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use of Antec's:
ROXY EC system (with Magic Diamond electrode)

ORIGINAL PAPER

Electrochemistry-mass spectrometry for mechanistic studies and simulation of oxidation processes in the environment

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Abstract Electrochemistry (EC) coupled to mass spectrometry (MS) has already been successfully applied to metabolism research for pharmaceutical applications, especially for the oxidation behaviour of drug substances. Xenobiotics (chemicals in the environment) also undergo various conversions; some of which are oxidative reactions. Therefore, EC-MS might be a suitable tool for the investigation of oxidative behaviour of xenobiotics. A further evaluation of this approach to environmental research is presented in the present paper using sulfonamide antibiotics. The results with sulfadiazine showed that EC-MS is a powerful tool for the elucidation of the oxidative degradation mechanism within a short time period. In addition, it was demonstrated that EC-MS can be used as a fast and easy method to model the chemical binding of xenobiotics to soil. The reaction of sulfadiazine with catechol, as a model substance for organic matter in soil, led to the expected chemical structure. Finally, by using EC-MS a first indication was obtained of the persistence of a component under chemical oxidation conditions for the comparison of the oxidative stability of different classes of xenobiotics. Overall, using just a few examples, the study demonstrates that EC-MS can be applied as a versatile tool for mechanistic studies of oxidative degradation pathways of xenobiotics and their possible interaction with soil organic matter as well as their oxidative stability in the environment. Further studies are needed to evaluate the full range of possibilities of the application of EC-MS in environmental research.

Keywords Degradation · Xenobiotics · Environment · Electrochemistry · Mass spectrometry

Introduction

The fate of chemicals in the environment in terms of persistence and degradation behaviour is a field of increasing interest for environmental research [1]. Numerous xenobiotics, such as pesticides and veterinary antibiotics as well as their derivatives directly influence the ecosystem (e.g. due to liquid manure). Some of these compounds undergo further chemical and/or microbial transformations after exposure to aquatic and/or terrestrial systems. Veterinary antibiotics are probably already metabolized prior to expulsion. Ultimately, numerous mechanisms contribute to the successive degradation of these substances. Besides hydrolysis under acidic or basic conditions, microbial conversions are common main degradation mechanisms. Light-induced reactions at surfaces in terrestrial and aquatic systems also contribute to the range of chemical conversions [2, 3]. Redox reactions in the environment are often supported by metal or metal-oxide catalysis, sometimes mediated by UV irradiation [4, 5]. All these reactions typically cover a time frame from several hours up to a few days. However, there are substances that remain as persistent organic pollutants in the soil for years or even decades [6, 7]. For new xenobiotics, there is often no reliable information about the possible degradations they

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could undergo in nature. This may even prohibit their authorization as a commercial product. Consequently, there is a need for rapid methodologies to cope with this problem. Indeed, degradation and metabolism processes are traditionally observed indirectly by extraction of degradation products (e.g. [8–11]). In addition, expensive and time-consuming lysimeter and field studies are applied.

Since oxidation is one degradation pathway in environmental chemistry [12], we aimed to use known EC-MS techniques [13–17] as a screening tool. In this way, we investigated the use of electrochemistry to simulate known oxidative degradations or even predict potential degradation mechanisms. Interestingly, electrochemical oxidation is already commonly used in wastewater treatment [18, 19] although no comparison of this method with natural degradation has yet been published.

Oxidation stability/reactivity and persistence data of well-known xenobiotics are indeed available in the literature, especially from wastewater treatment research [20]. For example, s-triazine pesticides such as atrazine are known to be very persistent [21]. Veterinary antibiotics such as sulfadiazine and tetracycline are less persistent and form a number of metabolites [2], and tetracycline is known to degrade even in solution [22].

While previous studies with EC-MS compared reactions in an electrochemical cell, almost exclusively with respect to mammalian metabolism, this study will extend the method to more environmental issues. The study discusses three aspects of the metabolism of xenobiotics in the environment: (1) the comparison of the electrochemical degradation of sulfadiazine—a typical sulfonamide used as a veterinary antibiotic—with the metabolites known from the literature, (2) the chemical reaction of sulfadiazine with a model substance for soil organic matter to demonstrate a model system for the formation of non-extractable residues and (3) the comparison of the reactivity of three strongly differing xenobiotics (*atrazine, sulfamethoxazole and tetracycline)* under oxidative conditions in the electrochemical cell with their known trends of persistence or stability in the environment.

The aim is to establish an approach for achieving better understanding or prediction of the transformation of chemicals in the environment by using pure substances in solution. This approach is still provisional and will not replace soil or lysimeter experiments under real conditions. However, it would provide first information on the outcome of these long-term experiments.

Experimental

Chemicals and instrumentation

All solvents and chemicals were used as received from the commercial suppliers. Sulfadiazine (99.9%) and tetracycline (95%) were purchased from Sigma Aldrich (Steinheim, Germany). Sulfamethoxazole (99.9%) and atrazine (97.4%) were analytical standards from Riedel-de-Haen (Seelze, Germany). Catechol (99.5%) was obtained from Fluka (Buchs, Switzerland). Ammonium acetate (p.a.), acetonitrile and methanol (both LiChrosolv purity) were purchased from Merck KGaA (Darmstadt, Germany). Formic acid was obtained from ROMIL (Cambridge, UK). Water of high purity (18.2 MΩcm) was produced by a *MilliQ plus 185* (Millipore, Molsheim, France).

MS experiments were carried out using an ESI-LTQ-FT Ultra (ThermoFisher Scientific, San Jose, CA, USA) equipped with a 7 T supra-conducting magnet. The MS was combined with a commercial EC-cell setup from Antec Leyden (The Netherlands). It consisted of a ROXY EC system (Antec, The Netherlands) for single compound screening equipped with a thin-layer cell (ReactorCell™, Antec, The Netherlands). An infusion pump was used in all experiments. The ROXY conductive diamond electrode (Magic Diamond™, Antec, The Netherlands) was used as a working electrode and HyREF™ (Pd/H_2) as the reference electrode. The inlet block that is made from conductive material was the auxiliary (counter) electrode. The spacer of 50-μm thickness is placed between the working and counter electrodes, giving the cell volume of approximately 500 nL. EC System is controlled by Dialogue software (Antec, The Netherlands). The working electrode potential was applied in range from 0–2,500 mV to find optimal conditions for metabolite generation by means of user programming and executed automatically. After each change of the cell potential mass spectra were recorded. Each MS acquisition was started by contact closure signal send by ROXY potentiostat. A capillary from the EC cell was directly coupled to the ESI ion source of the hybrid mass spectrometer. The temperature-sensitive EC reactions were performed at a constant temperature of 35 °C.

Mass spectrometric conditions

The mass spectrometer was used in positive mode and calibrated following a standard optimization procedure for all voltages and settings with the appropriate calibration solution suggested by the supplier, composed of caffeine, the peptide MRFA and ultramark. Therefore, the settings of the ion optics varied slightly from day to day. The ion source parameters varied with different analytes: the spray voltage ranged between 3.5 and 4.0 kV; the capillary voltage varied between 3 and 42 V; and the tube lens varied between 45 and 105 V. No sheath or aux gases were used; the transfer capillary temperature was set to 275 °C. Mass spectra were recorded in full scan from 90–600 *m/z*, first with the linear trap, followed by Fourier transform ion cyclotron resonance (FTICR) mass spectra (measured at a

resolution of 100,000 at 400 *m/z*). Collision-induced dissociation (CID) experiments were performed in the LTQ with helium as collision gas.

Electrochemical oxidation

The EC was used in the same way as described elsewhere [15, 23]. In all cases, a solution of xenobiotic (20 μM) passed through the electrochemical cell at a flow rate of 10 μl/min. A constant voltage (DC) or a potential ramp with a slope of 10 mV/s was applied. The residence time of the analyte at the working electrode was 3 s (500 nl cell volume at a flow rate of 10 μl/min). All oxidations were performed using a glassy carbon (GC) and a boron-doped diamond (BDD) electrode. In most of the experiments, BDD electrodes yielded a higher amount of oxidized species compared with GC electrodes. Since the oxidation products were identical under both conditions, the BDD material was the electrode of choice. The experiments varied with respect to different parameters such as pH, content of organic solvent, ionic strength of aqueous part to achieve good oxidation behaviour with the example of sulfadiazine. The highest number of oxidation products was observed in a 5-mM ammonium acetate solution at neutral pH. Oxidation in pure water was inefficient, evidently due to the lack of charge carriers. To minimize ion suppression in MS experiments, the buffer concentration was further reduced to at least 200 μM without a noticeable decrease in oxidation efficiency. By varying the content of organic solvent (10%, 30% and 50% methanol or acetonitrile), the electrospray is supported and adsorption of the analytes to the electrode surface can be suppressed. The addition of 30% methanol gave the best results in signal intensity and total ion current stability, while adsorption phenomena were not observed and there was no problem with the oxidation of methanol.

The optimized conditions were also used for the other xenobiotics to allow a reasonable comparison. Cyclovoltammetric measurements were performed in the same buffer at a scan speed of 50 mV/s in the range from −0.3 to 2.0 V. Oxidation of catechol in the presence of sulfadiazine was conducted at a glassy carbon electrode since catechol did not oxidize at a BDD electrode (not shown).

In many studies, the EC-LC-MS coupling is used instead of EC-MS to prevent quenching of the ions of interest. In this study, the main focus was on comparison, not on quantification. Therefore, the simpler and, above all, faster direct coupling of EC to the MS was applied allowing higher detection speed for putative instable metabolites. As a result, it was found that the complete oxidation mechanism for sulfadiazine was elucidated without prior separation of the metabolites.

Results and discussion

Comparison of sulfadiazine metabolites formed in the environment and by chemical oxidation in the electrochemical cell

Sulfadiazine was chosen as a test compound for a comparison of derivatives generated by EC oxidation since its behaviour in environmental systems is well described. It forms a number of metabolites as known from the literature [11, 24, 25]. Most of them can be extracted from soil. Metabolites of sulfadiazine are demonstrated to be formed by typical chemical/biochemical transformations, whereas some probably also arise directly by chemical oxidation. We assumed that these metabolites can also be formed by the EC-MS setup used.

Figure 1 shows the mass spectra of the pure sulfadiazine by flow injection (upper part) before and after EC treatment (lower part). The arrows indicate some of the additional peaks formed in the EC. Setting the mass spectrometer to the individual masses found in the infusion experiment allowed the voltage dependence to be determined during the generation of the metabolites as shown in Fig. 2. This profile is characteristic of all experiments described in this paper. The starting material significantly decreases at voltages higher than 1,100 mV, and some metabolites reveal a maximum and probably undergo further chemical conversions at higher voltages. Others only appear at higher voltages. In general, the mechanism of the conversion may be different in aqueous solution for low voltage compared with high voltage due to the high overpotential for oxygen evolution at BDD electrodes, which allows OH-radical formation [26]. Therefore, in general, a potential ramp for the whole voltage range was performed.

The structures of the generated masses were first elucidated by recording the exact masses with FTICR-MS. The elemental composition/molecular formula was then created (Table 1). The next step was CID fragmentation experiments in the LTQ: applying the known masses produced under optimal EC conditions. Fragmentation was performed once or twice in the LTQ and the results recorded, usually in the FTICR (Table 2). By combining these and earlier results about the cyclovoltammetric behaviour of sulfadiazine at low voltages [27], it is possible to suggest an oxidative degradation mechanism for sulfadiazine as given in Fig. 3.

As the first step in the conversion process, a two-electron oxidation is proposed in agreement with the literature [26]. It must be noted that the intermediates shown may also occur with consecutive one-electron oxidations. By considering the appearance of the coupling product (*m/z*=340) and the *p*-iminoquinone (*m/z*=108), a reactive anilinium cation was deduced. However, aniline itself was not detected in the study.

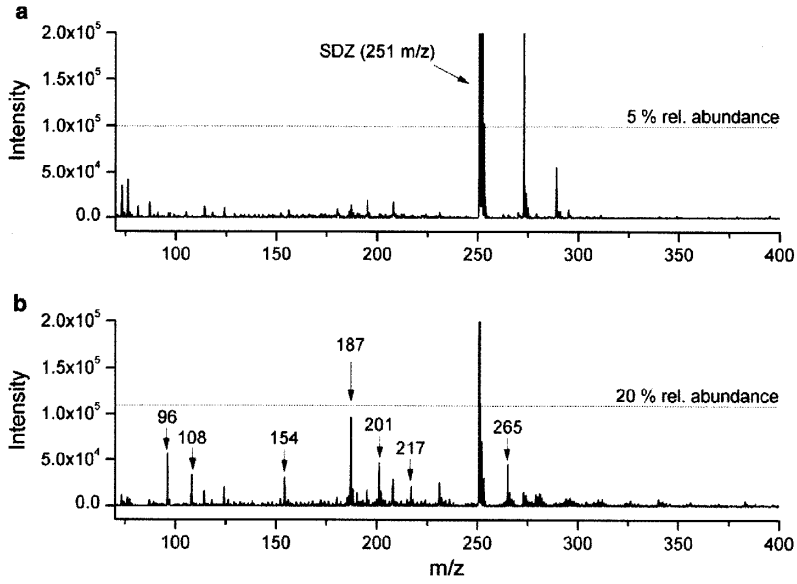


Fig. 1 **a** Mass spectrum of pure sulfadiazine (*SDZ*) without voltage applied to the electrochemical cell. **b** Mass spectrum of SDZ after electrochemical oxidation. Highlighted *m/z* ratios are related to oxidation of SDZ. EC conditions: 10-µl/min flow at a BDD working electrode, 2,500 mV vs. reference electrode. Sample: 40-µM SDZ in 200-µM NH_4OAc, pH 6.8/MeOH 70:30 (*v/v*)

The correlation of the metabolites found in the oxidative electrochemical conversion had to be evaluated with other metabolism studies and with the metabolism found in the environment. In the study by Sukul, three types of metabolites were found [24]: (1) products hydroxylated in the heteroaromatic ring, (2) reactions of the amine group to form acetyl and formyl groups and (3) the oxidation products aniline, 2-aminopyridine and 4-(2-iminopyrimidine-1(2H)-yl)aniline.

In this study, three typical EC reactions were observed: (1) the introduction of oxygen in the aromatic ring is obtained (*m/z*=201, 217, 265, 108), which has not previously been described in sulfadiazine degradation, (2) the loss of SO_2 (*m/z*=187) as a typical degradation step also found in soil/aquatic/biological systems and (3) the cleavage of the sulfadiazine molecule at the sulfonamide group, which is a relevant hydrolysis reaction in environmental systems.

The hydroxylation and the acetyl/formyl derivatization could not be observed here, because the EC experiments were performed in buffered solution without any additives such as oxidizing agents. However, three products found in the photochemical study by Sukul were identified under EC conditions. Two of these three products (aniline and aminopyrimide) were not found in soil or manure because they are expected to form bound residues [24]. Finally, only 4-(2-iminopyrimidine-1(2H)-yl)-aniline was detected in the environment [24]. Overall, the products derived by EC oxidation are comparable to the products of photochemical conversation. While some of the obviously more stable intermediates of the EC-MS experiment were found in soil

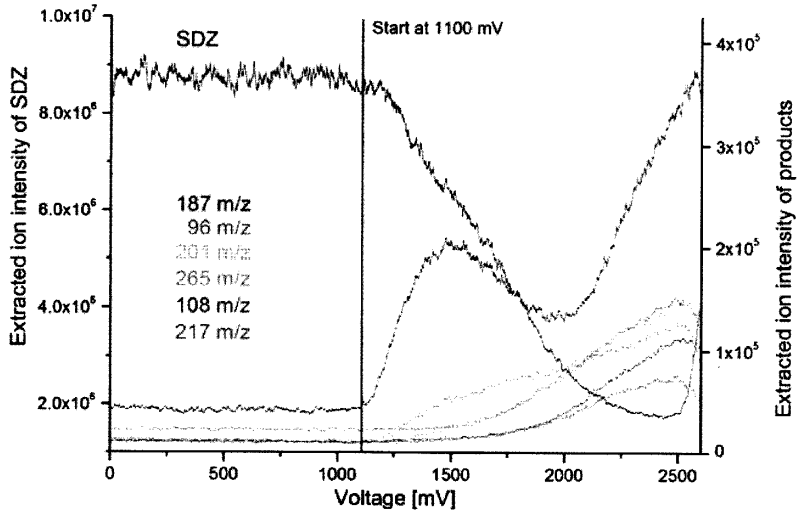


Fig. 2 Effect of oxidation potential on selected *m/z* ratios. Mass voltammogram was measured in flow injection mode while a potential ramp from 0 to 2,500 mV was applied with a slope of 10 mV/s. EC conditions same as in Fig. 1

Table 1 High-precision FTICR-MS masses and corresponding elemental composition of the metabolites of sulfadiazine generated by EC

Measured mass (Da)	Formula[a]	Deviation (ppm)
251.05977	$C_{10}H_{11}N_4O_2S_1$	0.20
265.03908	$C_{10}H_9N_4O_3S_1$	0.35
187.09776	$C_{10}H_{11}N_4$	−0.34
201.07713	$C_{10}H_9N_4O$	0.21
217.07208	$C_{10}H_9N_4O_2$	0.36
96.05563	$C_4H_6N_3$	0.10
108.04439	C_6H_6NO	0.00
340.08658	$C_{16}H_{14}N_5O_2S_1$	0.91

[a] All formula correspond to the protonated species

systems [24], others are strictly related to oxidation at the aromatic amine, a mechanism which is not involved in oxidative biotransformations or photochemistry. Indeed, some species, e.g. the anilium cation, are rather reactive and would be expected to undergo reactions with soil organic matter forming so-called non-extractable components. At this point, the analytical approach provides important indications about structural elements or functional groups which can occur in complex soil matrices.

To confirm these first findings, the metabolism of the sulfonamide sulfamethoxazole was also investigated and showed similar results. As expected, oxidation of the aromatic ring was observed (268.03859 Da, $C_{10}H_{10}O_4N_3S$ and −0.05 ppm) besides the breakdown at the sulfonamide group (99.05531 Da, $C_4H_7N_2O$ and 0.21 ppm) and the loss of SO_2, (190.09750 Da, $C_{10}H_{12}N_3O$ and 0.06 ppm), which has also been found for other sulfonamides [25, 27]. In Fig. 4, the CID spectrum of one breakdown product is shown. From the two possible configurations, one structure was identified by the loss of CNH. This is similar to earlier investigations with sulfadiazine and comparable sulfonamides [2, 24, 28]. Indeed, for sulfonamides most of the known derivatives are related to microbial or photocatalytic transformations while fewer derivatives are attributed to abiotic oxidation.

The direct coupling of the electrochemical cell with the mass spectrometer also allows the detection and structure elucidation of reactive species. Typically, these products would be hard to isolate in environmental samples. Because of their low concentrations and expected strong adsorption to the soil matrix, the structural elucidation of such compounds is rather difficult. This makes the EC-MS technique valuable for environmental chemistry. The opportunity of a fast method to determine the chemical degradation of a new substance in the environment means that it would be possible to assess a chemical compound before it is emitted into the environment. Especially, its behaviour

Table 2 Confirmation of the metabolites generated by EC by means of CID-generated fragment ions with LTQ-MS and/or FTICR-MS

Precursor ion	Fragment ion[a]	Formula	Deviation	Fragmentation
265.03908	235.04107	$C_{10}H_9N_3O_2S_1$	0.30	–NO
	233.06701	$C_{10}H_9N_4O_3$	0.40	–S
	201.07715	$C_{10}H_9N_4O$	0.31	$-SO_2$
265≥235	217.03050	$C_{10}H_7N_3OS$	0.30	$-H_2O$
	171.07916	$C_{10}H_9N_3$	0.36	$-SO_2$
187.09776	170.07121	$C_{10}H_8N_3$	−0.37	$-NH_3$
	160.08687	$C_9H_{10}N_3$	−0.34	–HCN
	145.07597	$C_9H_9N_2$	−0.38	–HN=C=NH
201.07713	171.07913	$C_{10}H_9N_3$	0.18	–NO
	184.05058	$C_{10}H_6N_3O$	0.23	$-NH_3$
	173.08221	$C_9H_9N_4O$	0.21	–CO
217.07208	189.07714	$C_9H_9N_4O$	0.28	–CO
	199.06150	$C_{10}H_7N_4O$	0.31	$-H_2O$
	200.04551	$C_{10}H_6N_3O_2$	0.28	$-NH_3$
	171.07913	$C_{10}H_9N_3$	0.18	$-NO_2$
	187.07409	$C_{10}H_9N_3O$	0.41	–NO
	148.05053	$C_7H_6N_3O$	−0.06	–HN=C=O
96	69	–	–	–HCN
	68	–	–	$-N_2$
108	80	–	–	–CO
	81	–	–	–HCN
340	322	–	–	$-H_2O$

[a] Fragment ions listed according to their intensities

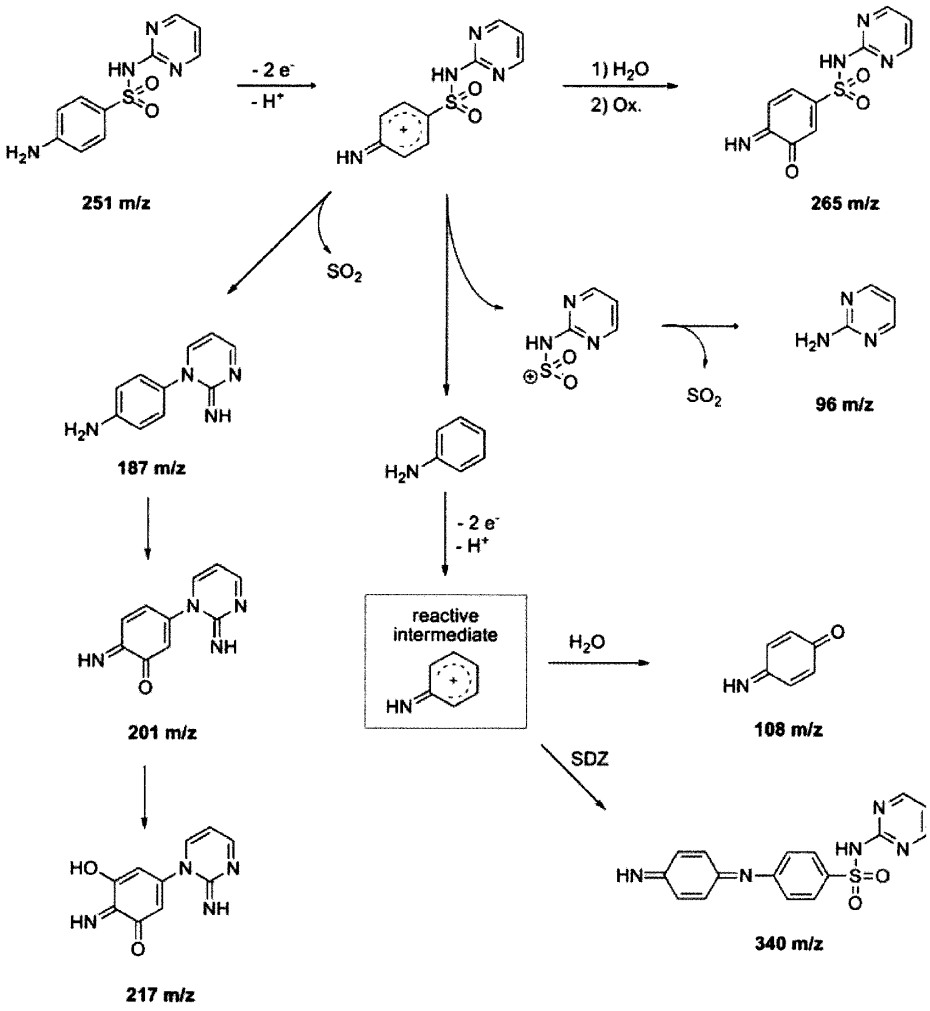


Fig. 3 Proposed reaction scheme of SDZ. The *m/z* ratios shown correspond to the protonated species

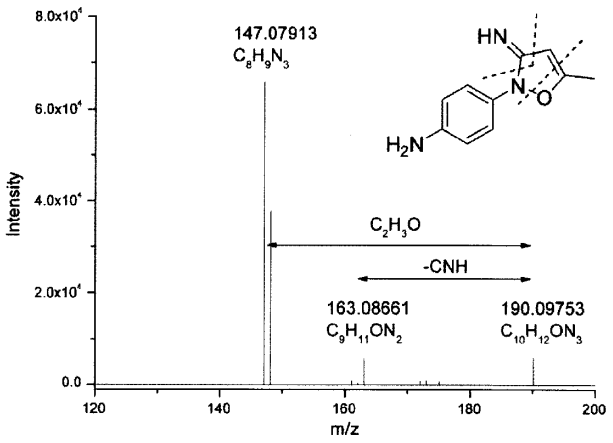


Fig. 4 High-resolution CID spectrum of main degradation product of sulfamethoxazole

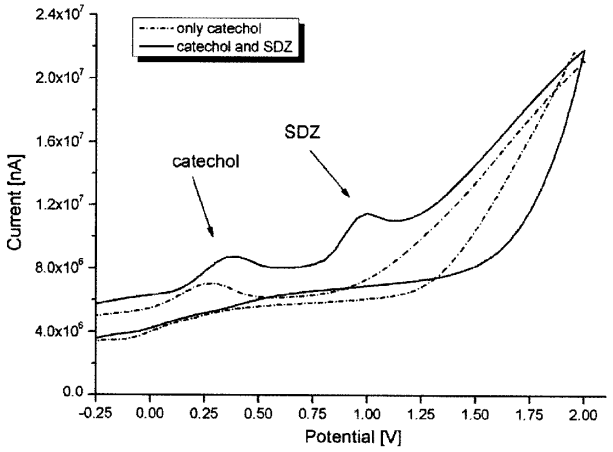
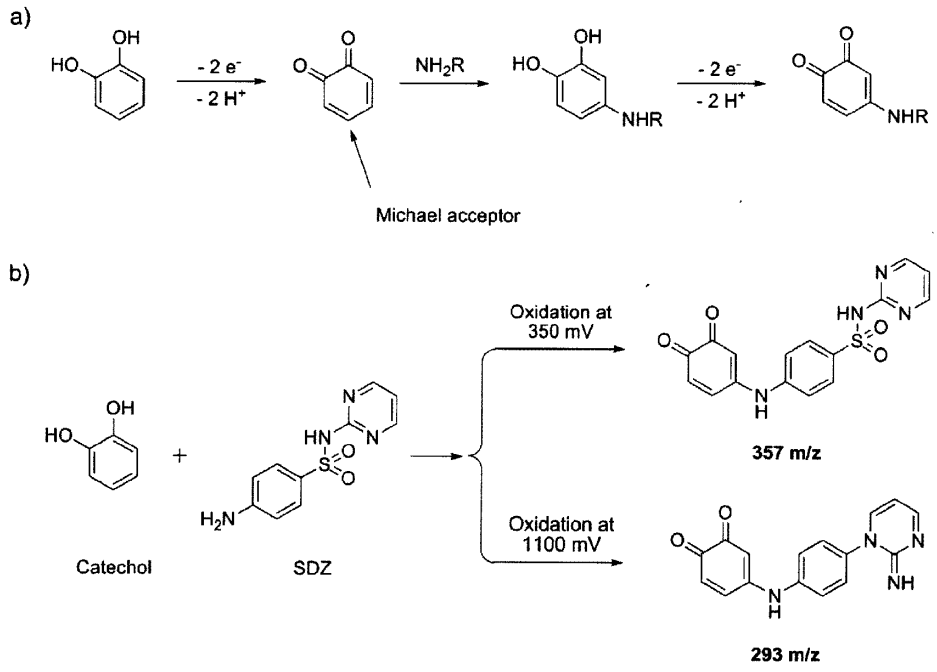


Fig. 5 Cyclovoltammetric (*CV*) behaviour of catechol and catechol together with sulfadiazine



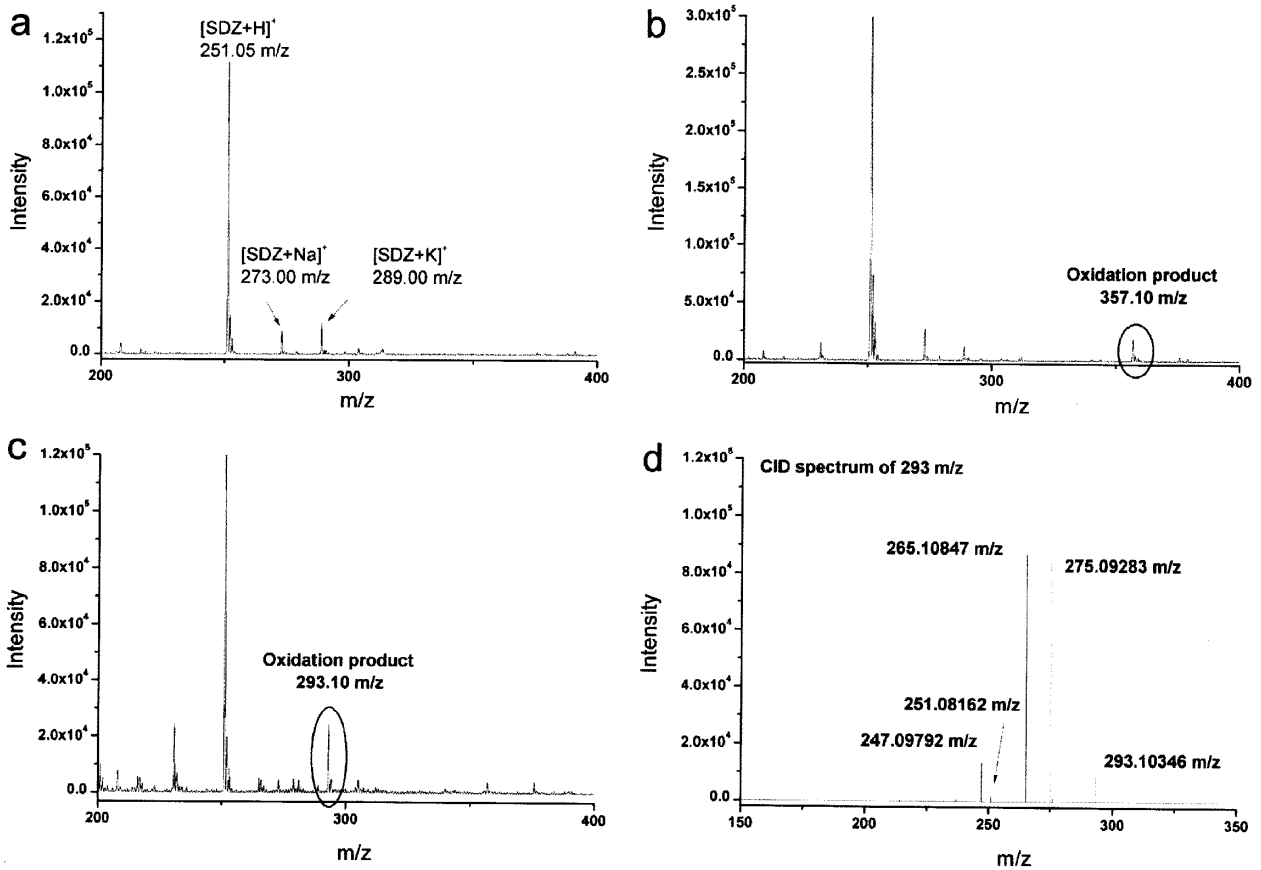


Fig. 6 **a** Assumed reaction scheme of catechol with an *N*-nucleophile under oxidative conditions. **b** Products obtained while applying a constant voltage to a solution containing catechol and SDZ. Sample: 10-μM SDZ, 20-μM catechol in 200-μM NH_4OAc, pH 6.8/MeOH 70:30 (*v/v*). EC conditions: 10 μl/min flow at a glassy carbon electrode. The *m/z* ratios shown correspond to the protonated species

Fig. 7 **a** Mass spectrum in the positive mode of a mixture of 10 μM sulfadiazine with 20-μM catechol in 200-μM NH_4OAc, pH 6.8/MeOH 70:30 (*v/v*) without applied voltage to the electrochemical cell. **b** Mass spectrum of the sulfadiazine—catechol mixture after electrochemical oxidation (400 mV). **c** Mass spectrum of the sulfadiazine—catechol mixture after electrochemical oxidation (1,100 mV). **d** High resolved MS^3-spectrum of the sulfadiazine—catechol reaction product after electrochemical oxidation (1,100 mV) 357→293 Da

Table 3 Confirmation of one EC-generated coupling (1,100 mV) product between sulfadiazine and catechol by CID-generated fragment ions with FTICR-MS

[a] Fragment ions are listed according to their intensities

Precursor ion	Fragment ion[a]	Formula	Deviation	Fragmentation
293.10346		$C_{16}H_{13}N_4O_2$	0.54	
	265.10847	$C_{15}H_{13}N_4O$	0.35	–CO
	275.09283	$C_{16}H_{11}N_4O$	0.31	$-H_2O$
	247.09792	$C_{15}H_{11}N_4$	0.39	$-CH_2O_2$
	251.08162	$C_{15}H_{11}N_2O_2$	0.46	–HN=C=NH

with respect to photochemistry and metal(-oxide)-mediated electron transfers is a field where EC-MS is capable of predicting putative derivatives of xenobiotics. This may be a field of application for EC-MS in environmental chemistry.

Model reaction for the chemical binding of xenobiotics to soil

Many chemicals may undergo chemical conversions with the organic matrix of the soil. The elucidation of these transformation mechanisms is difficult because reaction products are often no longer extractable from the soil matrix. In recent years, a number of structures of non-extractable residues (NER) have been found; some reaction mechanisms have been identified, and model substances and model reactions have been demonstrated [29, 30].

Based on these results, it is expected that some of these reactions are related to oxidative conditions. This would allow the use of EC-MS as a tool for performing model reactions to identify the products alone and those fixed to the organic carbon matrix in a short time frame. As reported recently [31], sulfonamide antimicrobials undergo a Michael addition with appropriate structural elements of organic matter in soil. A model substance for organic matter in soil is catechol [30]. Therefore we investigated whether catechol reacts with sulfadiazine by a Michael addition with the formation of the expected products. Figure 5 shows the cyclovoltammetric behaviour of catechol and catechol together with sulfadiazine. The cyclovoltagramms show that catechol is first oxidized at 350 mV without any reaction with sulfadiazine.

The oxidation of catechol in the presence of sulfadiazine leads to new species as stated in Figs. 6 and 7.

Using high resolution mass spectrometry data, including CID spectra, made it possible to identify the new derivatives (Table 3).

Figure 7a presents the mass spectrum of a mixture of sulfadiazine and catechol in buffer before voltage is applied in the EC cell. The catechol ionizes under this conditions only in the negative mode ($(M-H)^-$ 109.02963 Da, 1.2 ppm) and fails therefore generally in all positive mode spectra. After applying increasing voltages, the two compounds detected are the coupling products of sulfadiazine with catechol ($(M+H)^+$ 357.06639 Da, 3.3 ppm; 400 mV; Fig. 7b) as well as of catechol with the major degradation product of sulfadiazine ($(M+H)^+$ 293.10357 Da, 0.91 ppm; 1,100 mV; Fig. 7c). In addition, a reaction product of catechol with the buffer is found.

The new coupling product of sulfadiazine and catechol (m/z=357) was in agreement with the expected Michael addition. Proof of principle was given by the appearance of the coupling product of catechol with the major degradation product of sulfadiazine (m/z=293) at a higher potential, as also found for the oxidation of sulfadiazine (1,100 mV; see Fig. 2). Fragment ions from CID spectra are given in Table 3 and Fig. 7d, respectively. At least for this first example, EC-MS is demonstrated to be an easy and fast tool for the prediction of possible non-extractable xenobiotic structures. Together with the intermediates of the sulfadiazine degradation shown in Fig. 3, information is obtained on chemical structures of the reaction of xenobiotics and their metabolites with soil components. The elucidation of the chemical structures of NERs is an extremely difficult analytical research field.

Comparison of the oxidative stability/reactivity of atrazine, sulfamethoxazole and tetracycline

Figure 2 presents the example of the mass traces versus voltage ramp for all metabolites obtained from sulfadiazine. This gives a first idea of the stability of the compounds under oxidative conditions. In further investigations atrazine, sulfamethoxazole and tetracycline were studied with respect to their oxidative stability or degradability.

It was assumed that atrazine is only slightly reactive in the EC cell, because its reactivity under oxidative conditions in the environment is also rather low [21, 32].

Table 4 Decrease of peak heights for three selected xenobiotics at different pH

pH	Decrease of $(M+H)^+$		
	Atrazine (%)	Tetracycline (%)	Sulfamethoxazole (%)
3	6	62	75
7	14	62	81
10	2	46	78

Atrazine is known to degrade in the environment starting with a hydrolysis [33, 34]. In fact, it was found that atrazine does not form detectable metabolites under the conditions used above. Only by using harsh conditions with Fenton's reagent and with long reaction times could metabolites be obtained, as already described elsewhere [20].

The comparison of the decrease in the $(M+H)^+$ peak height of the three xenobiotics between 0 and 2,000 mV was investigated. Because the pH dependence of these chemicals is different, the comparison was performed for several pH values (Table 4). A comparison of the three substances for each pH shows the expected order. Atrazine only degrades slightly, whereas sulfonamide and tetracycline degrade to a much larger extent. Though environmental conditions would be expected to be mainly acidic, the degradation order by oxidation is also found to be valid for basic conditions.

In view of these preliminary results, EC-MS seems to be an appropriate tool to predict the environmental persistence of xenobiotics. However, further studies are necessary to verify this assumption for other classes of compound.

Conclusions

Understanding of behaviour of xenobiotics in the environment is essential to manage potential risks. The challenges here are the high number of chemicals, the wide range of chemical and physical properties, the complexity of the environmental system and the great effort needed to understand the behaviour of a substance.

In this study, EC-MS was applied as a purely analytical approach to evaluate the oxidation behaviour of a few selected, well-investigated xenobiotics. Though this is a pilot study some interesting results were achieved by the EC-MS approach. It is demonstrated that the same degradation products of sulfadiazine can be obtained as in photochemical experiments. In addition, the complete oxidative degradation mechanism can be also elucidated and potential degradation products can be identified. Thus, EC-MS allows, for example, ecotoxicologists to give a first estimation of possible toxic metabolites. For the three examples used in the study, the oxidative stability of the xenobiotics shows the same trend as their persistence in the environment. The very fast EC-MS approach might thus provide initial information on which chemicals need a more extensive investigation with respect to potential persistence. Finally, the reaction of sulfadiazine with catechol leads to the expected chemical structure of a model substance for organic matter in soil. This field of application for EC-MS might help soil chemists to elucidate the mechanisms of the formation and the structural elements of non-extractable residues.

In general, EC-MS is worth further evaluation as a tool for the assessment of the environmental behaviour of xenobiotics—besides broadening the basis for the preliminary results presented here preparative EC-MS might also give additional benefits for environmental research. If a metabolite or a xenobiotic/organic matter complex generated in EC-MS is relevant for environmental research, EC-MS can be used as a synthesis method for further ecotoxicological or physicochemical studies.

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