



**BIOAVAILABILITY ASSESSMENT OF
ENDOCRINE-DISRUPTING CHEMICALS IN
SOIL AND SEDIMENT**

A thesis submitted in fulfilment of the degree of

Doctor of Philosophy

by

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CERTIFICATE OF AUTHORSHIP/ORIGINALITY

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I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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PREFACE

The study of the bioavailability of endocrine-disrupting chemicals (EDCs) was carried out in the ISO 9001: 2000 certified laboratory at the NSW Department of Primary Industries, Wollongbar, NSW, Australia. This study aims to assess the hazard of EDCs, particularly DDT and atrazine in laboratory soil and sediment with the application of passive samplers. Semipermeable membrane devices (SPMDs) are a recently developed passive sampling tool specifically for monitoring hydrophobic contaminants (Van Zwieten *et al.*, 2001). The devices consist of lipid (cod liver oil) spread into a thin film inside sealed polyethylene lay-flat tubing. Lipophilic compounds permeate the polyethylene membrane and partition into the lipid where they are concentrated, depending on their physico-chemical parameters. The utility of SPMDs in providing bioavailability information has been assessed in this study. The determination of the concentrations and compositions of lipophilic compounds, such as DDTs taken up by the SPMDs provides a measurement of the levels of these compounds that are bioavailable to living organisms.

In recent years there has been increasing awareness of the endocrine-disrupting effects of organic contaminants such as chlorinated pesticides. DDT is one such pesticide that is of great environmental concern, due to its toxicity and longer persistence in the environment. Although DDT use was banned in 1970, DDT is still found in aquatic environments (Erdogrul *et al.*, 2005). Alarmingly, DDT is biomagnified, that is, its concentration increases with an increasing trophic level in aquatic food chains (Cullen & Connell, 1992; Kidd *et al.*, 2001).

Exposure to certain EDCs contributes to adverse effects in some wildlife species (Burlington & Linderman, 1950). There is evidence indicating a causal link between exposure to endocrine-disrupting pollutants and reproductive abnormalities observed in wild fish, birds, reptiles, and mammals (Helle *et al.*, 1976; Fry & Toone, 1981; Fry *et al.*, 1987; Fox, 1992; Guillette *et al.*, 1994; Jobling *et al.*, 1998). In amphibians, exposure to endocrine-disrupting pollutants can feminise gonadal differentiation, resulting in female-biased sex-ratios at metamorphosis (Kloas *et al.*, 1999; Hayes *et al.*, 2002; Mackenzie *et al.*, 2003; Levy *et al.*, 2004).

Endocrine disruption has also emerged as a human health issue (Bitman *et al.*, 1968). For example, exposure in the early stages of life to naturally occurring hormones could produce harmful health effects, including cancer, in young adults (Dunn & Green, 1963; Takasugi & Bern, 1964; Foresbert, 1969). Furthermore, EDCs have also been linked to declining human male reproductive health, such as reduced sperm quality/counts (Handelsman, 2001; Carlsen *et al.*, 1992; Sharpe & Skakkebaek, 1993) and increased occurrence of testicular cancer (Toppari & Skakkebaek, 2000). Furthermore, a Japanese study has confirmed that the increases in hypospadias in human males and accelerated puberty in girls are due to exposure to endocrine-disrupting chemicals (Mori, 2000).

This thesis consists of six chapters. Four chapters report on experimental work and these have been prepared as papers in a format suitable for publication in a refereed scientific journal. These four chapters are preceded by a general introduction (Chapter I) to the thesis, which gives an overview of endocrine-disrupting chemicals and their effects on biota, including humans. Chapter II is a study on the kinetic uptake of

atrazine into SPMDs from pure water. This chapter tests whether SPMDs are suitable for assessing the risk of bioaccumulation of atrazine, including six of its congeners, from pure water. The study showed the uptake of atrazine by cod-liver-oil-filled SPMDs had low bioaccumulation, which was similar to that by living organisms.

In the north of New South Wales, Australia, the contamination of soil from DDT use in cattle dips poses a potential environmental risk to soil and aquatic biota. Chapter III presents a comparative study between the kinetics of uptake of DDT by cod-liver-oil-filled semipermeable membrane devices (SPMDs) and earthworms (*Eisenia foetida*) in both pure water and dip soil. In this chapter, earthworms were used in the aquatic and soil terrestrial systems to estimate the bioavailability of DDT and its congeners (*o,p'* & *p,p'*-DDE, DDD and DDT). Both linear regression and non-linear regression were used to calculate the rate of kinetic uptake of different sampling tools. The kinetic uptake rate by earthworms in the aquatic system was 1.7 times faster than the uptake rate for the SPMDs. However, the kinetic uptake rate by earthworms in soil was found to be 1 to 4.3 times slower than the uptake rate for the SPMDs.

To assess the bioaccumulation of DDT from soil and sediment, SPMDs containing cod liver oil were used. These experiments are presented in Chapter IV. The SPMDs were exposed three times to the same sediment. Non-linear regressions were used to predict the maximum bioavailability of DDT in different dip soils that were submerged as aquatic sediments. DDT was sequestered from the sediment to SPMDs, and the sequestration decreased as the fraction of organic contaminants decreased. This confirms the suitability of the SPMD technique for the assessment of DDT bioavailability.

In Chapter V, DDT-contaminated soils were placed in laboratory aquaria to mimic the natural soil erosion into creeks. This study focused on the changes in environmental risk (measured as DDT availability) under aerated and non-aerated sediment conditions over time. The exponential decay model presented in this chapter demonstrates that the risk of DDT residues decreased as sediment aged. The final chapter of the thesis (Chapter VI) summarises the key findings of the whole study and provides recommendations for future research and management of EDC-contaminated soil and sediment.

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ACRONYMS AND ABBREVIATIONS

AATSE	Australian Academy of Technological Sciences & Engineering
APECs	Alklyphenol polyethoxycarboxylates
APEOs	Alklyphenol polyethoxylates
APs	Alkylphenols
APVMA	Australian Pesticides and Veterinary Medicines Authority
ATSDR	Agency for Toxic Substances and Diseases Registry
ATZ	Atrazine
BCF	Bioconcentration factor
BMF	Biomagnification factor
cm	Centimetre
cm ²	Square centimetres
DDD	1,1-dichloro-2,2-bis(p-chlorophenyl)ethane
DDE	1,1-dichloro-2,2-bis(p-dichlorodiphenyl)ethylene
DDT	Dichloro-diphenyl-trichloroethane
DBP	4,4'-dichlorobenzophenyl
DEA	Diethylatrazine
DEHA	Diethylhydroxyatrazine
DFO	Department of Fisheries and Oceans
DIA	Deisopropylatrazine
DIHA	Deisopropylhydroxyatrazine
DMF	Dimethylformamide
DOM	Dissolved organic matter
EDCs	Endocrine-disrupting chemicals
EPA	Environmental Protection Agency

FWPRDC	Forest & Wood Product Research & Development Corporation
g	gram
GC	Gas Chromatography
GC/MS	Gas Chromatography-Mass spectrometry
HA	Hydroxyatrazine
HPLC	High-performance liquid chromatography
HT	2-hydroxyterbutylazine
kg	Kilograms
K_{oc}	Soil sorption coefficient on an organic carbon basis
K_{ow}	Octanol-water partition coefficient
LDPE	Low-density polyethylene
LOQ	Limit of quantitation
LP	Liverpool Plains
LPWQP	Liverpool Plains Water Quality Project
mg	Milligram
mg/kg/d	Micrograms per kilogram per day
mL	Millilitre
mm	Millimetre
$\mu\text{g}/\text{kg}$	Micrograms per kilogram
$\mu\text{g}/\text{L}$	Micrograms per litre
$\mu\text{g}/\text{mL}$	Micrograms per millilitre
μm	Micrometre
MCL	Maximum contaminant levels
MIA	Murrumbidgee Irrigation Aarea
MRLs	Maximum residue limits

MTBSTFA	<i>N</i> -(<i>tert</i> -Butyldimethylsilyl)- <i>N</i> -methyltrifluoroacetamide
MTD	Maximum tolerated dose
NHMRC	National Health and Medical Research Council
NP	Nonylphenol
NSW	New South Wales
OP	Octylphenol
PAD	Passive accumulation devices
PAHs	Polyaromatic hydrocarbon
PCBs	Polychlorinated biphenyls
POCIS	Polar organic chemical integrated samplers
PTFE	Polytetrafluoroethylene
RO	Reverse osmosis
rpm	Revolutions per minute
SPE	Solid-phase extraction
SPMDs	Semipermeable membrane devices
SPME	Solid-phase microextraction
STPs	Sewage treatment plants
TBT	Tributyltin
TT	Triazine Tolerant
UK	United Kingdom
USA	United States of America
US EPA	United States Environmental Protection Agency
UV	Ultraviolet
WHO	World Health Organization
WA	Western Australia

PUBLICATIONS AND CONFERENCES

Parts of the research presented in this thesis have appeared in the following journal and conference presentations.

Phanchai Menchai, Lukas Van Zwieten, Stephen Kimber, Nazir Ahmad, P. Suresh, C. Rao and Grant Hose. 2008, Bioavailable DDT residues in sediments: Laboratory assessment of ageing effects using semi-permeable membrane devices. *Environmental Pollution*, Vol. 153, pp. 110-118.

Phanchai Menchai, Lukas Van Zwieten, Stephen Kimber, Nazir Ahmad and Grant Hose. Semipermeable membrane devices (SPMDs): Addressing the risk, not the residue. In abstracts of Pacificchem 2005. American Chemical Society, Honolulu, Hawaii, HI, USA.

Lukas Van Zwieten, Phanchai Menchai, Stephen Kimber, Nazir Ahmad, Joshua Rust and Grant Hose. Assessing risk of pesticide residues in aquatic and freshwater ecosystems. In abstracts of Pacificchem 2005. American Chemical Society, Honolulu, Hawaii, HI, USA.

ABSTRACT

There are many methods currently available to assess the risk of chemical bioaccumulation in an organism. Many of these methods are either very difficult to implement, being costly and time-consuming, or contain flaws which may affect the final result. In this study we used semipermeable membrane devices (SPMDs) containing cod liver oil to assess the bioavailability of lipophilic and hydrophilic organic contaminants. This SPMDs proved to be an excellent method for this study.

Atrazine is a hydrophilic endocrine-disrupting chemical and is likely to be taken up by SPMDs. Atrazine congeners were accumulated far less than the parent compound. The uptake of atrazine by SPMDs from pure water was rapid and reached equilibrium within 48 hours. The study also showed low bioaccumulation (0.05 – 13.5%), which is consistent with living organisms. Consequently, the SPMD method was appropriate for assessing atrazine.

Organochlorine pesticide DDT was readily taken up by the SPMDs. Approximately 76% of the total DDT from spiked water was accumulated by SPMDs after 180 days of exposure. However, only 5% of total DDT was taken up from field-collected contaminated soil and only 10% from a synthetic spiked soil after 35 days of exposure. Based on the percentage uptakes, *o,p'* & *p,p'*-DDD congeners were more bioavailable than any other DDT congeners (such as *o,p'* & *p,p'*-DDE, and *o,p'* & *p,p'*-DDT). Up to 10% of *o,p'* or *p,p'*-DDD was taken up from the field-collected soil and 20% was taken up from freshly spiked soil.

Kinetic uptakes of total DDT and six congeners by cod-liver-oil-containing SPMDs and earthworms were compared both in pure water and from soil and sediment. The correlation coefficients (r) between the SPMDs' uptake and the earthworms' uptake (*Eisenia foetida*) at 14 days of *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT, and total DDT were 0.96, 0.74, 0.80, 0.98, 0.95, 0.81, and 0.99, respectively. Unexpectedly, the kinetic uptake rate by earthworms in the aquatic system was 1.7 times faster than the uptake rate for the SPMDs. However, kinetic uptake rate by earthworms in soil was 1 to 4.3 times slower than the uptake rate for the SPMDs. The key advantage of SPMDs is 1) their ability to predict long term accumulation of the chemicals, 2) they provide more precise estimates of uptake than the earthworms, and 3) SPMDs require only simple preparation and give clean samples for chromatography. Even though earthworms can be cultured in the laboratory under controlled conditions, and can be tested in a variety of soil types, earthworm uptake rates were variable and experiments repeatedly failed.

The available Σ DDT and congeners in the contaminated dip soil decreased over time as they were sequestered into the SPMDs. The uptake was greatest at the first exposure and decreased with subsequent exposures. The bioaccumulation factors of DDT were in the range of 157 to 2,125 during the first 35 days of exposure and decreased over subsequent sampling periods. The non-linear regression model was used to predict the maximum uptake of DDT by SPMDs. The percentage DDT uptake of the two spiked soils and field-collected sandy soil reached asymptote after 150 days, with 11% to 13% of maximum uptake—that is the amount of chemical taken up as a proportion of the initial soil/sediment. After 70 days of exposure, 3.5% of DDT was predicted its maximum uptake in heavy clay and clayey sand soils. Of all the

DDT congeners, *p,p'*-DDD was the most bioavailable. Approximately 30% of *p,p'*-DDD in freshly spiked soil was taken up by SPMDs.

The initial risk of studied EDCs added to the environment is high because these chemicals may be readily bioavailable, but this risk decreases over time. A mathematical model was developed to enable eventual inclusion of the DDT in environmental risk assessments and it was effectively used to explain changes in DDT bioavailability over a one-year exposure period. Soil with a higher clay proportion or with higher organic carbon was shown to have a lower environmental risk. For example, clay soil exhibited the risk at the commencement of the incubation with 3.3% of available DDT residue. As the sediments aged, either under aerated or non-aerated conditions, the bioavailable DDT fraction decreased in all soil types, following first-order exponential decay.