# THIACLOPRID LEACHING IN SOIL AS A CONSEQUENCE OF TREATED WASTEWATER REUSE FOR AGRICULTURAL PURPOSES.

José Antonio Rodríguez Liébana, Aránzazu Peña and Mª Dolores Mingorance
Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), c/ Profesor Albareda, 1. 18008 Granada (Spain). joseantonio.rodriguez@eez.csic.es; arancha@eez.csic.es; mdmingor@eez.csic.es

**ABSTRACT:** The leaching behaviour of a neonicotinoid insecticide, thiacloprid, was assessed using soil columns irrigated with wastewater and with ammonium sulphate at a concentration similar to that corresponding to wastewater. Results indicate that thiacloprid was very mobile under all the effluent conditions, as expected from its polar nature. Wastewater increased the velocity through the soil columns as compared with the control, as well as increased the total amount of infiltrated thiacloprid.
**Key words:** Soil columns, mobility, pesticide, low quality waters

## INTRODUCTION

Treated effluents from urban origin are being considered for land irrigation especially in countries with periodic water shortage. Irrigation with these effluents, apart from avoiding their disposal, can also provide organic matter and nutrients to soils of poor fertility such as those normally encountered in arid or semiarid areas. However, treated effluents may affect the leaching behaviour of contaminants applied to soil with agronomical purposes, such as pesticides (Müller et al., 2007).

Pesticides are found in surface and groundwaters, because they can leach with the waterfront and reach the vadose zone. The threat of pesticide environmental fate is especially severe when using polar contaminants whose properties, such as water solubility, are indication of preferential mobility through the soil profile, unless they rapidly degrade in soil. These polar pesticides are gaining popularity to circumvent some drawbacks related with highly hydrophobic pesticides, such as bioaccumulation or bioaugmentation and are usually not affected by strategies oriented to maintain them in the upper soil layers by reducing their mobility (Hernández-Soriano et al., 2007; Delgado-Moreno & Peña, 2008).

Neonicotinoids, a new class of insecticides, have outstanding potency and systemic action for crop protection against piercing-sucking pests, and they are highly effective for flea control on cats and dogs, with low toxicity to mammals, birds and fish (Tomizawa and Casida, 2005). Neonicotinoid insecticides bind at the postsynaptic nicotinic acetylcholine receptor, a specific neural pathway that is more abundant in insects than in warm-blooded animals, thus having lower affinity for vertebrates relative to insects. Among them imidacloprid, is one of the most widely used insecticides. Another insecticide from the same family, thiacloprid, recently introduced, has been the aim of our study.

The leaching behaviour of the relatively polar insecticide thiacloprid has been investigated. The effect of irrigating soil columns with treated wastewater or with a salt solution was assessed.

## METHODS

A calcareous silt loam soil (31% sand; 58 % silt; 11 % clay) (Typic xerofluvent) was sampled from the upper layer (< 2 mm) of the Vega de Granada (SE Spain), a fertile plain lying on a large aquifer. It has 21 % water content at field capacity (1/3 bar), 1.1 % organic carbon (OC) content, pH 8.5 (1/2.5 soil/water ratio), 7.9 cmol(+) $kg^{-1}$ cation exchange capacity and 25 % $CaCO_3$.

Influent solutions consisted in (a) MilliQ (MQ) water as control, (b) treated wastewater (TWW) from the effluents of the secondary sedimentation tank in the city of Granada, with pH 7.5, 0.1 S $m^{-1}$ conductivity, 23 mg $L^{-1}$ suspended solid content and 30 mg $L^{-1}$ OC content and (c) a $(NH_4)_2SO_4$ 5 mM solution.

Thiacloprid (THIAC) from Dr. Ehrenstorfer (98% purity) was used. Its water solubility is 0.18 g $L^{-1}$ and its octanol-water partition coefficient (log $K_{ow}$) 1.26 (Tomlin, 2003).

## Leaching experiments

The experiments were carried using polypropylene columns (2 cm i.d.; 10 cm long). The soil was packed to a mean bulk density of 1.2 ± 0.1 g $cm^{-3}$ (simulated field density). Ground dry soil (5 g) was spiked with 1 mL of a THIAC solution at 100 mg $L^{-1}$ in acetone. After solvent evaporation, the fortified soil sample was carefully stirred with a spatula and added to the top of the soil column.

A constant pressure head (98 Pa) was applied on the soil column for steady state flow conditions, allowing the influent solutions to flow through the soil under positive pressure head. The test columns were carried out in triplicates and the experiments took place at room temperature (20 °C) and without sun protection, due to THIAC stability under sunlight irradiation (unpublished data).

A tracer solution was applied on the top soil before the beginning of elution for testing column performance. At regular intervals, leachate aliquots, collected with a fraction collector (Model frac-920, General Electrics), were weighed and stored at -20°C until chemical analysis. The breakthrough curves (BTCs) (pooled results from the triplicate columns) were drawn by plotting leachate concentration versus the relative pore volume ($V/V_0$).

Leachate concentration was fitted to the deterministic nonequilibrium CDE model by non-linear least-squares analysis (Toride et al., 1999).

## Chemical analysis

THIAC concentration in soil and leachates was determined by HPLC-DAD (Agilent Series). A 10-µl sample, after filtration by GHP Acrodisc filters (0.45 µm), was injected into a Zorbax RX C8 column (15 cm x 2.1 mm i.d.), protected by a guard column Eclipse XDB-C8 (1.25 cm x 2.1 mm i.d.) at a flow rate 0.2 ml $min^{-1}$, the mobile phase consisting of a 50:50 (v:v) mixture of acetonitrile/water and wavelength detection 245 nm. Calibration was performed by triplicate injection of standard solutions between 0.1 and 10 mg $L^{-1}$ ($R^2$ 0.998). Retention time for thiacloprid was 3.1 min.

Solution pH was measured with a Eutech pHmeter, model Cyberscan pH 2100 and solution EC, using an XS Instruments conductometer, model CON 510.

## RESULTS AND DISCUSSION

The only report found in the literature concerning THIAC sorption on soil (Oliver et al., 2005), did not correlate pesticide retention with soil characteristics such as OC content, clay content or pH.

The cumulated THIAC amount showed (Figure 1) that more pesticide was eluted from the soil columns with TWW than with $(NH_4)_2SO_4$ or MQ. In general, THIAC appears in the first leachates only when TWW or $(NH_4)_2SO_4$ are used as the influents. Both solutions seem to enhance the pesticide linear velocity which increases the risk of an early arrival to groundwater.

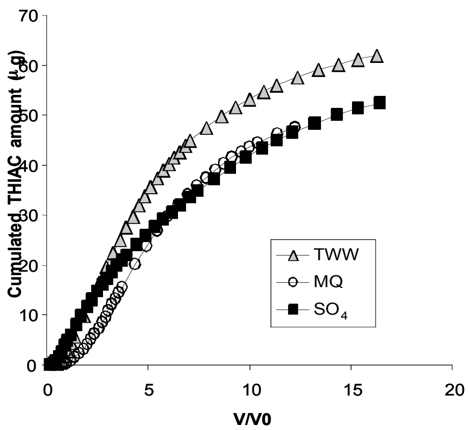

*Figure 1. Cumulated THIAC amount leached from the soil columns with the different influents*

Experimental data on insecticide leaching behaviour are well fitted ($R^2$ = 0.988-0.992) to the non-equilibrium CDE model, as can be seen in Figure 2. The peak maxima of both infiltration fluids, TWW and $SO_4$, appeared slightly anticipated relative to the control solution, MQ. For TWW and $SO_4$ the BTCs showed extended tailing which, according to Abu-Zreig et al. (2000), is an indication of non-equilibrium transport phenomena.

The solution pH after 3 pore volumes increased for all the solutions, a fact in accordance with elution from a calcareous soil. Electrical conductivity remains constant after approximately 3 pore volumes (Table 1). This is an indication that both influent solutions, TWW and $SO_4$, do not leach more ions, when compared to control MQ water.

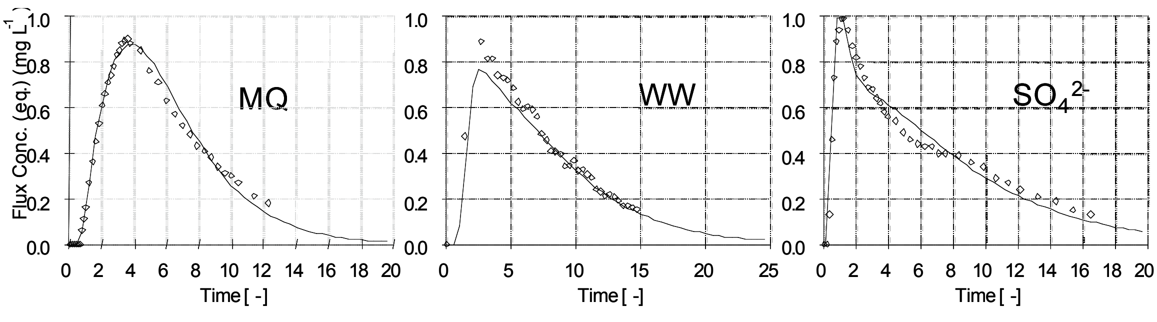


*Figure 2. THIAC concentration in the leachates collected from soil columns eluted with MQ, TWW or $(NH_4)_2SO_4$ solution. Experimental data (○) and data fitted (-) to the deterministic nonequilibrium CDE model.*

The total amount of infiltrated THIAC was ranged as TWW (59 μg) > $SO_4$ (52 μg) > MQ (47 μg). Irrigation water quality will therefore have an effect on the mobility of pesticides, even in the case of relatively polar compounds. Further research is required with soils of different characteristics to verify the mechanisms taking place.

*Table 1. pH and electrical conductivity (EC) of the influent solutions and the leachates*

| | MQ | | TWW | | $SO_4$ | |
|---|---|---|---|---|---|---|
| | Influent | Final | Influent | Final | Influent | Final |
| pH | 7.6 | 9.5 | 7.6 | 9.2 | 6.2 | 8.6 |
| EC (mS $cm^{-1}$) | 0.7 $10^{-3}$ | 0.6 | 0.9 | 1.2 | 1.2 | 1.6 |


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