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Uptake, elimination and biotransformation of N-ethyl perfluorooctane sulfonamide (N-EtFOSA) by the earthworms (*Eisenia fetida*) after *in vivo* and *in vitro* exposure

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ABSTRACT

N-ethyl perfluorooctane sulfonamide (N-EtFOSA) is commonly known as the active ingredient of sulfluramid. It can be degraded to perfluorooctane sulfonic acid (PFOS) in biota and environment. Earthworms (*Eisenia fetida*) were exposed with N-EtFOSA to examine the bioaccumulation, elimination and metabolism of N-EtFOSA by the earthworms after *in vivo* and *in vitro* exposure. N-EtFOSA could be biodegraded in quartz sands to perfluorooctane sulfonamide (FOSA) and PFOS. In the *in vivo* tests, in addition to parent N-EtFOSA, three metabolites, including perfluorooctane sulfonamide acetate (FOSAA), FOSA and PFOS also accumulated in earthworms as a result of N-EtFOSA biotransformation, with FOSA as the predominant metabolite. The bioaccumulation factor (BAF) and uptake rate coefficient (k_u) of N-EtFOSA from sand were 20.4 and 2.41·d^{-1}, respectively. The elimination rate constants (k_e) decreased in the order FOSAA (0.130·d^{-1}) > N-EtFOSA (0.118·d^{-1}) > FOSA (0.073·d^{-1}) > PFOS (0.051·d^{-1}). The biotransformation of N-EtFOSA in earthworm was further confirmed by the *in vitro* test involving incubation of earthworm homogenates with N-EtFOSA. This work provides evidence on the accumulation and transformation of N-EtFOSA in terrestrial invertebrates and will be helpful to explore the indirect sources of FOSA and PFOS in environmental biota.

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1. Introduction

Per- and poly-fluoroalkyl substances (PFASs) have been worldwide used as surfactants and surface protectors in various industrial and commercial applications (Loi et al., 2011). PFASs include perfluoroalkyl acids (PFAAs) and their precursors, which have been recognized as environmental pollutants due to their global occurrence in environment, bioaccumulative properties and toxicological characteristics (Paul et al., 2009). Perfluorooctane sulfonic acid (PFOS) is one of the most predominant PFAAs. PFOS and related substances based on perfluorooctane sulfonyl fluoride (POSF) chemistry were added to the list of the Stockholm Convention on Persistent Organic Pollutants (POPs) for global elimination in 2009. But, many related perfluorooctane sulfonamides have also been manufactured in many countries under use exemptions (Gilljam et al., 2016). These sulfonamide substances are also known as "PFOS-precursors" (PreFOSs) which are less persistent and can be transformed to highly persistent and globally distributed PFOS in the environment and biota (Martin et al., 2010; Mejia Avendano and Liu, 2015; Rhoads et al., 2008). Identified PFOS precursors include perfluorooctane sulfonamidoethanols (FOSEs) and perfluorooctane sulfonamides (FOSAs). N-ethyl perfluorooctane sulfonamide (N-EtFOSA, $C_8F_{17}SO_2NHCH_2CH_3$) is an important PreFOS which is used as an active ingredient in sulfluramid, a pesticide for controlling leaf-cutting ants, cockroaches and termites (Gilljam et al., 2016). N-EtFOSA is being demanded in a wide range of commercial products in some developing and newly industrialized countries (Gilljam et al., 2016; UNIDO, 2012). The environmental fate of the current used N-EtFOSA has and continues to receive considerable attention.

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PreFOSs can be found in water (Boulanger et al., 2004), soil (Houtz et al., 2013), indoor air (Eriksson and Kärrman, 2015), consumer products (Fromme et al., 2009; Heydebreck et al., 2016; Ye et al., 2015), wildlife (Pan et al., 2014) and humans (Bonefeld-Jørgensen et al., 2014; Gebbink et al., 2015). N-EtFOSA is not only toxic to biota and humans (Bonefeld-Jørgensen et al., 2014; Case et al., 2000; Pan et al., 2014; Slotkin et al., 2008) but also can be degraded to the more stable and toxic ultimate metabolite PFOS (Benskin et al., 2013; Chen et al., 2015; Fu et al., 2015; Martin et al., 2010; Plumlee et al., 2009; Zhao et al., 2016). Tomy et al. (2004a) firstly reported that N-EtFOSA is likely present in Arctic biota and is biotransformed to perfluorooctane sulfonamide (FOSA). Biotransformation of PreFOSs at different trophic levels has been demonstrated *in vivo* and *in vitro*, such as FOSA in rainbow trout (Brandsma et al., 2011) and common carp (Chen et al., 2015), N-ethylperfluorooctane sulfonamide acetate (N-EtFOSAA) in invertebrate organism (Higgins et al., 2007), N-EtFOSA in rainbow trout (Tomy et al., 2004b) and top Arctic mammalian predator (arctic polar bear, beluga whale, and ringed seal) liver microsomes (Letcher et al., 2014), N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE) in earthworms (Zhao et al., 2016) and rat liver slices (Xu et al., 2004).

Due to the widely existence of PreFOSs in soil (Meng et al., 2013; Tan et al., 2014), they can be taken up by terrestrial animals living in soil. Earthworms comprise 80% of the soil fauna biomass (Smidova et al., 2015) and are able to bioaccumulate perfluoroalkyl acids (PFAAs) neutral precursors, such as N-EtFOSE (Zhao et al., 2016), FOSA (Zhao et al., 2018) and 10:2 fluorotelomer alcohol (10:2 FTOH) (Zhao and Zhu, 2017), and then biotransformed to terminal product PFAAs in soil-earthworm systems. Thus, neutral PreFOSs pose a serious environmental threat to indigenous organisms living in soil. But, the bioaccumulation and biotransformation of N-EtFOSA in earthworms has not yet been investigated or documented.

Hence, in the present study, the uptake, elimination and biodegradation of N-EtFOSA in earthworms (*Eisenia fetida*) were investigated to understand the accumulation and metabolism of N-EtFOSA in earthworms. Quartz sands were used for exposure tests to provide an inert matrix which could minimize interference of the degradation by microbes in soil. This was accomplished through *in vitro* assays involving incubation of earthworm homogenates with N-EtFOSA.

2. Materials and methods

2.1. Chemicals

The standard of perfluorooctane sulfonate (PFOS, 98%) was purchased from Shanghai Aladdin Reagent Co., Ltd. (China). Perfluorooctane sulfonamide acetate (FOSAA) and perfluorooctane sulfonamide (FOSA) were from Wellington Laboratory (Guelph, ON, Canada). N-ethyl perfluorooctane sulfonamide (N-EtFOSA, 97%) was obtained from Shanghai Macklin Biochemical Co. Ltd. (China). Tetrabutyl ammonium hydrogen sulfate (TBAHS) was purchased from J&K Chemical Ltd. (Shanghai, China). β-nicotinamide adenine dinucleotide phosphate ($NADP^+$) was from Biosharp (Hefei, China). Glucose-6-phosphate Na2 (Glc-6-PO_4) and glucose-6-phosphate dehydrogenase (G6PDH) were purchased from Sigma-Aldrich (China). Methanol of high-performance liquid chromatography (HPLC) grade was obtained from Dikma Technology Inc., USA. Methanol (HPLC grade) and methyl tert-butyl ether (MTBE) for extraction and other chemicals were bought from Dalian Bono Biochemical Reagent Ltd. (Dalian, China). Milli-Q water (18.2 MΩ) was used throughout the study.

2.2. In vivo earthworm exposure tests

Mature earthworms (*Eisenia fetida*) were obtained from an earthworm culturing farm, located in Shenyang, China. All earthworms were maintained in a laboratory culture box filled with agriculture soil (Panjin, China) at the laboratory conditions (22−27 °C) for 14 d. Earthworms were removed from the soil, washed with distilled water and allowed to depurate on moist filter paper for 24 h before the experiment was commenced.

A stock solution of technical N-EtFOSA at 400 μg mL^{-1} was prepared in methanol, and then it was diluted with water to the desired concentration with methanol (0.01% v: v) for test aqueous solutions. Earthworms were exposed in a 250 mL glass beaker containing 200 g of rinsed and sterilized quartz sands (mean diameter of 1 mm) and 50 mL of test aqueous solution containing N-EtFOSA. The original N-EtFOSA concentration spiked in the sand was 0.78 nmol g^{-1} dry weight (dw), and the moisture of the sand was adjusted every day to keep approximately 20% (by weight). There were 33 containers for N-EtFOSA treatment, and each container held 10 test earthworms (approximately 3 g wet weight). Earthworms were randomly sampled after 1, 2, 4, 6, 8 and 10 d to study the uptake kinetics, and at each sampling time, three beakers (10 earthworms/beaker) were sacrificed (n = 3). For excretion kinetics, the earthworms were sifted from the N-EtFOSA spiked sand at the end of exposure (10 d), washed with distilled water and transferred into 15 glass beakers (250 mL) containing 200 g of clean quartz sands. Each beaker added 10 test earthworms. Earthworms were then sampled from each beaker on days of 12, 14, 16, 18 and 20. Earthworms which were exposed to the quartz sands with distilled water but without N-EtFOSA were set up as the contamination blank. Each treatment was conducted in triplicates (n = 3). All the beakers were capped with aluminum foil and kept in dark at 22 ± 2 °C. The collected earthworms were washed with deionized water, and allowed to purge on clean filter paper for 24 h, wiped with clean towel paper, weighed immediately and stored at −20 °C before chemical analysis.

Spiked quartz sands without earthworms were set up as earthworms-free controls and the sands were collected from the glass beakers on days of 0, 1, 2, 4, 6, 8 and 10 d. The sand samples were freeze-dried for 48 h in a lyophilizer (FD-1A-50, Beijing Boyikang Instrument Ltd.) and then stored in polypropylene (PP) tubes before chemical analysis. Detailed information on estimation of degradation rate constant and degradation half-life of N-EtFOSA in earthworms-free control sand is provided in the Supporting Information (SI).

2.3. In vitro incubation

The *in vitro* assays were performed on the basis of the methods in previous studies with some modifications (Chen et al., 2015; Renoux et al., 2000). Fifty acclimatized earthworms, which were exposed in non-spiked sterilized quartz sands for 48 h and purged on wet filter paper for two-cycles of 24 h, were homogenized using a mechanical homogenizer in cold buffer (4 °C, 0.1 M 21 phosphate buffer at pH 7.4, 1 mM ethylenediaminetetraacetic acid, 0.15 mM KCl) solution at a ratio of 1 g homogenate per 4 ml of buffer. The *in vitro* incubations were conducted in a series of polypropylene (PP) tubes (50 mL, autoclaved before use) in which 50 μL of N-EtFOSA solution in methanol (8 μg mL^{-1}), 3.95 mL of 0.05 M phosphate buffer (pH 7.4), 500 μL of premixed NADPH (nicotinamide adenine dinucleotide phosphate) regenerating solution (containing 1.6 mM $NADP^+$, 3.3 mM Glc-6-PO_4, 0.4 U·mL^{-1} G6PDH, and 3.3 mM magnesium chloride), and 0.5 g of earthworm homogenates were added. The initial exposure concentration of N-EtFOSA was set at 1.03 nmol g^{-1} wet weight. Reaction mixtures were vortexed and

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