Illicit drugs - environmental occurrence, fate and toxicity

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DECLARATION

I declare that:

This thesis presents work carried out by myself and does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any university. To the best of my knowledge it does not contain any materials previously published or written by another person except where due reference is made in the text; and all substantive contributions by others to the work presented, including jointly authored publications, are clearly acknowledged.

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Signed _____ Date: 19 February 2016

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LIST OF ABBREVIATIONS

ATSs	Amphetamine-type stimulants
MAP	Methamphetamine
MAS	Methylamphetamine sulphate
PSE	Pseudoephedrine
P2P	Phenyl-2-propanone
MDMA	3, 4-methylenedioxymethamphetamine
COC	Cocaine
BE	Benzoylecgonine
EME	Ecgonine methyl ester
THC	Δ^9-tetrahydrocannabinol
LSD	Lysergic acid diethylamide
ECs	Emerging contaminants
K_d	Sorption coefficient
DOC	Dissolved organic carbon
OC	Organic carbon
RGR	Relative growth rate
ROS	Reactive oxygen species
WWTPs	Wastewater treatment plants
HPLC-MS	High performance liquid chromatography - mass spectroscopy

ABSTRACT

Illicit drugs are those compounds whose non-medical use is prohibited by international legislation and mainly belong to the classes of opiates, cocaine, cannabis, amphetamines and ecstasy-group substances (UNODC, 2007; Hall et al., 2008). These chemicals have been proven to be toxic to humans and animals in that they cause numerous and potentially precarious side effects. Reports on illicit drugs and their metabolites ending up in the environment have been increasing worldwide. These problems occur mainly due to human consumption and also disposal into sewage networks by the illegal manufacturesrs. Although, the reported environmental concentrations of illicit drugs are low, their potent pharmacological properties and the mixing of illicit drugs along with similar compounds in soil and water could be toxic to non-target organisms and pose a risk to human health. The data available on the environmental occurrence and distribution pattern of illicit drugs in Australia (i.e. South Australia), fate in soil and water and ecotoxicity on aquatic and terrestrial biota are limited given that previously published research has focused mainly only on sewage epidemiology and human health. This thesis focuses on the: (a) occurrence and distribution pattern of illicit drugs and their metabolites in South Australian wastewater (influent and effluent), surface waters, sewage sludge and sediments; (b) fate of illicit drugs in soils; and (c) toxicity of illicit drugs and their metabolites to biota including daphnia, duckweed, and earthworms.

The occurrence and distribution patterns of illicit drugs and their metabolites in specific regions of South Australian wastewater, sewage sludge, surface waters and sediments were investigated. Results indicated that 3 out of 6 illicit drugs were found to be present in wastewaters were at concentrations ranging from 12 to 1670 ng L^{-1}. Methamphetamine (MAP) was the only test compound detected in sewage sludge (2 µg kg^{-1} dry samples). In surface waters MAP, 3, 4-methylenedioxymethamphetamine (MDMA) and benzoylecgonine (BE) were recorded in 4 out of 20 test locations with a concentration of 5 to 11 ng L^{-1}. Hence, water from wastewater treatment plants (WWTPs) could be the primary source of illicit compounds contaminating the environment. Although the environmental concentrations of these contaminants are low, their impact on aquatic organisms and risk to human health cannot be overlooked.

The sorption and desorption patterns of MAP and MDMA (alone and as mixture) were determined in three different soils using batch equilibration experiments. MAP and MDMA reached equilibration within 12 h with initial rapid uptake and then gradually reached equilibrium. Sorption data were analysed employing the Langmuir and Freundlich models, and the results showed that the Freundlich model is the best fit and described the sorption process of MAP and MDMA (alone and as mixture) in three test soils. Sorption of the illicit drugs in soils followed the order: MAP > MAP mixture > MDMA mixture > MDMA. The sorption

coefficient (K_d) was positively correlated with soils' organic carbon (OC), dissolved organic carbon (DOC) and clay for MAP, while for MDMA it was clay, OC and DOC. In addition, the following soil characters such as cation exchange capacity (CEC) > electrical conductivity (EC) > sand were negatively correlated irrespective of the treatments. Furthermore, desorption was assessed when the sorbed particles were released into solution in the following order: MAP > MAP mixture > MDMA > MDMA mixture. These findings could provide an insight into the sorption and desorption patterns, and inform us about the transport and fate of MAP and MDMA in the environment and also their risk assessment.

The persistence of cocaine was investigated in a laboratory experiment for 120 days involving three different South Australian soils under both non-sterile and sterile conditions. Cocaine degrades very rapidly in a non-sterile condition in all three test soils (half-life between 2.2 and 3.9 days) compared to sterile condition (half-life between 40.8 and 54.1 days). Cocaine degradation products such as benzoylecogonine (BE) and ecgonine methyl ester (EME) were detected in both conditions. BE was relatively stable for a period of time in non-sterile soil compared to cocaine.

Chronic toxicity of illicit drugs (MAP, PSE and cocaine) to earthworm (*Eisenia fetida*) was studied in a soil. No mortality was recorded even at the highest concentration, and results showed loss in weights for all treatments. Chronic exposure of adult earthworms to MAP, PSE and cocaine showed changes in their morphology and behaviour. Their reproduction capacity also declined especially above 20 mg kg^{-1} concentration. Exposure at concentrations of 50 – 200 mg kg^{-1} significantly reduced both cocoon and juvenile stages. Earthworm chronic exposure to cocaine induced and significantly increased DNA damage, olive tail moment, and lipid peroxidation at > 1 mg kg^{-1} and had a significant impact on total antioxidant capacity at > 25 mg kg^{-1}. Overall, these finding suggests that soil contamination with illicit drugs does constitute a threat to soil biota and the environment

The acute and geno-toxicity of MAP, PSE, MDMA and cocaine to a freshwater cladoceran, *Daphnia carinata* were studied in both cladoceran and natural water collected from local creeks. The cladoceran toxicity followed the order: cocaine > MAP > MDMA > PSE. All these test chemicals were relatively less toxic in non-sterile compared to sterile natural water, which may be due to the influence of varied physico-chemical and biological parameters of natural water. In all the test media, MAP, PSE and MDMA were found to be relatively stable while cocaine was metabolized to BE and ecgonine methyl ester (EME). Also, these chemicals at lower concentrations in water had significant genotoxic effects on *D. carinata* in comparison to the controls, suggesting that even low level chronic exposure of these compounds to *D. carinata* can cause serious harm, including developmental and reproductive toxicity.

The toxic effects of commonly abused illicit drugs and a precursor were assessed by examining their impact on duckweed (*Lemna minor* L.), a common aquatic plant. Growth attributes (frond numbers, fresh weight and relative growth rate) and biochemical parameters (chlorophyll and proline) content was affected with the increase in the concentrations of illicit drugs. Of these parameters, fresh weight was the most appropriate indicator for validating the effects of illicit drugs. The toxicity of these compounds was followed the order: cocaine > MAP > MDMA > PSE. Overall, the results demonstrate the usefulness of *L. minor* L. as an illicit drug's aquatic toxicity indicator for reliable assessment of phytotoxic potential of complex aquatic systems.