Supporting Information

Removal of the iodinated X-ray contrast medium diatrizoate by anaerobic transformation

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15 pages, 5 tables, 4 figures

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Materials and methods

Chemicals, standards and solvents

Diatrizoate, dansyl chloride, formic acid (LC-MS grade), acetonitrile and methanol (both LC-MS grade) were purchased from Sigma-Aldrich (Steinheim, Germany). 3,5-bis(acetylamino)benzoic acid (TP 236) was obtained from ChemBridge (San Diego, CA, USA). 3-acetamido-5-aminobenzoic acid (TP 194), iron(III) chloride, barium chloride dehydrate, ammonium acetate, sodium hydroxide, glacial acetic acid, hydrochloric acid (25%), sulphuric acid (96%) and gelatin were purchased from Merck (Darmstadt, Germany). 3,5-diaminobenzoic acid (DABA) was provided by TCI Europe (Eschborn, Germany). Sodium acetate and 1,10-phenanthroline hydrochloride monohydrate were purchased from C. Roth (Karlsruhe, Germany). Ultrapure water was obtained from a Milli-Q water purification system (Millipore, Darmstadt, Germany). Nitric acid (65%, p. a.) was purchased from Merck (Darmstadt, Germany) and subboiled prior use by means of a subboiling unit (DST-1000) from Savillex (Eden Prairie, MN, USA).

Environmental samples

Groundwater (grab samples) from different depths, including Fe(III) and Mn(IV) reducing zones, was sampled from two wells that are influenced by infiltrating water from a polishing pond receiving the effluent of a conventional WWTP (Figure 1a). The first well (GW1) is directly connected to the infiltrating water of the pond, while the second well (GW2) is located approximately 55 m downstream of GW1, corresponding to a travel time of approximately 2 years. At the time of sampling, oxygen was not detectable in both wells. In GW1 and GW2

ferrous iron concentrations were 2.1 mg/L and 0.16 mg/L, Mn(II) concentrations were 0.30 mg/L and 0.17 mg/L, sulfate concentrations were 130 mg/L and 100 mg/L, sulfide concentrations (semi-quantitative determination with colorimetric test kit by Merck, Darmstadt, Germany) were <0.1 mg/L in both samples, and redox potentials were approximately 70 mV and 180 mV, respectively.

Grab samples were taken from the effluents of two technical wetlands (TW) fed by the WWTP effluent mentioned above (Figure 1b). TW1 is a subsurface flow wetland (SSF) consisting of sand mixed with straw and TW2 is a pond covered with floating plants. An additional 24 h composite sample was taken from the corresponding WWTP effluent. At the time of sampling, in the effluents of TW1 and TW2 oxygen concentrations were 0.14 mg/L and 0.09 mg/L and redox potentials were -90 mV and -40 mV, respectively.

In total, 40 sets of samples were taken over a period of 5 months from three consecutive reactors of a pilot WWTP (Figure 1c): a conventional denitrifying and nitrifying reactor (R0, HRT 12 h, 3 d composite samples from the effluent) and two anaerobic reactors (R1, HRT 5.75 d, grab samples from the aqueous phase in the reactor; R2, HRT 5.75 d, 3 d composite samples from the effluent). During sampling of R2 a contact with oxygen could not be avoided, however, the redox potential of the sampled water (cooled down to 4 °C) was still < -200 mV after the three days. The reactors were operated as sequencing batch reactors, each operated in parallel cycles of 3 h. Oxygen dosing in R0 was regulated to keep the oxygen concentration in the reactor between 1 mg/L and 3 mg/L during nitrification. Prior to the transfer to R1, oxygen was depleted to <0.1 mg/L in R0. Acetate was dosed into R1 to achieve a sufficient denitrification and to establish strictly anaerobic conditions. In R1 and R2 the oxygen concentrations (on-line monitored) remained always < 0.01 mg/L. In R1 the redox potential (on-

line monitored) decreased to < -200 mV until the end of a cycle and remained < -200 mV in R2 throughout a cycle. Ferrous iron concentrations (determined at the end of a cycle in the aqueous phases of the reactors, method provided above) were < 2 mg/L (i.e. < LOQ) in both R1 and R2. The dissolved sulfide concentrations (determined with photometric test kits (Hach-Lange, Düsseldorf, Germany) at the end of a cycle in the aqueous phases of the reactors, starting from the 3rd month of sampling, n = 19) were up to 2.22 mg/L in R1 and up to 1.87 mg/L in R2. Sulfate concentrations (determined in the composite samples at the same time points as the sulfide concentrations; method provided above) were 88 ± 17 mg/L in R0, 65 ± 13 mg/L in R1 and 66 ± 12 mg/L in R2. Diatrizoate concentrations were measured in all composite samples. After method development, concentrations of diatrizoate TPs were measured in a set of samples (R0, R1, R2) covering a 3 d period.

Photometric determination of ferrous iron and sulfate concentrations

For the determination of ferrous iron and sulfate concentrations in the batch experiments, samples were taken and filtered (0.45 µm regenerated cellulose syringe filters, C. Roth, Karlsruhe, Germany) under an argon atmosphere. Samples for the determination of ferrous iron were stabilized with HCl at a concentration of 15 mmol/L before they were removed from the argon atmosphere.

Determination of ferrous iron concentrations: Ferrous iron was determined by complexation with 1,10-phenanthroline. The procedure was modified from the Standard methods for the Examination of Water & Wastewater.[1] 2 mL sample aliquots were incubated at room temperature for 5 min with 500 µL of a 0.5% (w/w) aqueous solution of 1,10-phenanthroline

hydrochloride monohydrate and 500 µL of an ammonium acetate buffer (100 g ammonium acetate, 50 mL ultrapure water and 125 mL glacial acetic acid replenished with ultrapure water to 250 mL). The absorbance of the formed complex at 510 nm was determined, and quantification was realized by means of an external calibration ranging from 0.1 mg/L to 15 mg/L (20 points).

Determination of sulfate concentrations: Sulfate concentrations were determined by precipitation with barium chloride based on the method of Tabatabai.[2] 3 mL sample aliquots were incubated for 1 h at room temperature with 150 µL of a 40 g/L solution of barium chloride dihydrate in 2.5 g/L gelatin gel and 300 µL 1 N HCl. The turbidity caused by the precipitated barium sulfate was determined by measuring the absorbance at 420 nm. Quantification was realized by means of an external calibration ranging from 0.4 mg/L to 50 mg/L (11 points).

Identification of transformation products

Analysis of TPs via LTQ Orbitrap Velos ESI FT-MS (LC-ESI-HR-MS^n): Chromatographic conditions were similar to those used for quantification by LC-ESI-MS/MS (see below). The ESI source parameters were set as follows: capillary temperature, 275 °C; capillary voltage, 2.7 kV; heater temperature, 350 °C; sheath gas flow rate, 45 AU; aux gas flow rate, 20 AU; S-lens RF level, 69%. Data dependent acquisition was used to gain MS^2 and MS^3 spectra as follows: a full scan (100 – 800 *m/z*, positive mode) was performed followed by MS^2 for the most intense ion with an intensity of >10,000 and MS^3 scans for the two most intense MS^2 fragments with intensities >1,000. Collision induced dissociation (CID) and high-energy collision dissociation (HCD, only MS^2) with normalized collision energies of 20% and 40%, respectively, were used for fragmentation. In addition, dynamic exclusion was applied (exclusion of masses for which

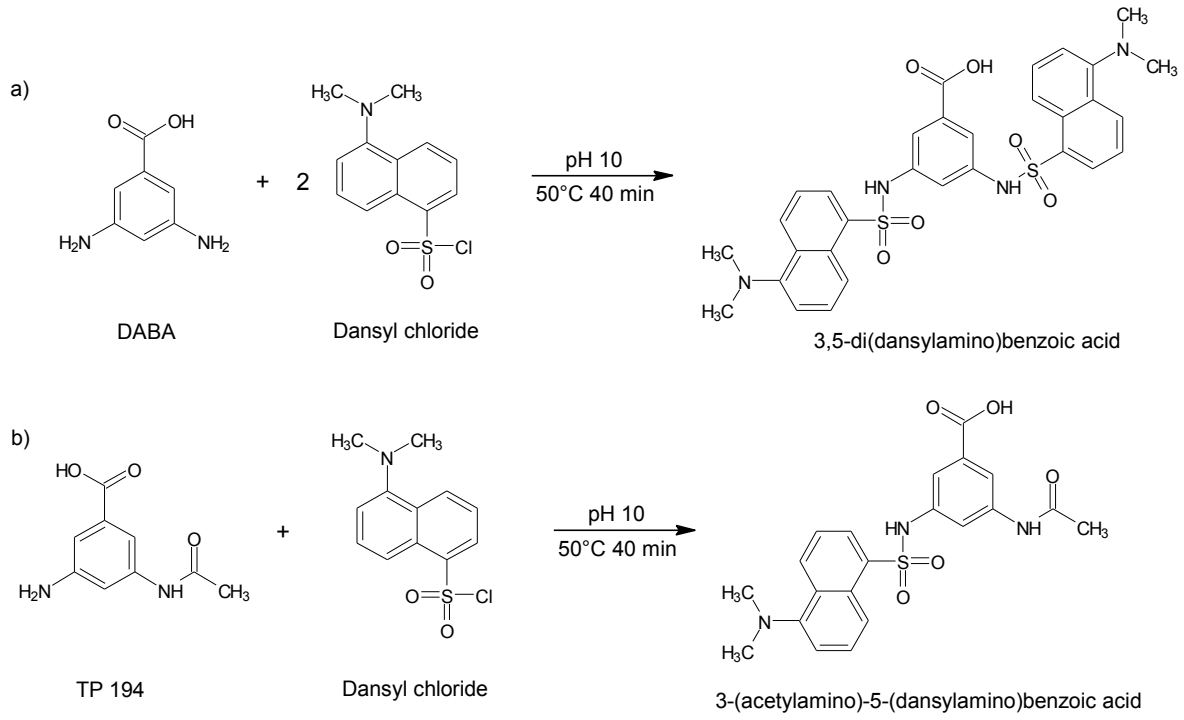
three MS^n experiments have been performed; exclusion duration: 30 s) enabling also MS^n experiments for less abundant ions (e.g., during co-elution of different substances).

Preparation of samples

Solid phase extraction(Dugo, Vilasi et al. 2006): Different types of adsorbents (Oasis HLB, 200 mg, 33 µm, Waters, Milfort, USA; Isolute ENV+, 500 mg, 90 µm, Biotage, Uppsala, Sweden; Bakerbond SDB1, 200 mg, J.T. Baker, Deventer, the Netherlands; ENVI-Carb Plus, 400 mg, Supelco, Bellefonte, USA; Strata SAX, 500 mg, 55 µm, Phenomenex, Aschaffenburg, Germany; Oasis WAX, 150 mg, 30 µm, Oasis MAX, 150 mg, 30 µm; Oasis MCX, 60 mg, 30 µm, each Waters, Milford, USA), pH values of the sample, and different elution solvents were tested using 200 mL of groundwater spiked with 500 ng/L of diatrizoate and each of the commercially available non-iodinated TPs 236, 194 and DABA. In addition, the groundwater samples were spiked with 50 µL of a sample from a batch experiment (initial diatrizoate concentration: 10 mg/L) containing most TPs to assess also the absolute recoveries of TPs for which no reference standards were available. Based on the results of these tests, the following method was developed: A sample volume of 20 mL was adjusted to pH 2.6 – 2.8 with 3.5 M sulfuric acid. Bakerbond SDB1 cartridges (200 mg, 3 mL, J.T. Baker, Deventer, the Netherlands) were conditioned with 3 x 2 mL methanol and 4 x 2 mL groundwater (pH 2.6 – 2.8). After loading the samples onto the cartridges, the cartridges were dried with nitrogen gas. The analytes were eluted with 5 x 2 mL methanol, the eluate was reduced to 0.1mL under a light nitrogen gas stream, and 1.9 mL of ultrapure water were added.

Derivatization: In the samples of batch experiment VI spiked with 5 µg/L diatrizoate and in the environmental samples the amino groups of the TPs 194 and DABA were derivatized with dansyl chloride (Scheme S1). The procedure was modified from Dugo et al.[3] 900 µL sample aliquots were incubated with 50 µL of a 0.75 mM dansyl chloride solution in acetonitrile and 50 µL of a 7.5 mM Na_2CO_3 buffer solution (pH 10) at 50°C for 40 min.

Scheme S1. Derivatization of a) DABA and b) TP 194 with dansyl chloride.



Quantitative Analysis of samples

Liquid chromatography – inductively coupled plasma – mass spectrometry (LC-ICP-MS): Quantification was realized using an HPLC 1260 Infinity system from Agilent Technologies (Waldbronn, Germany) coupled with an ICP-sector field-mass spectrometer (ICP-SF-MS) Element 2 (Thermo Scientific, Bremen, Germany). Coupling of the LC unit with the ICP-SF-MS

instrument was realized with a peltier-cooled quartz spray chamber PC^3 (4 °C) and a µ-flow PFA-ST ES-2040 nebulizer (both from Elemental Scientific Inc., Omaha, NE, USA). A Hydro-RP column (250 mm x 3 mm, 4 µm; Phenomenex, Aschaffenburg, Germany) was used for chromatographic separation. Mobile phase A was 0.1% formic acid in ultrapure water, mobile phase B was 0.1% formic acid in methanol. The gradient of A was as follows: 0 – 20 min 85%, 21.5 – 24 min 10%, 24.6 – 27 min 2%, 27.6 – 28.5 min 85%. The column oven was set to 40 °C, flow rate to 0.4 mL/min and injection volume was 20 µL. By means of a T-piece and a peristaltic pump (circa 100 µL/min) diluted HNO_3 (6.5%) was added post-column to achieve further acidification of the HPLC effluent to abet ionization in the ICP source. The ICP-SF-MS parameters applied are listed in Table S1.

Table S1. ICP-SF-MS parameters applied

	LC/ICP-SF-MS	**FI approach**
power [W]	1,500	1,500
nebulizer gas flow rate [L/min]	0.75-0.86	0.75
aux gas flow rate [L/min]	0.7	0.7
cool gas flow rate [L/min]	16.0	16.0
dwell time [ms]	10	20
passes; runs	1, 2.530	1, 4.000
nuclides/isotopes monitored	^{115}In, ^{127}I	^{115}In, ^{127}I
run time	38 min 3 s	02 h 0 min 9 s
internal standard flow [mL/min]	~ 0.12 – 0.13	~ 0.12 – 0.13

For total iodine determination a flow-injection (FI) approach (5 µL injection volume) was applied bypassing the autosampler of the HPLC via an electronic switching valve (FCV-14AH, Shimadzu, Japan); the pump-flow rate was set to 0.4 mL/min @ 15% B. Samples were injected manually (disposable syringes, 1 mL, Braun, Melsungen, Germany).

Liquid chromatography – electrospray ionization – tandem mass spectrometry (LC-ESI-MS/MS): Quantification was realized using an Agilent HPLC system (1260 Infinity, Agilent Technologies, Waldbronn, Germany) coupled with an API 5500 QTrap MS (Applied Biosystems, Langen, Germany) operated with ESI in positive ionization mode. A Hydro-RP column (250 mm x 3 mm, 4 µm; Phenomenex, Aschaffenburg, Germany) was used for chromatographic separation. Mobile phase A was 0.1% formic acid in ultrapure water, mobile phase B was 0.1% formic acid in acetonitrile. The gradient of A was as follows: 0 – 2 min 100%, 12.5 min 45%, 15 – 18 min 10%, 18.5 – 27 min 100%. The column oven was set to 40 °C, flow rate to 0.4 mL/min and injection volume was 25 µL. For complementary measurements to allow for peak assignment of the iodinated TPs in the LC-ICP-MS chromatograms, the chromatographic conditions were chosen as for LC-ICP-MS measurements (see description above).

Detection was accomplished by multiple reaction monitoring (MRM). Two transitions (MRM1 for quantification, MRM2 for confirmation) were monitored for each analyte. Optimization of the compound specific parameters (declustering potential, collision energy, cell exit potential) was performed in continuous flow mode (10 µL/min) injecting derivatized and non-derivatized aqueous standard solutions (0.1 – 10 µg/L) or (for the TPs which were not available as analytical standards) undiluted samples from the batch experiments spiked with 10 mg/L containing the TPs (Table S2).

Table S2. Precursor, product ions and MS parameters used for LC-MS/MS detection

Compound	MRM1 [*m/z*]	MRM2 [*m/z*]	DP[a] [V]	CE[b] (MRM1/MRM2) [eV]	CXP[c] (MRM1/MRM2) [V]
Diatrizoate	615 → 361	615 → 233	80[d]	26 / 63	10 / 8
TP 488	489 → 235	489 →193	30	30 / 65	10 / 10
TP 362	363 → 194	363 → 152	30	30 / 50	10 / 10
TP 320	321 → 152	321 →194	50	40 / 40	10 / 10
TP 278	279 → 152	279 → 108	50	40 / 40	10 / 10
TP 236	237 → 219	237 → 177	60	20 / 25	15 / 12
TP 194	195 → 153	195 → 107	65	20 / 35	12 / 7
TP 194 derivatized	428 →177	428 →170	80	25 / 35	12 /15
DABA	153 → 92	153 → 80	32	25 / 40	15 / 13
DABA derivatized	619 → 385	619 → 368	120	30 / 30	35 / 30

[a] DP = Declustering potential, [b] CE = Collision energy, [c] CXP = Cell exit potential, [d] MRM2: 40 V

Method validation: Absolute recoveries of the SPE method were determined in triplicate by spiking 200 mL groundwater (pH 2.6 – 2.8) with 50 µL of a sample from the batch experiments containing all iodinated TPs and with 500 ng/L of diatrizoate and each of the commercially available non-iodinated TPs 236, 194 and DABA. The spiked groundwater samples were subjected to the SPE procedure described above. Absolute recoveries were calculated as the ratio of peak areas of the samples subjected to SPE and the standard solutions diluted in ultrapure water. HPLC column recovery for iodinated compounds by LC-ICP-MS measurements was determined by comparing the sum of iodine concentrations from all peaks in the chromatograms with total iodine concentrations in the samples obtained from flow injection with external calibration.

Limits of quantification (LOQ) were determined by extra- or interpolation from spiked samples as the concentrations at which the signal to noise ratios were > 10 for quantification (MRM1) or > 3 for confirmation (MRM2), respectively.

Results and discussion

Dissipation of diatrizoate in batch experiment 2

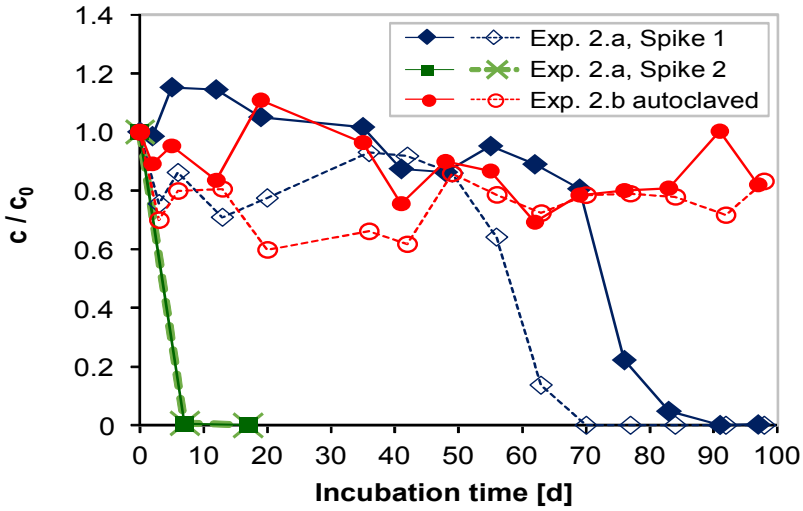


Figure S1. Time series of diatrizoate concentrations in two replicates of experiment 2.a after first and second spike each, and in two autoclaved replicates of experiment 2.b. Solid and dashed lines represent the results of both replicates of each experiment.

Identification of transformation products

The fragments of diatrizoate and its anaerobic TPs resulting from MS^n experiments are listed in Table S3.

Table S3. Precursor and product ions of diatrizoate and its anaerobic TPs obtained by MS^n experiments using LTQ-Orbitrap-MS with electrospray ionization in the positive ionization mode. TPs are named after their nominal mass and not the measured high resolution mass $[M+H]^+$.

Compound	m/z	Mass error [ppm]	Elemental composition	Proposed fragmentation
Diatrizoate	614.7775	-0.48	$C_{11}H_{10}O_4N_2I_3$	$[MH]^+$
	487.8719	-1.13	$C_{11}H_{10}O_4N_2I_2$	$[MH-I]^+$
	360.9674	-1.09	$C_{11}H_{10}O_4N_2I$	$[MH-I-I]^+$
	318.9572	-0.75	$C_9H_8O_3N_2I$	$[MH-I-I-C_2H_2O]^+$
	233.0556	-0.66	$C_{11}H_9O_4N_2$	$[MH-I-I-HI]^+$
	192.0530	-0.48	$C_9H_8O_3N_2$	$[MH-I-I-I-C_2H_2O]^+$
	148.0392	-0.60	$C_8H_6O_2N$	$[MH-I-I-HI-C_2H_3NO-CO]^+$
TP 488	488.8808	1.09	$C_{11}H_{11}O_4N_2I_2$	$[MH]^+$
	470.8692	-1.14	$C_{11}H_9O_3N_2I_2$	$[MH-H_2O]^+$
	361.9756	-0.67	$C_{11}H_{11}O_4N_2I$	$[MH-I]^{+\cdot}$
	235.0713	-0.27	$C_{11}H_{11}O_4N_2$	$[MH-I-I]^+$
	193.0608	-0.37	$C_9H_9O_3N_2$	$[MH-C_2H_2O-I-I]^+$
TP 362	362.9841	-0.20	$C_{11}H_{12}O_4N_2I$	$[MH]^+$
	344.9727	-0.90	$C_{11}H_{10}O_3N_2I$	$[MH-H_2O]^+$ (F1)[a]
	236.0791	-0.25	$C_{11}H_{12}O_4N_2$	$[MH-I]^{+\cdot}$ (F2)[a]
	217.0608	-0.04	$C_{11}H_9O_3N_2$	$[MH-HI-H_2O]^+$ (F3)[a]
	194.0686	0.29	$C_9H_{10}O_3N_2$	$[MH-I-C_2H_2O]^{+\cdot}$ (F4)[a]
	190.0739	1.37	$C_{10}H_{10}O_2N_2$	$[MH-I-H_2O-CO]^{+\cdot}$ (F5)[a]
	152.0579	-0.91	$C_7H_8O_2N_2$	$[MH-I-C_2H_2O-C_2H_2O]^{+\cdot}$ (F6)[a]
TP 320	320.9733	-1.06	$C_9H_{10}O_3N_2I$	$[MH]^+$
	194.0686	-2.85	$C_9H_{10}O_3N_2$	$[MH-I]^{+\cdot}$
	152.0580	-4.00	$C_7H_8O_2N_2$	$[MH-I-C_2H_2O]^{+\cdot}$
TP 278	278.9622	-0.76	$C_7H_8O_2N_2I$	$[MH]^+$
	260.9517	-0.81	$C_7H_6ON_2I$	$[MH-H_2O]^+$

	234.9727	-0.46	$C_6H_8N_2I$	$[MH-CO_2]^+$
	232.9572	0.57	$C_6H_6N_2I$	$[MH-H_2O-CO]^+$
	152.0579	-0.72	$C_7H_8O_2N_2$	$[MH-I]^{+\cdot}$
	151.0503	-0.62	$C_7H_7O_2N_2$	$[MH-HI]^+$
	108.0680	-1.94	$C_6H_8N_2$	$[MH-I-CO_2]^{+\cdot}$
TP 236	237.0874	1.59	$C_{11}H_{13}O_4N_2$	$[MH]^+$
	219.0760	-2.05	$C_{11}H_{11}O_3N_2$	$[MH-H_2O]^+$
	195.0761	-1.89	$C_9H_{11}O_3N_2$	$[MH-C_2H_2O]^+$
	191.0812	-2.12	$C_{10}H_{11}O_2N_2$	$[MH-H_2O-CO]^+$
	177.0656	-1.78	$C_9H_9O_2N_2$	$[MH-C_2H_2O-H_2O]^+$
TP 194	195.0768	1.70	$C_9H_{11}O_3N_2$	$[MH]^+$
	177.0658	-0.59	$C_9H_9O_2N_2$	$[MH-H_2O]^+$
	167.0815	-0.03	$C_8H_{11}O_2N_2$	$[M+H-CO]^+$
	153.0658	-0.68	$C_7H_9O_2N_2$	$[MH-C_2H_2O]^+$
	149.0707	-1.34	$C_8H_9ON_2$	$[MH-CO-H_2O]^+$
	138.0661	-10.8	$C_8H_{10}O_2$	$[MH-C_2H_3ON]^+$
	135.0553	-0.29	$C_7H_7ON_2$	$[MH-C_2H_2O-H_2O]^+$
	109.0759	-1.42	$C_6H_9N_2$	$[MH-C_2H_2O-CO_2]^+$
	107.0602	-1.35	$C_6H_7N_2$	$[M+H-H_2O-CO-C_2H_2O]^+$
DABA	153.0662	-2.00	$C_7H_9O_2N_2$	$[MH]^+$
	135.0552	-0.37	$C_7H_7ON_2$	$[MH-H_2O]^+$
	109.0759	-1.15	$C_6H_9N_2$	$[MH-CO_2]^+$
	107.0602	-1.73	$C_6H_7N_2$	$[MH-H_2O-CO]^+$
	92.0493	-2.02	C_6H_6N	$[MH-H_3N-CO_2]^+$

[a] F1 – F6: labelling of fragments in Figure S2

In Figure S2 the proposed fragmentation pathway of TP 362 is shown exemplarily. The main fragments of TP 362 resulted from the cleavage of iodine (iodine radical and HI), acetyl moieties (ketene, C_2H_2O) and the carboxylic moiety (H_2O and CO). The cleavage of one iodine confirmed that only one instead of three iodine atoms are present. Moreover the cleavage of two ketenes and CO + H_2O revealed that the amide moieties and the carboxylic group of diatrizoate remained unaltered. Hence, based on the exact mass (362.9841 +/- 0.20 ppm) leading to the sum formula

($C_{11}H_{12}O_4N_2I$) as well as on the MS^2 spectra TP 362 could be identified as di-deiodinated diatrizoate (3,5-diacetamido-iodobenzoic acid).

However, the exact positions of the deiodination and deacetylation reactions could not be determined by MS^n fragmentation. For this NMR measurements are required which were impossible since the isolation of pure reference standards from the batch experiments failed (data not shown). Accordingly to the methodology presented for TP 362, the chemical structures of the other detected TPs were determined.

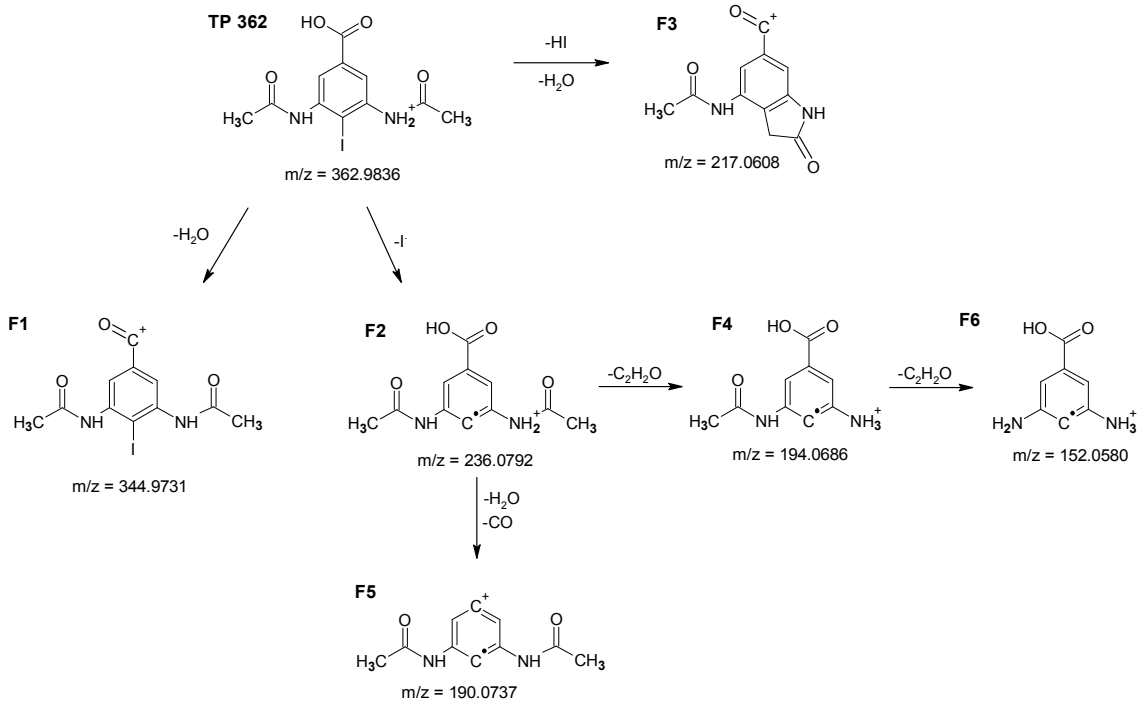


Figure S2. Proposed fragmentation pathway of TP 362 determined by LC-LTQ-Orbitrap MS with theoretical m/z ratios. The positions of cleaved iodines and ketene groups as well as charges have been assigned arbitrarily.

Transformation pathway

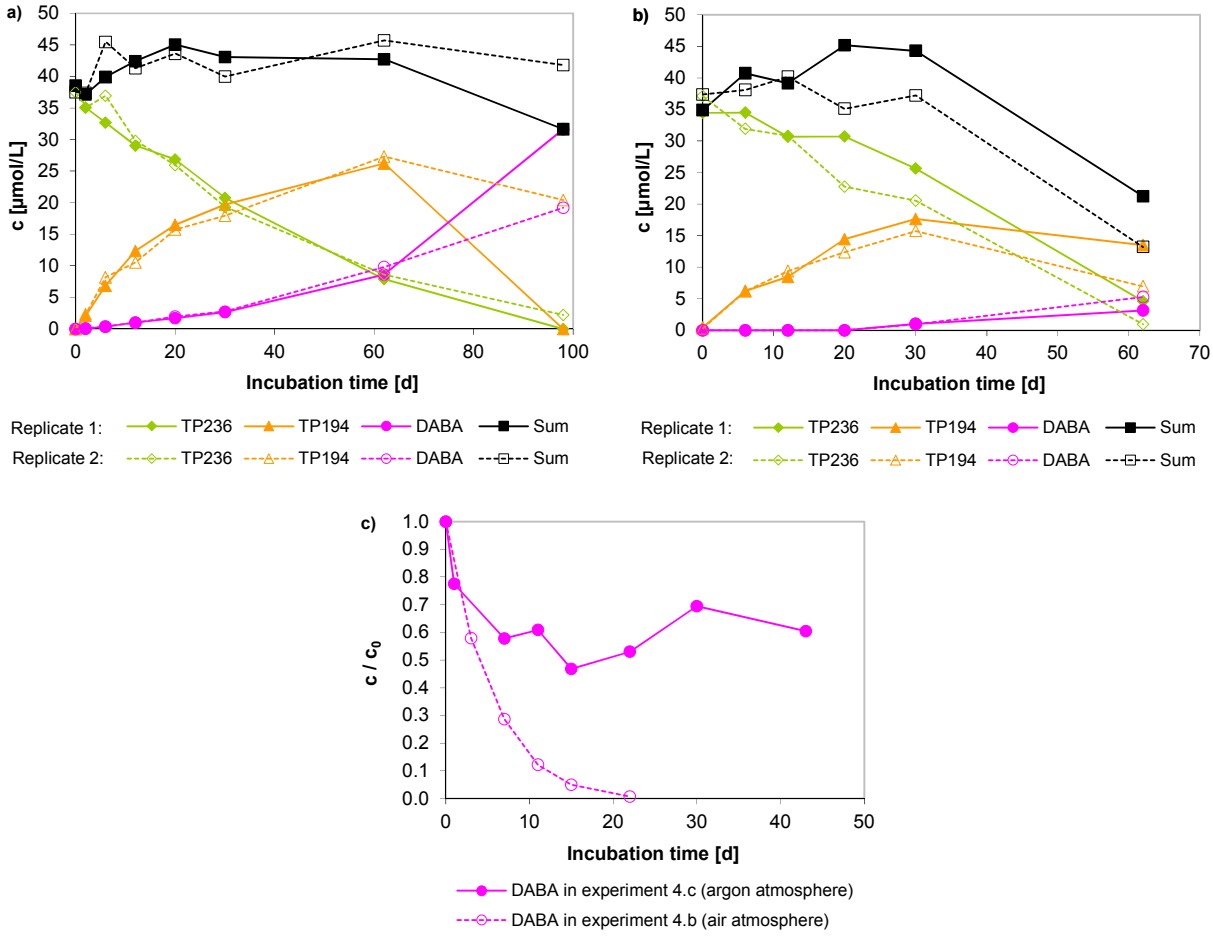


Figure S3. Concentrations of the TPs 236, 194 and DABA a) during incubation of TP 236 (c_0 = 10 mg/L) under an argon atmosphere (Experiment 3, n = 2) and b) under an air atmosphere (Experiment 4 a, n = 2). The dashed and solid lines represent the results of the two replicates; c) during incubation of DABA (c_0 = 10 mg/L) under an argon and an air atmosphere in experiments 4b and 4c. The 40% decrease of DABA within the first 6 d under argon atmosphere is presumably caused by spiking of DABA before strictly anaerobic conditions had been developed in the batch system.

Method to close mass balances

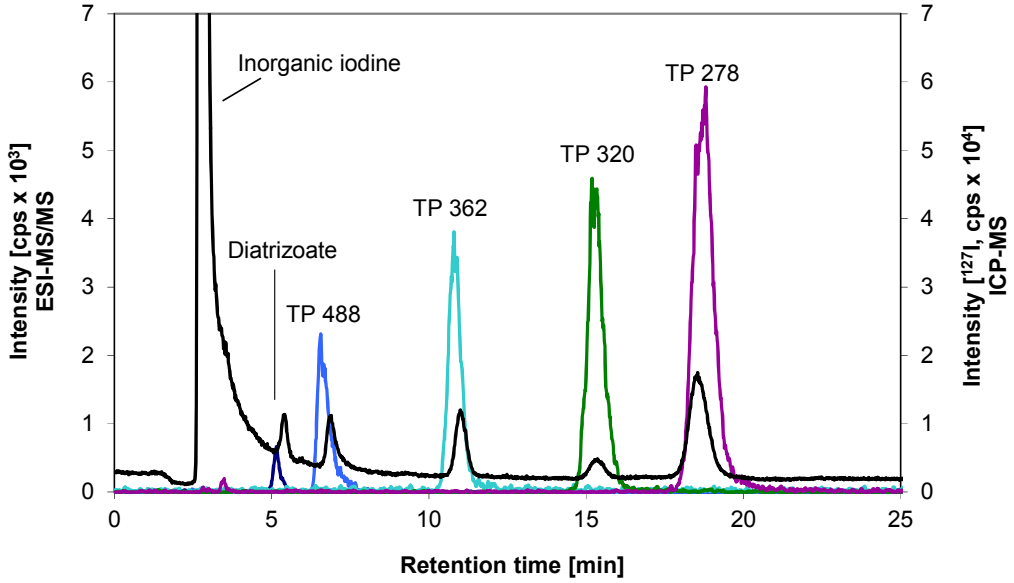


Figure S4. Peak assignment for LC-ICP-MS measurement (black line) of iodinated diatrizoate TPs with complementary LC-ESI-MS/MS measurement (coloured lines are extracted ion chromatograms of the single TPs).

Table S4. LOQs of the different quantification methods used for the quantification of diatrizoate and its anaerobic TPs in the batch experiments. LOQs are given in µg/L. The values in brackets represent the molar ratio (in percent) of the LOQ of TPs to the lowest spiked molar concentration of diatrizoate (5 µg/L, batch experiment 5).

quantification method	Diatrizoate	TP 488	TP 362	TP 320	TP 278	TP 236	TP 194	DABA
LC-ICP-MS	0.2 (3)	0.2 (5)	0.3 (10)	0.25 (10)	0.25 (10)			
SPE + LC-ICP-MS	0.02 (0.3)	0.02 (0.5)	0.03 (1)	0.03 (1)	0.25 (10)			
LC-ESI-MS/MS					0.06 (3)	0.03 (2)	0.1 (6)	0.5 (40)
Derivatization + LC-ESI-MS/MS							0.07 (5)	0.02 (2)

Table S5. Absolute recoveries of diatrizoate and its anaerobic TPs by SPE enrichment of the batch experiments with SDB1 cartridges (arithmetic means and standard deviations, n = 3).

	Diatrizoate	**TP 488**	**TP 362**	**TP 320**	**TP 278**	**TP 236**	**TP 194**	**DABA**
absolute recovery [%]	97 ± 13	78 ± 14	94 ± 10	87 ± 12	11 ± 3	97 ± 9	26 ± 1	< 5

References

(1) American Public Health Association, American Water Works Association, Water Environment Federation, *Standard methods for the examination of water and wastewater*, APHA-AWWA-WEF: Washington, D.C., 2005.

(2) Tabatabai.M.A., Rapid method for determination of sulfate in water samples. *Environmental Letters* **1974**, 7, (3), 237-243.

(3) Dugo, G.; Vilasi, F.; La Torre, G. L.; Pellicano, T. M., Reverse phase HPLC/DAD determination of biogenic amines as dansyl derivatives in experimental red wines. *Food Chemistry* **2006**, 95, (4), 672-676.