



Thiosteranes in samples impacted by fecal materials and their potential use as marker of sewage input



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ABSTRACT

Sewage impacted soil, sludge and water samples were studied to understand the occurrence and formation of thiosteranes and to determine the relevance of these compounds as tracers for sewage input into the environment. Soils were collected from wastewater irrigation fields (Wrocław, Poland), water from the Nexapa River Basin (Mexico), which also received wastewater and wastewater treatment plant (WWTP) effluent, and water and sludge from the Norman WWTP (USA) at different treatment stages. Thiosteranes represented a high proportion of the steroid fraction in the Wrocław irrigation field and the Nexapa River Basin samples. Small amounts of thiosteranes were found in anaerobically digested sludge from the Norman WWTP. A good correlation between coprostanone and thiosterane concentrations suggests thiosteranes were produced by stanone sulphurization under anoxic conditions. Thiosterane stability under anoxic and suboxic conditions indicates their potential use as tracers for environmental input of sewage products or land application of sewage sludge.

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1. Introduction

Fecal contamination is a widespread issue as it affects urbanized areas as well as rural zones and wild regions throughout the world. It is one of the most important causes of water quality degradation as it is often associated with pathogenic organisms (Sims and Wolf, 1994) and it causes an increase in nutrient concentrations which is favorable to alga proliferation (Mainstone and Parr, 2002) and leads to eutrophication of the system (Hilton et al., 2006). Fecal materials can originate from different sources including wildlife, various agricultural activities, domesticated animals, land application fields, urban runoff, and failing onsite wastewater disposal systems. The presence of fecal material and, more precisely, the associated pathogenic organisms is a major health issue especially when the water is used for recreational activities and/or as a supply for drinking water because they can be responsible for many diseases (McNinch et al., 2009; Pond, 2005).

Some sterols, referred to as fecal sterols or fecal stanols, can be used to track fecal contamination as they are formed by sterol

biohydrogenation in the digestive track of many warm-blooded animals (Martin et al., 1973). Coprostanol, which is derived from cholesterol by reductive bacteria during digestion (Grimalt et al., 1990), is the major fecal stanol encountered in human feces (Leeming et al., 1996). It has been used extensively to track fecal contamination from wastewater, septic tank sewage and wastewater treatment plants (WWTP) (Carreira et al., 2004; Chou and Liu, 2004; Grimalt et al., 1990; Leeming et al., 1997; Mudge et al., 1999; Sojinu et al., 2012; Standley et al., 2000; Takada et al., 1997). However in many cases the use of a single compound does not allow source identification (Blanch et al., 2006) and it is often necessary to integrate other tracers or tools to determine precisely the origin of contamination (Biache and Philp, 2013; de Abreu-Mota et al., 2014; Derrien et al., 2011; Gourmelon et al., 2010; Jardé et al., 2009; Martins et al., 2014).

Thiosteranes started to arouse interest in a geological and environmental context as they have been detected in various samples such as sedimentary rocks (Jiamo et al., 1991; Schaeffer et al., 1995), crude oils (Jiamo et al., 1991; Lu et al., 2013), sediments (Louati et al., 2001; Safi, 2004), sewage sludge and compost samples (Mejía et al., 2008; Rushdi et al., 2013). It has been proposed that thiosteranes are formed in marine and lacustrine sediments via incorporation of the thiol group into Δ^2 sterenes (double

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Table 1

Summary of the collected samples, their origins, the extraction and fractionation techniques and the molecular analyses performed. (WWTP: wastewater treatment plant, MeOH: methanol, DCM: dichloromethane, SPE: solid-phase extraction, TMAH: tetramethylammonium hydroxide, TMSH: trimethylsulfonium hydroxide, BSTFA: N,O-bis(trimethylsilyl)trifluoroacetamide).

Sample type	Origin	Extraction/derivatization	Fractionation	Molecular analyses
Soil	Wroclaw irrigation field (Poland)	Soxhlet extractions (DCM/MeOH, v/v 93/7)	Non polar <i>n</i> -hexane soluble fraction	Qualitative GC-MS analyses
		Pyrolysis with methylation (TMAH) of extracted soil residue	DCM soluble fraction	Qualitative GC-MS analyses
Primary sludge	Krotoszyn WWTP (Poland)	Soxhlet extractions (DCM/MeOH, v/v 93/7)	Solvent fractionation; <i>n</i> -hexane soluble fraction	Qualitative GC-MS analyses
		Pyrolysis with methylation (TMAH) of extracted residue	DCM soluble fraction	Qualitative GC-MS analyses
Water and particulate	1999–2000: Nexapa River (Mexico)	Liquid–liquid and Soxhlet extractions (DCM).	Liquid chromatography on alumina/silica separation columns (for identification only)	Qualitative (identification) and quantitative GC-MS analyses.
	2003–2004: Nexapa River, creeks and sewer discharges			
Water, particulate and sludge	2012–2013: Nexapa River and Izúcar WWTP	SPE (ethyl acetate) and sonication (MeOH and DCM/acetone v/v 1/1)	Cleanup on silica column of particulate extracts	Quantitative GC-MS analyses with derivatization (TMSH)
	Norman WWTP (USA)	SPE (DCM) and sonication (MeOH, DCM/MeOH v/v 1/1 and DCM)	liquid chromatography on alumina and silica separation column	Quantitative GC-MS analyses with derivatization (BSTFA)

bond located in C2) (Louati et al., 2001), the A or B ring, or the side chain of sterols or derivatives (Jiamo et al., 1991). The commonly observed 2α - and 3β -thiosteranes with the thiol group bound in ring A strongly supports their origin via addition of H_2S (origin-anaerobic degradation) across the Δ^2 double bond of the sterenes (Schaeffer et al., 1995). Mejía et al. (2008) have previously stated that selective formation of 3β -thiosteranes occurs in sewage sludge samples, and their concentrations increase after the anaerobic digestion process during the sludge treatment. Their occurrence in such samples should be explored in order to determine if these compounds can be used as additional tracers to monitor sewage inputs. However it is necessary to understand the mechanism for the selective formation of the 3β -thiosteranes in this context and this is still unclear.

Therefore, the aim of the present study was to explore the occurrence of thiosteranes in various kinds of samples from different environmental media impacted by fecal material/sewage contamination in order to understand mechanisms of their formation in different contexts and evaluate their potential as tracers to monitor sewage input. Four groups of samples were studied and screened for thiosteranes. The first set of samples consisted of soils from fields irrigated by municipal effluent in the Wroclaw area (Poland). The second set of samples consisted of primary sludge collected from the WWTP in Krotoszyn (Poland). The third set of samples consisted of water collected from the Nexapa River Basin (Mexico) and sludge collected from a WWTP located in that area (Navarro Frómata and Philp, 2007). The fourth sample set consisted of water and sludge collected from WWTP in Norman (OK, USA) at different stages of the treatment. Comparison of thiosterane distributions in diverse sample sets such as those described above, originating from different localities and geochemical environments, is innovative. It is anticipated that such a study should shed some light on the mechanisms involved in the formation of thiosteranes during anthropogenic processes.

2. Experimental

It should be noted that the results in this study represent three independent studies. After the studies had been completed and as a result of discussions and meetings it was decided to combine the results from these three studies into one comprehensive paper rather than three separate publications. As a result it is inevitable

that there will be some variations in the collection methods and analytical procedures. However the overall aim of all the studies was to investigate the distribution of the thiosteranes in all of these samples and that common goal was achieved. Table 1 summarized the different samples, extractions, fractionation and analyses.

2.1. Study areas and sample pre-treatments

2.1.1. Irrigation fields-wroclaw osobowice in Poland

These irrigation fields cover 1100 ha and have been intensively irrigated with municipal wastewater since the end of the 19th century. Wastewater was discharged into the irrigation fields from settling ponds via an irrigation channel. Six sites were sampled (Fig. S1) and five of them (site 1–5) were located along, or close to, the irrigation channel. Site 6 was located in a runoff area and has not been affected by the irrigation for the last 15 years. A reference sample (site 0) represented by a sandy soil, similar in nature to the soils taken at the other sites, was taken from outside the irrigation field. All samples were collected from a soil layer located 10 cm below the surface. Eh and pH were measured and the obtained values (0.180 mV and 6.37, respectively) placed the soil in the sub-oxic category according to Sposito (2008). After collection, soils were air-dried and stored at room temperature prior to further analyses.

2.1.2. The Krotoszyn WWTP, Poland

The WWTP of Krotoszyn is located 100 km north to Wroclaw (Poland). Raw primary sludge containing 91.3% of water was collected from the Krotoszyn WWTP. Alkaline hydrolysis was applied to the sludge in order to check its impact on the thiosterane distribution and stability. Lime suspension (217.5 g at 20% w/w concentration) was added to 10 kg of sludge to obtain a concentration of 5% $Ca(OH)_2$ based on the sludge dry weight (dw). The treated sludge was homogenized by stirring for a 10 week period. Each week, 47 mL of the treated sludge, containing the equivalent of 4 g of dry sludge initial mass, was collected for analyses. A sample (46 mL) of raw sludge (4 g dw) (without any treatment) was also taken as a reference sample. The samples were then filtered and dried, before being extracted.

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