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Fast low-pressurized microwave-assisted extraction of benzotriazole, benzothiazole and benezenesulfonamide compounds from soil samples

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ABSTRACT

Benzotriazoles (BTRs), benzothiazoles (BTs) and benzenesulfonamides (BSAs), compounds largely used in industrial and household applications, are ubiquitous emerging contaminants. In this work a novel, straightforward procedure for the simultaneous determination of two BTRs (1H-benzotriazole, 5-methyl-1H-benzotriazole), three BTs (benzothiazole, 2-hydroxybenzothiazole, 2-methylthiobenzothiazole) and two BSAs (benzenesulfonamide, toluenesulfonamide) in soil has been developed. The target analytes were extracted from soil by a single low-pressurized microwave-assisted extraction (MAE) cycle (120 °C, 10 min) and quantified by high-performance liquid chromatography with UV detection. For all the seven analytes, quantitative extraction yields (72–119%, $n=4$) were observed from recovery tests on soil samples (1 g) spiked with 5, 10 and 50 mg kg^{-1}, using 4 mL water-methanol (85:15) as extracting solution. For the lower concentrations levels (100, 250 and 500 μg kg^{-1}), the analytes were extracted from soil samples (2–3 g) using 6 mL methanol, and the extract was pre-concentrated by evaporation before analysis; recoveries in the range 70–117% were obtained ($n=4$). Suitable intra-day and inter-day precision were observed, with values of relative standard deviation generally below 6% and 11% ($n=4$), respectively. Linearity was evaluated in the concentration range 0.5–10 mg L^{-1} by matrix-matched standards, obtaining $r^2 > 0.9996$. The experimental method quantification limit (MQL) was 100 μg kg^{-1}. The entire procedure has been successfully applied to the analysis of real impacted soil samples.

1. Introduction

Among the various classes of environmental pollutants, benzotriazole (BTR), benzothiazole (BT) and benzenesulfonamide (BSA) derivates are important emerging contaminants and increasing attention is being devoted to their occurrence, behavior and fate. These compounds are high-volume production chemicals, largely used in industrial and household applications. In particular, BTRs are mainly employed as anticorrosive additives in several anti-icing fluids and as silver protectors in dishwater detergents; BTs as vulcanization accelerators and biocides; BSAs as plasticizers and intermediate synthesis products for pesticides, drugs and artificial sweeteners, like saccharin [1].

The base chemical structure of BTRs consists of a five-member ring with three nitrogen atoms sharing a C–C bond with a benzene ring, while BT derivates present a five-member 1,3-thiazole ring attached to a benzene ring by a common C–C bond; BSAs have a benzene or toluene ring with a sulphonamide group substituent. The molecular structures of the compounds here studied are presented in Fig. 1.

All these compounds are characterized by good chemical stability, high polarity and water solubility, and resistance to biodegradation [1]. Differently from other micropollutants such as sulfa drugs [2], herbicides [3] and fluoroquinolone antibiotics [4,5], also photochemistry under natural conditions as abiotic transformation path is scarcely efficient in their removal from contaminated ecosystems, as reported for BTRs [6], unless working under hard irradiation conditions or advanced oxidation processes [7]. Moreover, the relatively low octanol–water partition coefficients (K_{ow}) strongly favor the mobility in water phase [1,8].

Such physical–chemical properties are at the basis of their wide diffusion in the environmental aquatic compartments, as a results of wastewater effluent discharge from municipal and industrial sewage treatment plants, that ensure only a partial abatement [7,9]. Indeed, BTRs, BTs and BSAs have been frequently detected in actual waters at concentrations almost ranging from 1 to 100 μg L^{-1} [9]. There is concern about their presence in the

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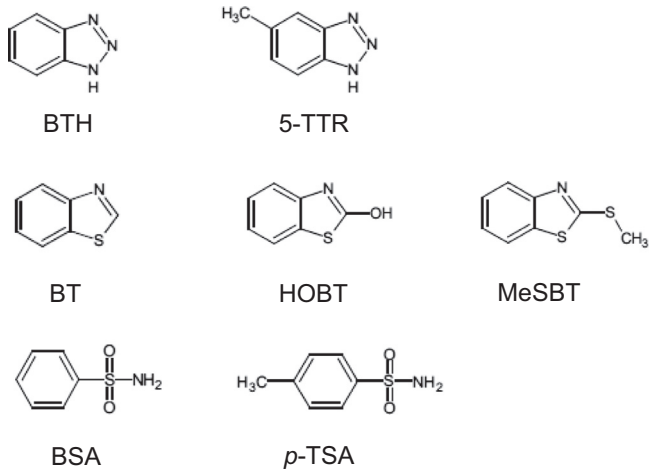

Fig. 1. Molecular structures of the selected compounds: 1-H-benzotriazole (BTH), 5-methyl-1-H-benzotriazole (5-TTR), benzothiazole (BT), 2-hydroxybenzothiazole (HO-BT), 2-methylthiobenzothiazole (MeSBT), benzenesulfonamide (BSA) and *para*-toluenenesulfonamide (*p*-TSA).

environment due to the adverse effects on wildlife and human health. With regard to this, BTRs were proved to be phytotoxic, mutagenic in bacteria, estrogenic in fish and, in particular, 1-H-benzotriazole (BTH) is also suspected to be human carcinogen and endocrine disrupting compound; BTs are dermal sensitizers and related to mutagenicity in microorganisms and carcinogenity in humans [10]. More limited information is currently available for BSAs, although a moderate toxicity has been attributed to *para*-toluenesulfonamide (*p*-TSA), and further studies are actually required [11].

Beside surface waters also soil contamination needs to be considered, as only few data are currently available about the occurrence of BTRs, BTs and BSAs in soil and sediment [6]. It is reasonable to assume that BTRs, BTs, and BSAs can reach the terrestrial compartment through the application of sewage sludge, often reused as one of the most sustainable options for agricultural purposes. Indeed, the presence of such compounds in sludge has been recently ascertained, at concentrations up to some hundreds of nanograms *per* gram [12,13]. It should be also noticed that BTR levels up to 1700 and 13,000 μg kg^{-1} were determined in impacted soil and sediment collected near airports, respectively [14], as a result of the runoff from the application of aircraft de-icing/anti-icing fluids, that is a major contamination input [6,15]. In this context, it has to be underlined that BTRs were detected in soil also after two years after the cessation of de-icing activity, evidence of their environmental persistence [14]. Despite the relatively low K_{ow} values, different mechanisms are involved in sorption to soil, *viz.* hydrophobic interaction of the apolar portion of the molecule with organic matter, charge transfer and ion exchange with clay minerals, hydrogen bonding, and sorption with intraparticle diffusion [16]. It has been reported that BTRs sorption in top soils varies as function of the organic carbon content (0.3–1.7%), with sorption capacities up to several hundred mg kg^{-1} [16].

At present only few analytical methods are available for determination of BTRs, BTs or BSAs in sewage sludge, based on pressurized [10,12,17,18] liquid extraction, and Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) extraction [13]. Just one paper reports the extraction of three BTR derivates from soil [15] and another one for extraction of two BTRs from sediment [19]. Specifically for soil, it was found that a double vortex extraction in aqueous-organic phase prior chromatographic separation provided poor recovery (around 30%) [15]; on the contrary, a two-cycles liquid–solid extraction with methanol followed by solvent change prior solid-phase extraction and liquid chromatography gave recovery higher than 70% [19]. No analytical method is currently available for determination of BTRs, BTs and BSAs in soil.

This work presents a simple, straightforward and accurate procedure for simultaneous and quantitative extraction of two BTRs (1-H-benzotriazole, 5-methyl-1-H-benzotriazole), three BTs (benzothiazole, 2-hydroxybenzothiazole, 2-methylthiobenzothiazole) and two BSAs (benzenesulfonamide, *p*-toluenesulfonamide) from soil. The microwave procedure involves a single cycle low-pressurized microwave-assisted extraction, not yet tested for determination of such compounds in solid environmental matrices, followed by liquid chromatography UV detection. The extraction yields have been investigated at concentration levels ranging from 100 μg kg^{-1} to 50 mg kg^{-1}, to cover realistic situations. The analytical figures of merit of the method, i.e. selectivity, linearity, sensitivity, accuracy (trueness and precision), have been explicated, and the final procedure has been applied to the analysis of impacted soil samples, confirmed by mass spectrometry.

2. Experimental

2.1. Chemicals and materials

All the chemicals employed were reagent grade or higher in quality and used with no further purification. 1-H-benzotriazole (BTH, ≥99%), 5-methyl-1-H-benzotriazole (5-TTR, 98%), benzothiazole (BT, 96%), 2-hydroxybenzothiazole (HO-BT, 98%), 2-methylthiobenzothiazole (MeSBT, 97%), benzenesulfonamide (BSA, ≥98%), methanol (≥99.9%). HPLC gradient grade ACN was purchased by VWR (Milan, Italy). H_3PO_4 (85%, w/w), NH_3 (30%, v/v) and *para*-toluenesulfonamide (*p*-TSA, 99%) were obtained from Carlo Erba Reagents (Milan, Italy). Ultrapure water (resistivity 18.2 MΩ cm^{-1} at 25 °C) was produced in laboratory by a Millipore Milli-Q system. BTRs, BSAs and BTs stock solutions of 100 mg L^{-1} were prepared in methanol, and stored in the dark at 4 °C for a maximum of 1 month; working solutions of 0.5–10 mg L^{-1} were prepared daily.

2.2. Instruments and apparatus

A sequential low-pressurized microwave solvent extraction system, equipped with a volume independent IR temperature sensor, electromagnetic stirring and cooling device (Discover SP, CEM S.r.l., Cologno al Serio, Italy) was employed. A Sigma 2-16P centrifuge (Celbio S.p.a., Pero, Italy) was used after sample extraction.

The HPLC–UV system consisted of a Shimadzu (Milan, Italy) LC-20AT solvent delivery module equipped with a DGU-20A3 degasser and interfaced with a SPD-20A UV detector. A Thermo Scientific Accucore XL C18 (100 × 4.6 mm, 4 μm) column, purchased from Microcolumn (Lissone, Italy) coupled with a similar guard-column was used.

2.3. Sample collection and storage

A typical agricultural soil from South Lombardy plain, collected in Ferrera Erbognone (Pavia, Italy) was used as blank matrix for recovery tests and accuracy evaluation. The physico-chemical properties and mineralogical composition are reported in Table 1. After collection, the sample was left to dry at room temperature, homogenized and sieved (0.2 mm). Soil samples (1–3 g) were then fortified at different concentration levels (100, 250, 500 μg kg^{-1} and 5, 10, 50 mg kg^{-1}) into 5 mL weight-boats and stored overnight at room temperature to allow solvent evaporation and adsorption of the analytes to the matrix sites.

Natural-contaminated samples were collected (0–20 cm depth)