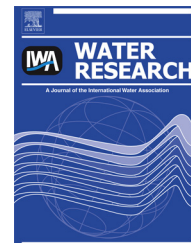


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# Degradation and transformation products of acetaminophen in soil

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## ABSTRACT

Acetaminophen is the most widely used human medicine. Trace levels of acetaminophen are frequently detected in treated wastewater and the impacted surface or groundwater resources. However, even though soil is a primary receiving compartment, the fate of acetaminophen in soil is poorly known, including in particular the potential for the formation of incomplete degradation products that may have altered biological activity and mobility. In this study, using both <sup>14</sup>C-labeling and LC-MS/MS techniques, we evaluated the dissipation routes and transformation pathways of acetaminophen in soils under a range of conditions. Throughout 120-d aerobic incubation, up to 17.0 ± 0.8% of <sup>14</sup>C-acetaminophen was mineralized, but mineralization was greatly inhibited after sterilization or amendment of biosolids. Immediately after treatment, the majority of <sup>14</sup>C-residue became non-extractable or bound, with the level accounting for 73.4–93.3% of the applied amount at the end of incubation. A total of 8 intermediates were identified, including 3-hydroxyacetaminophen, hydroquinone, 1, 4-benzoquinone, N-acetyl-*p*-benzoquinone imine, *p*-acetanisidide, 4-methoxyphenol, 2-hexenoic acid, and 1, 4-dimethoxybenzene. Mineralization and rapid conversion to bound residues suggest that acetaminophen is quickly detoxified in soil, decreasing the potential for off-site transport such as leaching or runoff. On the other hand, the formation of a large number of degradation intermediates, and their potential biological activity, may pose unknown risks, such as accumulation into edible plants. This risk warrants further investigation.

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## 1. Introduction

Pharmaceutically active compounds (PhACs) are detected in great prevalence in different environmental compartments such as surface water, groundwater, and soil. Consequently, contamination of natural resources by PhACs has come to the forefront of environmental research. Thousands of tons of PhACs, after human and veterinary medication, are excreted

non-metabolized or as active metabolites and emitted into the sewage system every year (Heberer, 2002). These compounds may then be continuously released into surface waters and even drinking water due to their continual daily replenishment, or enter terrestrial systems when sewage effluent is reused for irrigation, or when sewage sludge is applied as a fertilizer to agricultural land (Kinney et al., 2006; Ternes et al., 2004). Once in soil, PhACs can be transformed as a result of biotic and abiotic reactions, leading to changes in their

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chemical state. Incomplete degradation may convert some PhACs to intermediates with altered biological activity or mobility, leading to unknown risks for off-site transport or plant accumulation. However, the majority of studies to date have focused on environmental occurrence, removal efficiency during wastewater treatment, or non-target toxicological effects (Boxall et al., 2012; Heberer, 2002). In contrast, relatively little is known about degradation of PhACs in soil (Hamscher et al., 2002). In particular, transformation pathways of commonly occurring PhACs in soil, where most of these chemicals may be eventually deposited, are seldom investigated.

Acetaminophen (*N*-acetyl-*p*-aminophenol) is the most widely used over-the-counter and prescription pain medicine in the United States (Kaufman et al., 2002). For instance, during 2001–2005, 24–29 billion doses of acetaminophen in all forms were sold (FDA, 2008). Acetaminophen was one of the most frequently detected anthropogenic compounds in a national reconnaissance of 139 streams in 1999–2000 by the United States Geological Survey (Kolpin et al., 2002), where it was detected at 24% frequency with concentrations up to 10 µg/L. In a recent study, acetaminophen was further detected in groundwater used for public drinking water supply in California at levels up to 1.89 µg/L (Fram and Belitz, 2011). On the other hand, *in vitro* and *in vivo* studies on the metabolism of acetaminophen in human (e.g., Bessems and Vermeulen, 2001; Forte et al., 1984; Laine et al., 2009; Manyike et al., 2000; Patten et al., 1993; Tsikas et al., 2011) suggested that acetaminophen-induced hepatotoxicity was a major cause of acute liver failure (ALF) in the United States (Larson et al., 2005) and that reactive metabolites of acetaminophen may have contributed to the pathogenesis of drug-induced toxicity (Park et al., 2005). The hazard quotients derived from predicted environmental concentrations (PECs) for acetaminophen were 1.8 (Kim et al., 2007) and 7.1 (Stuer-Lauridsen et al., 2000), suggesting the potential environmental concerns and need for further investigation.

The objective of this study was to elucidate the degradation pathways of acetaminophen in soil, with an emphasis on the identification of incomplete degradation products. The effect of soil types, and organic matter amendment, and the role of microorganisms in degradation, were evaluated using different soils and treatments under aerobic conditions. Both <sup>14</sup>C labeling and LC-MS/MS were used in understanding the transformative pathways of acetaminophen in soil. This information will be valuable for obtaining a more holistic assessment of environmental risks of acetaminophen and other PhACs from the same chemical class.

## 2. Materials and methods

### 2.1. Chemicals

<sup>14</sup>C-Benzyl ring-labeled acetaminophen (radiochemical and chemical purity >99%, specific activity 48.7 mCi/mmol; see Fig. S1 for structure and <sup>14</sup>C labeling position) was purchased from American Radiolabeled Chemicals (St Louis, MO). Non-labeled acetaminophen, hydroquinone, 2-hexenoic acid and 1, 4-benzoquinone were purchased from Sigma–Aldrich

(St Louis, MO). *N*-acetyl-*p*-benzoquinone imine (NAPQI) and 3-hydroxyacetaminophen were obtained from Santa Cruz Biotechnology (Santa Cruz, CA). 4-Methoxyphenol and 1, 4-dimethoxybenzene were obtained from Acros Organics (Morris Plains, NJ) and *p*-acetanisidide was from TCI Europe NV (Zwijndrecht, Belgium).

A stock solution of <sup>14</sup>C-acetaminophen was prepared in methanol at 2000 mg/L by mixing the labeled and non-labeled acetaminophen at a final specific activity of 5 µCi/mg. All organic solvents and other chemicals used were of high-performance liquid chromatography (HPLC) grade.

### 2.2. Soils and biosolids

Three agricultural soils with different physico-chemical properties taken from the top 10 cm at locations in California were used in this study. San Emigdio fine sandy clay loam (University of California Research and Education Center, Irvine, CA), Grangeville medium loam (Scott Brother's Dairy Farms, Moreno Valley, CA), and Salinas silty clay (University of California Hansen Agricultural Center, Ventura County, CA), are abbreviated herein as soil A, B, and C, correspondingly. The soils were air-dried, homogenized and sieved with a 2-mm mesh to remove plant debris and then stored at 4 °C in the dark until use. A sample of biosolids was obtained from a local wastewater treatment plant using primary, secondary, and tertiary treatment stages. The wet material was centrifuged and the dewatered sludge contained 21.7% dry solids. The OC contents of the soils and biosolids were measured by combustion on a nitrogen/carbon analyzer (Thermo Finnigan, Woods Hole, MA) after digestion with HCl (1 M) to remove carbonates. The OC content of biosolids was 45.1%. Selected properties of the test soils are listed in Table 1. Soil sterilization was accomplished by autoclaving soil A at 121 °C for 45 min over three consecutive days followed by addition of sodium azide (200 mg/L) to suppress microbial activity during incubation.

### 2.3. Experimental setup

Degradation experiments were performed using five soil treatments: soils A, B, and C, sterilized soil A and biosolid-amended soil A. All non-sterilized soils were pre-incubated for 7 d prior to <sup>14</sup>C-acetaminophen addition after adjusting the soil moisture content to 40% of the soil water-holding capacity (WHC) to revive microbial activity. To minimize the potential effect of solvent, 20 µL <sup>14</sup>C-acetaminophen stock solution ( $4.44 \times 10^5$  dpm) in methanol was dispensed onto a 1.0-g (dry weight equivalent) soil subsample or biosolids in 40-ml amber glass vial. The treated soil was mixed with a spatula in a fume hood until the solvent was completely evaporated. The spiked subsample was then mixed with 9.0 g (dry weight equivalent) of the same type of soil, while the spiked biosolid sample was homogenized with 9.0 g soil A to simulate land application of biosolids (Brown et al., 2003; Sopper, 1993). The initial acetaminophen concentration was 4 µg g<sup>-1</sup>. Deionized water was added to adjust the soil moisture to about 60% of WHC. The sterilized soil A was similarly spiked with <sup>14</sup>C-acetaminophen. All treated samples were mixed on a shaker at a low speed for 2 h to achieve uniform distribution. Blank

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