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Investigation of the mechanism of uptake and accumulation of zwitterionic tetracyclines by rice (*Oryza sativa* L.)

M. Boonsaner [a,*], D.W. Hawker [b]

[a] Department of Environmental Science, Faculty of Science, Silpakorn University, Nakhon Pathom 73000, Thailand
[b] School of Environment, Griffith University, Nathan, Queensland 4111, Australia

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ABSTRACT

The uptake and accumulation of organic contaminants by plants can be detrimental to the plant itself as well as consumers. Tetracycline antibiotics are present at trace levels in soil and water. Under typical environmental conditions, they exist as zwitterions. Comparatively little is known of their uptake and accumulation by plants, or the mechanism by which this occurs. To examine this, rice (*Oryza sativa* L.) was employed, together with a static diffusion cell equipped with a cellulose membrane as a model for the uptake process. For rice, kinetic results suggested that the zwitterions were behaving similarly to neutral organic compounds, with a passive uptake process. The diffusion cell provided qualitatively similar results. When exposed to aqueous concentrations of zwitterionic tetracyclines of 50 mg L^{-1} over 15 days, no translocation to shoots or detrimental effects on plants was observed. Despite relatively low root lipid contents, concentrations in root tissue of greater than 1000 mg kg^{-1} (d.w.) were determined with maximum Root Concentration Factors of the order of 2000 L kg^{-1} (d.w.). Overall, for the tetracyclines investigated, kinetic and accumulation behavior in plants together with permeation in the diffusion cell were all governed by compound hydrophobicity.

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1. Introduction

Food crops may be contaminated with various organic pollutants through foliar or root uptake. Accumulation of organic contaminants can be detrimental to the plant itself, or since plants form the basis of food webs, provide an important exposure pathway to humans and other biota (Fryer and Collins, 2003; Kong et al., 2007). Antibiotics such as the tetracyclines are relatively non-volatile (Kowalski, 2008) and represent a group that would be uptaken from the interstitial water of soil via the roots. Studies on the uptake of tetracyclines by soybean (Boonsaner and Hawker, 2010) and alfalfa roots (Kong et al., 2007) showed that most of the compounds enter the plant via the root system and accumulate there without translocation.

Tetracyclines are reported to be the most widely used feed additive for livestock production but are poorly absorbed, with the majority being excreted unmetabolized, and released into the environment (Sassman and Lee, 2005). This results in a presence at trace levels in many soils and surface waters (Kong et al., 2007; Blackwell et al., 2007). They are ionizable species with p*Ka* values of approximately 3, 7 and 9 (Sassman and Lee, 2005). With neutral organics, physicochemical properties including the octanol/water partition coefficient (K_{OW}) and molecular size influence their diffusion and uptake into plants (Trapp, 2000). For tetracyclines, octanol/water partitioning behavior is better described by the pH dependent distribution ratio (D_{OW}) (Wells, 2006; Lützhøft et al., 2000). Similarly, aqueous solubility is pH dependent. Relevant physicochemical properties of some tetracyclines of interest are shown in Table 1. At pH $<$ 3.3, these tetracyclines have a net positive charge. However they exist predominantly as zwitterions at pH values typical of the natural environment (Sassman and Lee, 2005). A proposed structure for these zwitterions is shown in Fig. 1 (Avisar et al., 2010).

There has been little work on the uptake and accumulation of zwitterionic chemical species by plants despite its potential importance. Although overall neutral, Trapp (2009) has pointed out that D_{OW} values of zwitterionic forms of compounds are very different to those of analogous neutral uncharged species.

It is reasonably well established that for neutral nonionizable organics, the extent of uptake from soil water, as characterized by measures such as Root Concentration Factor (RCF), the ratio of concentrations in root tissue and soil interstitial water, is related to tissue lipid content and compound hydrophobicity (log K_{OW}) (McKone and Maddalena, 2007; Li et al., 2005). However the situation for zwitterionic species is largely unknown.

Kinetic aspects of uptake are even less clear. Wild et al. (2005) have proposed that the uptake of organics such as phenanthrene and anthracene by roots is linked to the uptake of water. Thus, passive diffusion has been argued to be a major transport process

* Corresponding author. Fax: +6634273047.
E-mail address: Maliwan@su.ac.th (M. Boonsaner).

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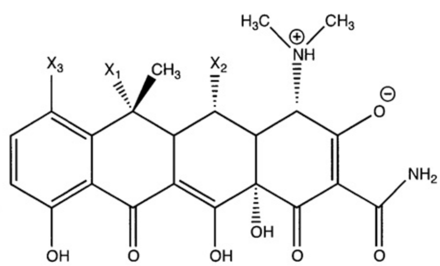
Table 1
Relevant physicochemical properties of the tetracyclines of interest.

Test compound	pK_a[a]			Isoelectric point[b]	Molecular weight[a]	Solubility[c] (mol L^{-1})	$\log D_{OW}$[c]
	pK_{a1}	pK_{a2}	pK_{a3}				
Tetracycline (TC)	3.3	7.68	9.3	5.49	480.9	7.8×10^{-4}	−2.18
Oxytetracycline (OTC)	3.27	7.32	9.11	5.30	496.9	8.9×10^{-4}	−2.30
Chlortetracycline (CTC)	3.3	7.44	9.27	5.37	515.3	2.5×10^{-4}	−1.46

[a] López-Peñalver et al. (2010).
[b] Sassman and Lee (2005).
[c] Wells (2006) and references therein. Data is relevant to pH=4.4, which reflects experimental conditions employed.



Tetracyclines	X_1	X_2	X_3
Tetracycline (TC)	OH	H	H
Oxytetracycline (OTC)	OH	OH	H
Chlortetracycline (CTC)	OH	H	Cl

Fig. 1. Proposed zwitterionic structure of tetracyclines of interest.

for such chemicals (Briggs et al., 1982; Li et al., 2005) since the amount of water transpired is in proportion to the amount of chemical moving into the plant (Collins et al., 2006; Dettenmaier et al., 2009).

For passive uptake, organic solutes must pass through a cell wall, membrane and aqueous phases (Trapp, 2000). Root cell walls may be regarded as an unstirred aqueous layer with polysaccharides such as cellulose providing added resistance (Trapp, 2000). Movement from external solution across a cell wall, membranes and aqueous phases can be described mathematically by the following expression for permeability (P e.g., m s^{-1}):

$$P=((R_D+R_M/K_{MW})^{-1}) \quad (1)$$

This assumes additive and independent resistances of aqueous phases including the cell wall (effectively an aqueous diffusion layer) (R_D) and potentially lipophilic phases such as the membrane (R_M). Eq. (1) also includes the membrane/water distribution coefficient of the diffusing chemical (K_{MW}) (Flynn and Yalkowsky, 1972). The latter is often related to the 1-octanol/water partition coefficient (K_{OW} or D_{OW}) (Gobas et al., 1986). Phase resistances are in turn related to the diffusion coefficient (D) of the chemical and the diffusion layer or barrier thickness (δ)

$$R_D=\frac{\delta_D}{D_D} \quad (2)$$

$$R_M=\frac{\delta_M}{D_M} \quad (3)$$

Combining Eqs. (1)–(3)

$$P=\frac{K_{MW}D_MD_D}{\delta_MD_D+K_{MW}\delta_DD_M} \quad (4)$$

This expression shows that two limiting situations may be delineated. For relatively hydrophilic compounds with $\log K_{OW}$ or $\log D_{OW}<2$, if $D_M \ll D_D$ such that $K_{MW}\delta_DD_M \ll \delta_MD_D$, Eq. (4) may be approximated by

$$P=\frac{K_{MW}D_M}{\delta_M} \quad (5)$$

Permeability under these circumstances would be a function of $\log K_{OW}$ or $\log D_{OW}$ (Trapp, 2000; Gobas et al., 1986). For more hydrophobic compounds, if resistance to diffusive transport in aqueous phases is governing and $D_D \ll D_M$ such that $\delta_MD_D \ll K_{MW}\delta_DD_M$, then permeability may be approximated by the following expression:

$$P=\frac{D_D}{\delta_D} \quad (6)$$

In this situation, little relationship with $\log K_{OW}$ or $\log D_{OW}$ would be expected. For ionizable organics, acid–base speciation is governed by ambient pH, so this would be an additional factor.

Dermal uptake of pharmaceuticals by humans involves traversal of cell walls and membranes together with aqueous phases. In order to help understand this process, parallel artificial membrane permeability studies are carried out (Loftsson et al., 2006). Artificial membranes employed for this purpose have included cellophane that is a porous material derived from cellulose (Manosroi et al., 2005; Santi et al., 1991). It has been used to represent a plant cell for diffusion or osmosis studies (Ansari et al., 2006). The diffusion coefficient of compounds through cellophane has been found to be related to the molecular size of a compound (Manosroi et al., 2005), but the permeation of large organic cations has also been found to be a function of pH (Santi et al., 1991). Since the permeability of cellophane is sensitive to speciation it may well be a suitable material to probe the accumulation of zwitterionics such as the tetracyclines by plant roots.

Rice (*Oryza sativa* L.) is a plant of considerable economic importance. It is regarded as the most important cereal crop in the world, serving as food for 50% of the world's population, and is the staple food for more than 80% of the people in Asia (Zhu and Wu, 2008). Thailand is a leading world exporter of rice. The soil of rice-growing areas may be contaminated by tetracyclines from previous aquaculture activities (Boonsaner and Hawker, 2010). Thus there are important practical reasons to employ rice when examining the behavior of plants exposed to tetracyclines.

The objective of this study then was to investigate the role of the physicochemical properties of zwitterionic tetracyclines in their uptake and accumulation from water by rice. Cellophane was employed in a parallel study to investigate the permeability of the same tetracyclines through a porous cellulose-based membrane such as might be encountered in root uptake.

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