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Degradation in soil of precursors and by-products associated with the illicit manufacture of methylamphetamine: Implications for clandestine drug laboratory investigation

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ABSTRACT

Key precursors and by-products in the Leuckardt, Nagai and dissolving metal reductive syntheses of methylamphetamine undergo degradation in soil as a result of biotic and abiotic processes. Furthermore, methylamphetamine is a product of the degradation of 1-(1′,4′-cyclohexadienyl)-2-methylaminopropane and N-formylmethylamphetamine.

These findings have implications for the forensic assessment of buried residues recovered from clandestine laboratory sites because markers used to infer the synthetic methods used might be absent as a result of degradation and because methylamphetamine might be present in residues as a result of degradation rather than as a direct result of its manufacture in the laboratory.

1. Introduction

A common theme with regards to clandestine drug laboratories is that operators are anxious to avoid detection by the authorities and members of the public. As disposal of chemical waste can attract undue attention, clandestine laboratory operators sometimes bury waste or dispose of it into domestic sewerage or wastewater systems. The analysis of buried waste can yield information as to the past or on-going manufacture of illicit drugs.

The aim of the work described in this article was to examine whether burial in soil has any affect upon the compounds used by forensic scientists to indicate the manufacture, or the particular route of manufacture, of methylamphetamine. Previous work [1] has indicated that phenyl-2-propanone (structure 1, Fig. 1), a key manufacturing by-product and precursor, is rapidly metabolized by soil microbes to yield a mixture of compounds that are in turn also metabolized.

The present work describes forensic implications arising from the degradation in soil of methylamphetamine (2, Fig. 1), N-formylmethylamphetamine (3, Fig. 1), 1-benzyl-3-methylnaphthalene (4, Fig. 1) and 1-(1′,4′-cyclohexadienyl)-2-methylaminopropane (CMP, 5, Fig. 1) and pseudoephedrine (6, Fig. 1), which are important markers in the Leuckardt, Nagai and dissolving metal reduction (DMR) methods, respectively.

2. Materials and methods

Soils used in this study were collected from Mawson Lakes (ML), Sturt Gorge (SG) and Waite Campus (WC), which are locations within the Adelaide metropolitan area in South Australia. The three soils are from urban backyard, Australian bushland and agricultural environments, respectively, and they exhibit a broad range of characteristics (see Table 1). Prior to their use the soils were freed of obvious plant material and other foreign matter, passed through a 2 mm sieve, and stored at 4 °C.

Two series of degradation studies were conducted: one under abiotic conditions where the soils were sterilized by autoclaving for three consecutive days at 121 °C for 20 min prior to spiking with compounds 2, 3, 4, 5 and 6; and one under biotic conditions where the soils were not sterilized prior to spiking. In each series the soils (5 g) were spiked with solutions of 2, 5 and 6 as their hydrochloride salts in water (2 g/L) at a dosage of 100 μg per gram of soil. N-formylmethylamphetamine and 1-benzyl-3-methylnaphthalene were added as solutions in acetone and hexane

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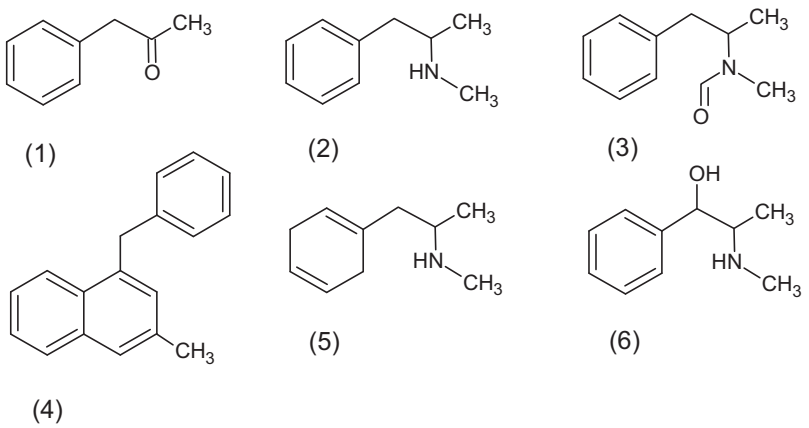

Fig. 1. Molecular structures for compounds of interest.

Table 1
Characteristics of soils used in this study.

Soil	pH (1:2.5 H_2O)	Electrical conductivity ($\mu S\,cm^{-1}$)	Cation exchange capacity ($cmol(p+)\,kg^{-1}$)	Organic carbon (%)	Textural class	Dissolved organic carbon ($\mu g\,mL^{-1}$)	Sand (%) Silt (%) Clay (%)
Waite Campus	5.64	965	17.42	2.26	Loam	3.90	42.5 42.5 15
Sturt Gorge	5.98	36	6.30	2.88	Sandy loam	5.84	60 25 15
Mawson Lakes	8.91	159	19.24	1.11	Sandy loam	8.71	55 25 20

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(20 g/L) at the same rate. Spiking solutions were passed through sterile 0.45 μm filters for the abiotic series of experiments.

Soils thus treated were kept in the dark at 25 ± 2 °C and 50% water holding capacity for up to 1 year prior to extraction of degradation products. Additional experimental details with regards to the spiking experiments can be found in Refs. [2,3].

A mixture of chloroform:acetonitrile:methanol:acetic acid (80:10:9:1) used in two steps (2× 20 ml) was found to produce the best extraction efficiency overall for all compounds except 1-benzyl-3-methylnaphthalene, which required the separate extraction strategy described below. For the two extraction steps the soils were vortexed with the solvent (1 min), placed on an electric shaker (1 h for the first extraction and 15 min for the second) and finally subjected to ultrasonic vibration for 5 min at 30 °C. The mixtures were centrifuged and the supernatants filtered through 0.22 μm Teflon filters. The filtrates were combined, evaporated under a stream of nitrogen and taken up in HPLC grade methanol for HPLC–MS analysis. The average recoveries for this extraction system are given in Table 2.

Table 2
Extraction average recoveries for each analyte in each soil.

Compound	Soil	Recovery (%)
2	Mawson Lakes	73.3 ± 3.46
	Sturt Gorge	51.4 ± 0.78
	Waite Campus	85.2 ± 0.21
3	Mawson Lakes	77.5 ± 3.69
	Sturt Gorge	88.3 ± 1.53
	Waite Campus	93.0 ± 1.26
4	Mawson Lakes	77.2 ± 1.34
	Sturt Gorge	83.7 ± 1.98
	Waite Campus	91.2 ± 1.27
5	Mawson Lakes	76.9 ± 11.02
	Sturt Gorge	48.3 ± 1.36
	Waite Campus	80.9 ± 0.94
6	Mawson Lakes	57.3 ± 8.81
	Sturt Gorge	33.8 ± 2.75
	Waite Campus	63.3 ± 4.70

Three steps were used to extract 1-benzyl-3-methylnaphthalene. The first step used acetone (10 ml) and this was followed by two extractions with ethyl acetate (10 mL). Each extraction step involved vortexing (1 min) followed by ultrasonic vibration (15 min at 30 °C). The extracts were filtered, the filtrates were combined and then evaporated under a stream of nitrogen before being taken up in chromatographic grade ethyl acetate for GC–MS analysis. The average recovery for this extraction process is also given in Table 2.

HPLC–MS analysis was performed using an Agilent 1100 series chromatograph equipped with a mass selective detector (Agilent 1100) and Chemstation software. Separation of analytes was achieved using a ZORBAX Eclipse XDB-C18 column (150 mm × 4.6 mm, 5 μm packing) operated at 25 °C. The mobile phase used was a time-programmed mixture of two solvents, A (20% methanol + 0.1% acetic acid + 10 mM ammonium acetate) and B (90% methanol + 0.1% acetic acid + 10 mM ammonium acetate) at a constant flow-rate of 0.8 mL/min. The mobile phase program was as follows: 0–8 min (100% A), 8–12 min (90% A + 10% B), 12–25 min (100% B), and 25–26 min (100% A). Electrospray ionization (ESI) was used in positive mode with nebulizer pressure in the spray chamber at 35 psig and drying gas at 12.0 L/min. The scan range was 100–350 Da, fragmentor 120, Gain EMV 3.0, Threshold 0.0, and step size 0.10. Propranolol was used as the internal standard all analyses included positive and negative control samples.

GC–MS was performed using an Agilent 6890 N chromatograph equipped with an Agilent 5973 mass selective detector and Chemstation software. The GC inlet was operated in splitless mode at 250 °C with helium as carrier gas in constant flow mode. Inlet pressure was 96.46 kPa, purge flow 49 mL/min, purge time 0.75 min, and total flow 52.8 mL/min. A DB-5 column (30 m × 0.25 mm × 0.50 μm) was used for separation with an initial flow of 1 mL/min. The temperature program was 90 °C for 2.50 min then 45 °C/min to 300 °C, which was held for 9.00 min. Mass spectral acquisition started after a 4 min solvent delay over a range of 50–550 Da. Phenanthrene was used as the internal standard. Limits of detection for each of the analytes are given in Table 3.

3. Results and discussion

Organic compounds in soil can degrade as a result of action by micro-organisms (i.e. biotic processes) or as a result of purely chemical processes such as hydrolysis, photolysis or oxidation, which take place without the involvement of organisms (i.e. abiotic