, photodegradation of imidazolinone herbicides was found to have a major impact on the behaviour of these herbicides in aqueous and soil matrices. The degradation of imidazolinone herbicides in the soil was enantioselective, however, the enantioselectivity tended to be compound-specific and was related to soil types. The findings of this study are expected to be useful for the manufacturers to decrease the amount of chemical load in the environment.

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