Degradation pattern of illicit drugs in soil

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Abstract
The abuse of illicit drugs has received worldwide attention due to their significant adverse impacts on human and the environment. The aim of the present work was to determine the degradation pattern of certain compounds (associated with the clandestine manufacture of illicit drugs) in soil. The target compounds include parent drug (methamphetamine and 3,4-methylenedioxymethamphetamine (MDMA)), precursors (pseudoephedrine), and by-products (1-(1,4-cyclohexadienyl)-2-methylaminopropane, N-formylmethylamphetamine, and 1-benzyl-3-methylnaphthalene). The environmental fate of the target compounds were evaluated in three different South Australian soils under non-sterile and sterile conditions. The results of the degradation study indicated that 1-benzyl-3-methylnaphthalene, methamphetamine, and N-formylmethylamphetamine persist for a long time in soil, MDMA and pseudoephedrine persist for a moderate time, and 1-(1,4-cyclohexadienyl)-2-methylaminopropane is not persistent. The role of biotic-abiotic soil processes on the degradation of target compounds was also varied significantly for different soils as well as with the progress in incubation period. The degradation of methamphetamine and 1-benzyl-3-methylnaphthalene can be considered as predominantly biotic as no measureable changes in concentrations were recorded in the sterile soils within one year period. The results of the present study revealed that the degradation pattern depends mostly on the soil conditions and the nature of the compound.

Key Words
Illicit drug, clandestine lab, methamphetamine, ecstasy, MDMA.

Introduction
Illicit drugs are those whose nonmedical use is prohibited by the international law and mainly belongs to the class of opiates, cocaine, cannabis, amphetamines type substances (ATSs), etc. (Hall *et al.* 2008; UNODC 2007). ATS comprise two groups of compounds: [1] the amphetamines group (e.g., amphetamine, methamphetamine) and [2] ecstasy group (e.g., 3,4-methylenedioxymethamphetamine (MDMA) and analogous compounds) (UNODC, 2008a). Amphetamine group drugs account for more than three-quarters of ATSs (UNODC 2008b) and currently demand the most attention of all the synthetic illicit drugs (EMCDDA 2007). Methamphetamine continues to be the most widely manufactured ATS and accounted for 68% of the amphetamine groups as per 2006 estimate (UNODC 2008a, b). In comparison to the plant based drugs (e.g., heroin, cocaine, cannabis, etc.), methamphetamine is relatively easy to manufacture in clandestine laboratories from commonly available chemicals (Sasaki and Makino 2006). Methamphetamine manufacture is typically located throughout East and South-East Asia, North America and Oceania due to easy availability of precursors and high demand (UNODC 2008a). In Australia, the ATS market is second only to the cannabis market and may continue to grow (ACC "Organized Crime in Australia" 2009). In 2006-07 ATS seizures accounted for 46% by weight of all drugs seized in Australia, a period when 356 clandestine laboratories were detected across Australia (ACC, "Illicit Drug Data Report, 2006-2007" 2008).

Illicit drugs are manufactured through variety of synthetic routes employing different illicit precursors most commonly in small clandestine labs and also in industrialized mega and super laboratories. The chemicals associated with these clandestine drug laboratories are often improperly disposed of in indoor or outdoor drains, directly on the ground, and in water bodies. In most cases, the exact contents of the waste products are unknown. These chemicals may then be exposed to different environmental compartments (i.e., soil, sediments, ground water, surface water, etc) through diverse processes (e.g., sorption, degradation, leaching, surface runoff, etc.). Thus, it is pre-requisite to systematically investigate the environmental behavior of these clandestine lab chemicals to assess the potential risk due to the release of these compounds into the environment. A series of reports have been published from different countries on the presence of illicit drugs in water bodies, but there is no report on the behavior of these compounds in soil.

The present work was conducted to investigate the degradation pattern of selected parent drug (e.g., methamphetamine and 3,4-methylenedioxymethamphetamine (MDMA)), precursors (e.g., pseudoephedrine), and the by-products (e.g., 1-(1,4-cyclohexadienyl)-2-methylaminopropane, N-formylmethylamphetamine, and 1-benzyl-3-methylnaphthalene) in soils.

Methods

The soils for the present work were collected from the Mawson Lakes, Sturt Gorge, and Waite Campus of South Australia, which are originally urban impacted backyard, bush, and agricultural land, respectively. The three soils were widely varied in terms of organic carbon, clay content, soil texture, pH, and surface area. The results of the present study employing test soils widely varying in their basic physico-chemical properties (Table 1) may be extrapolated to other soils around Australia to predict the behavior of the target compounds. The test soils were scanned for the presence of any target compounds and none were detected.

Table 1. Basic physico-chemical properties of the test soil.

Soil	Short name	pH (1:2.5 H_2O)	Electrical conductivity ($\mu S\text{-}cm^{-1}$)	Cation Exchange capacity (meq-100 g^{-1})	Organic carbon (%)	Dissolved Organic carbon ($\mu g\text{-}mL^{-1}$)	Particle size distribution			Textural class	B.E.T. Surface area ($m^2\text{-}g^{-1}$)
							Sand (%)	Silt (%)	Clay (%)		
wson Lakes	ML	8.91	159	19.24	1.11	8.71	55.0	25.0	20.0	Sandy loam	26.67
turt Gorge	SG	5.98	36	6.30	2.88	5.84	60.0	25.0	15.0	Sandy loam	9.36
ıite Campus	WC	5.64	965	17.42	2.26	3.90	42.5	42.5	15.0	Loam	4.59

In the present study, the degradation pattern was investigated at a single spiking level of 100 µg/g, 50% of maximum water holding capacity of soils, and at 25 ± 2^0C temperature for one year period. To avoid any chance of photodegradation, the soils were incubated in dark. 5 g of soil in individual amber colored screw cap vials of 40 mL capacity were spiked with the test compounds. The pre-incubated stabilized soils were used for both the non-sterile and sterile degradation studies. The soils (in individual vials) were sterilized by autoclave for three consecutive days at 121^0C for 20 min. The soils for both the non-sterile and sterile degradations were spiked with requisite amount of the freshly prepared stock solution. In case of the sterile degradation, the stock solutions were passed through sterile 0.20 µm filter and soils were spiked aseptically within a laminar air flow.

The analytical technique (including soil extraction, sample clean-up, and analysis involving HPLC-MS and GC-MS) was developed for precise quantification of the test compounds.

Results

In this work, degradation of the target compounds (e.g., methamphetamine, MDMA, pseudoephedrine, 1-(1,4-cyclohexadienyl)-2-methylaminopropane, N-formylmethylamphetamine, and 1-benzyl-3-methylnaphthalene) was studied both under non-sterile soil conditions (where both biotic and abiotic degradation can take place) and sterile conditions (where only abiotic degradation can take place) in all the three soils. Most of the compounds showed substantial degradation in the sterile soils indicating the possible role of the abiotic factors other than photolysis as the incubation was performed under dark throughout the experimental period. The resistance to degradation in non-sterile soils was found in the following descending order: 1-benzyl-3-methylnaphthalene > methamphetamine > N-formylmethylamphetamine > MDMA > pseudoephedrine > 1-(1,4-cyclohexadienyl)-2-methylaminopropane. The degradation of methamphetamine and 1-benzyl-3-methylnaphthalene showed a fairly steady pattern throughout the incubation period when compared in terms of the residual concentration.

No changes in concentrations of methamphetamine and 1-benzyl-3-methylnaphthalene were apparent in the sterile soils within one year period. MDMA, pseudoephedrine, and N-formylmethylamphetamine, were somewhat less stable while 1-(1,4-cyclohexadienyl)-2-methylaminopropane was very unstable.

The experimental data were fitted to regression equations considering first order reaction. The half-life values were calculated from the best fit lines of the logarithm of residual concentrations vs. time elapsed in the incubation period. The half-life values for the non-sterile degradation were recorded in the following ascending order: 1-(1,4-cyclohexadienyl)-2-methylaminopropane (0.8 to 8.3 days) < pseudoephedrine (3.7 to 30.1 days) < MDMA (15.4 to 59.0 days) < N-formylmethylamphetamine (35.0 to 43.6 days) <

methamphetamine (130.9 to 501.7 days) < 1-benzyl-3-methylnaphthalene (150.5 to 10034.3 days). However, the same for the sterile degradation were found to follow the order: 1-(1,4-cyclohexadienyl)-2-methylaminopropane (2.60 to 5.6 days) < MDMA (75.3 to 107.5 days) < N-formylmethylamphetamine (188.1 to 301.0 days) < pseudoephedrine (143.3 to 501.7 days).

Interestingly, 1-(1,4-cyclohexadienyl)-2-methylaminopropane showed the fastest degradation both under the non-sterile and sterile conditions. In addition, almost a parallel degradation pattern of 1-(1,4-cyclohexadienyl)-2-methylaminopropane both under non-sterile and sterile conditions indicated the dominant role of the soil abiotic factors compared to biotic components.

Conclusions

The results showed that the overall degradation mostly relies on the role of biotic and/or abiotic factors of individual soil plus the molecular nature of the target compound. Methamphetamine and certain synthetic by-products 1-benzyl-3-methylnaphthalene and N-formylmethylamphetamine recorded long persistence in the test soils which is not desirable and need further study to investigate their long term metabolism pattern and impacts of these compounds on the biota including their bioaccumulation potential.

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