

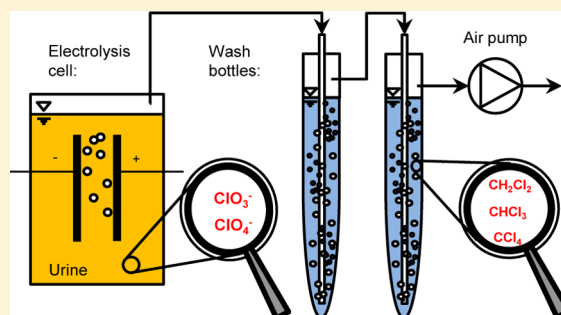
# Formation of Chlorination Byproducts and Their Emission Pathways in Chlorine Mediated Electro-Oxidation of Urine on Active and Nonactive Type Anodes

Hanspeter Zöllig, Annette Remmele, Cristina Fritzsche, Eberhard Morgenroth, and Kai M. Udert\*

Eawag, Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, 8600 Dübendorf, Switzerland

## S Supporting Information

**ABSTRACT:** Chlorination byproducts (CBPs) are harmful to human health and the environment. Their formation in chlorine mediated electro-oxidation is a concern for electrochemical urine treatment. We investigated the formation of chlorate, perchlorate, and organic chlorination byproducts (OCBPs) during galvanostatic (10, 15, 20 mA·cm<sup>-2</sup>) electro-oxidation of urine on boron-doped diamond (BDD) and thermally decomposed iridium oxide film (TDIROF) anodes. In the beginning of the batch experiments, the production of perchlorate was prevented by competing active chlorine and chlorate formation as well as by direct oxidation of organic substances. Perchlorate was only formed at higher specific charges (>17 Ah·L<sup>-1</sup> on BDD and >29 Ah·L<sup>-1</sup> on TDIROF) resulting in chlorate and perchlorate being the dominant CBPs (>90% of initial chloride). BDD produced mainly short chained OCBPs (dichloromethane, trichloromethane, and tetrachloromethane), whereas longer chained OCBPs (1,2-dichloropropane and 1,2-dichloroethane) were more frequently found on TDIROF. The OCBPs were primarily eliminated by electrochemical stripping: On BDD, this pathway accounted for 40% (dichloromethane) to 100% (tetrachloromethane) and on TDIROF for 90% (1,2-dichloroethane) to 100% (trichloromethane) of what was produced. A post-treatment of the liquid as well as the gas phase should be foreseen if CBP formation cannot be prevented by eliminating chloride or organic substances in a pretreatment.



## INTRODUCTION

Electrolysis is a versatile technology which is promising for on-site nutrient removal from urine because it allows for easy process control. The technology was applied for decentralized disinfection of drinking<sup>1</sup> and swimming pool water<sup>2</sup> and for on-site treatment of industrial wastewaters<sup>3,4</sup> or land fill leachate.<sup>5</sup> Electrolysis was also proposed to treat domestic wastewater on-site.<sup>6</sup> Thereby, the final goal, being it the disinfection of water or the removal of chemical substances, was primarily achieved by oxidation with active chlorine (Cl<sub>2</sub>, HOCl, and OCl<sup>-</sup>) which is produced in situ by the oxidation of chloride. This process is referred to as mediated or indirect electro-oxidation.

Urine contains high concentrations of chloride<sup>8</sup> potentially leading to strong active chlorine formation, high nutrient removal rates, and small reactors. It was shown that organic substances and ammonia can be readily removed with mediated electro-oxidation.<sup>6,9</sup> However, the unspecific nature of indirect oxidation resulted in the formation of chlorination byproducts (CBPs)<sup>10–12</sup> which could be a drawback of mediated electro-oxidation of urine.

Chlorate (ClO<sub>3</sub><sup>-</sup>) and perchlorate (ClO<sub>4</sub><sup>-</sup>) are important inorganic CBPs. They are the oxidation products of active chlorine species. Chlorate<sup>5,6,13,14</sup> and also perchlorate<sup>15–17</sup> were reported as products of mediated electro-oxidation. It is not completely clear under which conditions chlorate or perchlorate is the main product. The electrode material is an

important factor for the formation of perchlorate. Perchlorate formation was reported to be a bigger problem with boron-doped diamond (BDD) anodes than with mixed oxide electrodes.<sup>18</sup> Iridium oxide electrodes showed negligible perchlorate formation at low current densities. Furthermore, competing oxidation of chloride<sup>16,18</sup> or organic substances<sup>19</sup> was shown to reduce perchlorate formation. However, there is little knowledge about how these processes interact in a real, complex electrolyte such as urine and if competing reactions inhibit perchlorate formation.<sup>20</sup>

A second group of CBPs are organic chlorination byproducts (OCBPs). In batch electrolysis experiments, it was found that the concentration of OCBPs in the electrolyte increased initially, reached a maximum, and went back to zero.<sup>21</sup> This OCBP removal could result from the electrochemical degradation of OCBPs or from electrochemical stripping into the gas phase.<sup>22</sup> Most studies only analyzed the liquid phase while neglecting the gas phase as an emission pathway of OCBPs<sup>10,11,21,23</sup> or the complexity of real wastewaters was neglected by working with model substances if the gas phase was analyzed.<sup>22,24</sup> It remains unknown if OCBPs are mainly

Received: April 2, 2015

Revised: July 6, 2015

Accepted: July 27, 2015

Published: July 27, 2015



removed by electrochemical stripping or by electrochemical degradation in complex wastewaters.

In this study, we report on the fate of chlorate, perchlorate, and OCBPs during chlorine mediated electro-oxidation of real stored urine with nonactive type boron-doped diamond (BDD) and active type thermally decomposed iridium oxide film (TDIROF) anodes. We investigated if TDIROF leads to less perchlorate formation than BDD and if the high concentrations of chloride and organic substances prevent the formation of chlorate or perchlorate. We hypothesized that on TDIROF weaker chlorate and perchlorate formation would result in the formation of more OCBPs being eliminated primarily by electrochemical stripping into the gas phase.

## ■ EXPERIMENTAL SECTION

**Electrolysis Cell.** An undivided glass cell (400 mL) was equipped with a BDD (Si/BDD, BDD-film thickness: 3.0  $\mu\text{m}$ , B-doping: 800 ppm, sp3/sp2 ratio: 250, Adamant Technologies SA, La Chaux-de-Fonds, Switzerland) or a TDIROF (fabrication described elsewhere<sup>25</sup>) anode with 20  $\text{cm}^2$  of exposed surface area ( $A$ ). The cathode was made of steel (X5CrNi18-10, Hans Kohler AG, Zürich, Switzerland) with equivalent surface area. The electrodes were not pretreated except for intense rinsing with nanopure water. The distance between the electrodes ( $d$ ) was between 9 and 10 mm. A  $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$  (MSE, 0.64 V vs standard hydrogen electrode (SHE), ref 601, Radiometer analytical, France) reference electrode was employed to measure the anode potential ( $E_A$  in V) and was placed in a glass-blown Luggin capillary filled with saturated  $\text{K}_2\text{SO}_4$ . A magnetic stirrer (IKAMAG RCT basic, IKA, Staufen, Germany) ensured turbulence at a rotational speed of 750 rpm in all experiments. The temperature in the reactor was controlled below ambient temperature as indicated for each experiment to prevent condensation of OCBPs during transfer into the wash bottles (Colora thermostat, Colora Messtechnik GmbH, Lorch, Germany). The cell was covered with a glass lid and sealed up gastight with Teflon tape.

**Gas Wash.** The gas from the headspace was directed through Teflon tubes into two glass-blown wash bottles (WB, height: 40 cm, diameter: 2 cm, Glastechnik Rahm, MuttENZ, Switzerland) filled with dodecane ( $\geq 99\%$ , Merck, Darmstadt, Germany) to absorb volatilized OCBPs. The wash bottles were connected in series, and a constant air flow ( $Q_g = 18.0 \pm 0.7 \text{ mL} \cdot \text{min}^{-1}$ ) was ensured in all experiments by sucking air through the system with a vacuum pump (N816.1.2KN.18, KNF Neuberger AG, Freiburg, Germany). The gas flow was measured at the inlet to the headspace of the electrolysis cell with a flow meter (F-111D-HB-22-P, Bronkhorst High Tech, AK Ruurlo, The Netherlands) and at the outlet of the vacuum pump with a gas meter (L1, Wohlgroth AG, Zürich, Switzerland) and a bubble meter (Optiflow 520, Humonics, Fairfield, USA). The total amounts of the OCBPs were calculated by summing up the measured and calculated amounts in the liquid and gaseous compartments of the system (Supporting Information (SI), Figure S.1) and the mass removed in the aliquots. The amounts in the gaseous compartments were calculated by assuming equilibrium between the gas phase and the urine in the reactor or the gas phase and the dodecane in the wash bottles. Additionally, it was accounted for the mass lost out of wash bottle 2 ( $m_{\text{WB2,g}}$ ). This mass was calculated according to eq 1. Thereby, the concentration in the off-gas was calculated by assuming equilibrium between the gas bubbles leaving WB2 and the

dodecane phase. This was shown to be a reasonable assumption by modeling the OCBP concentrations in the rising gas bubble (SI, section B)

$$m_{\text{WB2,g}}(t_x) = \sum_{y=1}^{y=x} \left( \frac{1}{L_{16,\text{OCBP}}} \left( \frac{c_{\text{OCBP,WB2}}(y-1) + c_{\text{OCBP,WB2}}(y)}{2} \right) \int_{t_{y-1}}^{t_y} Q_g \cdot dt \right) \quad (1)$$

where  $t_x$  (s) is the time when aliquot  $x$  was taken,  $L_{16,\text{OCBP}}$  ( $\text{m}^3_{\text{gas}} \cdot \text{m}^{-3}_{\text{hexadecane}}$ ) is the partition coefficient of the particular OCBP between air and hexadecane (The partition coefficient for the air/dodecane system, which was not available, is very similar to the one of the air/hexadecane system (SI, section B), and  $c_{\text{OCBP,WB2}}(y)$  is the concentration of the OCBP in aliquot  $y$ .

**Recovery Experiment.** A recovery experiment was performed to show that OCBPs can be quantified with our experimental setup. Six OCBPs were quantified (dichloromethane, trichloromethane, tetrachloromethane, 1,2-dichloroethane, 1,2-dichloropropane, chlorobenzene) because of their high abundance in two preliminary electrolysis experiments with stored urine on BDD and TDIROF anodes (results not shown). Additionally, chloromethane was detected in significant amounts in these experiments but could not be quantified later due to a very low  $L_{16}$  value (SI, Table S.1). A spike solution ( $1 \text{ g} \cdot \text{L}^{-1}$ ) of the targeted OCBPs was prepared in ethanol (Merck), and 1.1 mL of this solution was spiked to 350 mL of nanopure water at time zero. The total amounts of the OCBPs were calculated as mentioned above to close the mass balances at 9 points in time within 8 h of experiment duration. In this experiment, the temperature in the electrolysis cell was controlled at 19 °C.

**Urine Electrolysis.** The electrolysis cell was filled with 350 mL of stored urine from the women's urine storage tank at Eawag (SI, Table S.2). Electrolysis was performed with a potentiostat which registered the current density  $j$  and  $E_A$  (PGU 10 V-1A-IMP-S, Ingenieurbüro Peter Schrems, Münster, Germany) under galvanostatic control at three current densities: 10, 15 (the data of the experiments at these two current densities can be found in the SI, section J), and 20  $\text{mA} \cdot \text{cm}^{-2}$ . The temperature in the electrolysis cell was controlled at 16.5 °C.

**Chemical Analysis.** Aliquots ( $\sim 13 \text{ mL}$ ) were taken with a syringe through a needle permanently installed in the glass lid for the wet chemical analysis. After the total COD analysis they were filtered with glass-fiber filters (0.45  $\mu\text{m}$ , Chromafil GF/PET, Macherey-Nagel, Düren, Germany). After dilution, chloride, chlorate, perchlorate, phosphate, sulfate, and nitrate were analyzed by ion chromatography (881 compact IC pro, Metrohm, Herisau, Switzerland). Ammonia, nitrite, and total COD were measured photometrically with cuvette tests (LCK 303, LCK 341, and LCK 314/614, Hach Lange, Berlin, Germany). The standard deviations of the wet chemical analyses were less than 5%. OCBPs were extracted from urine by taking aliquots ( $\sim 0.9 \text{ mL}$ ) with a gastight syringe. The unfiltered aliquots were added to 0.9 mL of dodecane in gas chromatography/mass spectrometry (GC/MS) glass screw-cap vials. The GC/MS vials were shaken for 10 s, and the solvent was allowed to separate for 30 min. Thereafter, 0.8 mL of the segregated dodecane phase on top of the sample was pipetted into another GC/MS glass screw-cap vial (1.5 mL). The dodecane aliquots ( $\sim 2 \text{ mL}$ ) from the wash bottles were taken

through a valve located at the bottom and pipetted into a GC/MS glass screw-cap vial. The dodecane samples were then analyzed by GC/MS (Thermo Scientific DSQII single quadrupole GC/MS, Restek, Bellefonte, USA) as described elsewhere.<sup>26</sup> Adsorbable organic halogens (AOX) were analyzed in a certified laboratory according to DIN EN 1485<sup>27</sup> (Labor Veritas, Zürich, Switzerland).

## RESULTS

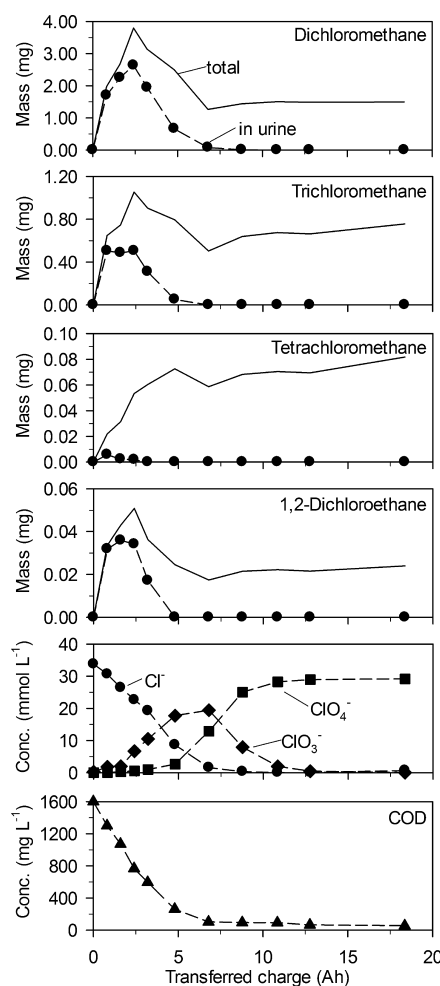
**Recovery Experiment of OCBPs.** The reliability of the new experimental setup for the measurement of OCBPs in the gas phase was tested with a recovery experiment prior to the actual experiments. The experiment showed that the experimental setup was suitable to quantify the targeted OCBPs during the electrolysis of urine. The average recovered masses over the 9 points in time were as follows:  $95 \pm 6\%$  (dichloromethane),  $99 \pm 2\%$  (trichloromethane),  $97 \pm 3\%$  (tetrachloromethane),  $98 \pm 3\%$  (1,2-dichloroethane),  $100 \pm 3\%$  (1,2-dichloropropane), and  $101 \pm 3\%$  (chlorobenzene). Detailed results are shown in section D of the SI.

**Chloride Removal and the Formation of Chlorate and Perchlorate.** At  $20 \text{ mA}\cdot\text{cm}^{-2}$ , chloride was constantly removed from urine in the beginning of each experiment as shown in Figure 1 and Figure 2 for BDD and TDIROF, respectively. However, chloride oxidation was more efficient on BDD. The chloride removal rates in the linear regions were  $8.3 \pm 0.3 \text{ mol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  on the BDD anode and  $5.5 \pm 0.2 \text{ mol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  on the TDIROF anode. This was surprising because in other studies TDIROF was shown to have a higher catalytic activity for chloride oxidation than BDD.<sup>28,29</sup>

The constant chloride removal in the beginning of the experiments implies that chloride oxidation was under current limited control on BDD and on TDIROF because the rate did not depend on the bulk concentration. At low chloride concentrations, the removal of chloride became mass transport limited which is apparent from the decreasing removal rate toward the complete removal of chloride.<sup>30</sup>

Chlorate was the dominant product of chloride oxidation on both electrodes (Figure 1 and Figure 2). On BDD, the chlorate production rate was  $6.3 \pm 0.7 \text{ mol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  until 5 Ah of transferred charge. On TDIROF, the production rate was  $4.7 \pm 0.7 \text{ mol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  up to 9 Ah corresponding to the slower oxidation of chloride on this anode. Neither the high concentration of chloride nor the one of organic substances prevented the formation of chlorate.

However, the presence of chloride or organic substances seemed to inhibit the formation of perchlorate in the beginning of the experiments (up to 3 Ah on BDD and up to 5 Ah on TDIROF), whereas impeding direct ammonia oxidation is unlikely due to low pH values close to the anode surface.<sup>25</sup> Strong perchlorate formation set in on both electrodes when the chloride concentration dropped below the chlorate concentration. At this point in time, the COD measurement was already comparatively low in the experiment with BDD ( $\sim 400 \text{ mgCOD}\cdot\text{L}^{-1}$ ), whereas with TDIROF it was still high ( $\sim 1200 \text{ mgCOD}\cdot\text{L}^{-1}$ ). This indicated that on BDD it might were the concentrations of chloride and organic substances that prevented perchlorate formation, whereas on TDIROF the presence of organics was less important. At the end of the experiments when all chloride was oxidized, the sum of chlorate and perchlorate accounted for 88% of the initial chloride concentration on BDD and for 96% on TDIROF, respectively.

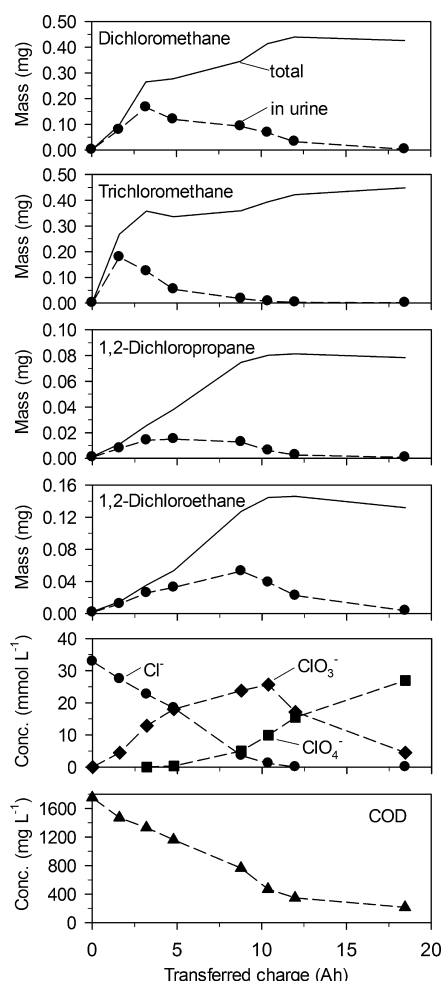


**Figure 1.** Concentrations in the cell and produced masses of OCBPs during the electrolysis of stored urine with a BDD anode at a current density of  $20 \text{ mA}\cdot\text{cm}^{-2}$ . The solid lines denote the total mass of OCBPs produced. The data with full symbols were measured in urine. Temperature:  $16.5^\circ\text{C}$ , electrode gap: 9 mm.

**Formation of OCBPs on BDD and TDIROF.** Figure 1 shows that a strong net production of the targeted OCBPs took place in the beginning of the electrolysis on the BDD anode (up to 2.5 Ah). Tetrachloromethane was the only OCBP which was produced until 5 Ah were transferred. This is an indication that tetrachloromethane was built from dichloromethane or trichloromethane through successive chlorination. Chlorobenzene was only found in traces ( $<3 \mu\text{g}$ ) close to the quantification limit ( $0.03 \text{ mg}\cdot\text{L}^{-1}$ ) in WB1. 1,2-Dichloropropane was detected (signal-to-noise ratio  $>3$ ) but could not be quantified.

After 2.5 Ah of transferred charge, the total amounts of the targeted OCBPs decreased dramatically except for tetrachloromethane. Since the OCBPs escaping in the off-gas of WB2 and the mass in the wash bottles were included in this calculation, the removal must have resulted from a process eliminating OCBPs in the system. More precisely, the elimination must have taken place in the electrolysis cell because the decrease in total mass came from a sharp drop in the mass measured in urine.

The formation of the targeted OCBPs on the TDIROF anode is shown in Figure 2. Dichloromethane and trichloromethane were the dominantly produced OCBPs. Tetrachloro-



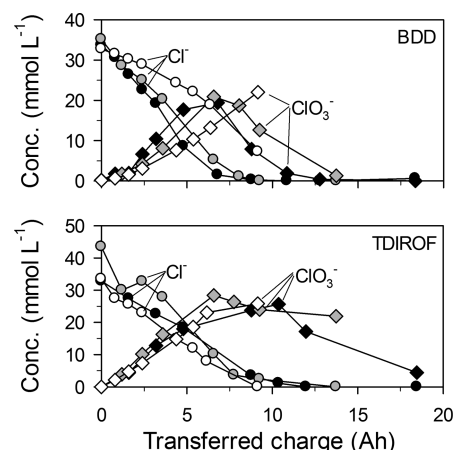
**Figure 2.** Concentrations in the cell and produced masses of OCBPs during the electrolysis of stored urine with a TDIROF anode at a current density of  $20 \text{ mA}\cdot\text{cm}^{-2}$ . The solid lines denote the total mass of OCBPs produced. The data with full symbols were measured in urine. Temperature:  $16.5^\circ\text{C}$ , electrode gap: 10 mm.

methane was not found with this anode. Compared to the BDD anode, larger amounts of 1,2-dichloroethane, 1,2-dichloropropane, and chlorobenzene (close to  $40 \mu\text{g}$ ) were produced. The net formation of dichloromethane and trichloromethane was strongest before 2.5 Ah, whereas 1,2-dichloropropane and 1,2-

dichloroethane were produced at a constant rate until all chloride was used up.

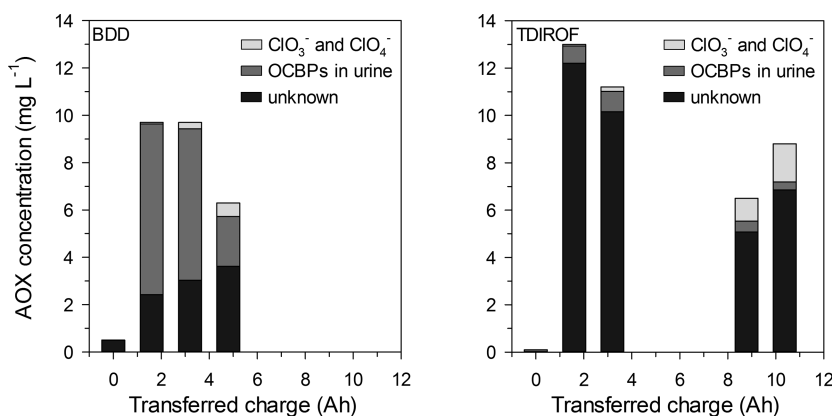
**Adsorbable Organic Halogens (AOX).** Electrolysis with the TDIROF anode yielded higher AOX concentrations than electrolysis with the BDD anode in the beginning of the experiments (Figure 3). However, only with the BDD anode a large fraction of the AOX concentrations could be explained with the OCBPs measured in the liquid phase. A small part of the AOX measurements could also be attributed to the interference of chlorate and perchlorate (SI, section E). The unknown AOX fractions could be chloramines or longer chained OCBPs that could not be detected with our GC/MS method because their boiling point is higher than the one of dodecane. Another possibility are untargeted OCBPs. In the preliminary experiments we also found chloromethane, bromomethane, chloroethane, 1,1-dichloroethane, and 2-chloropropane with the BDD and chloromethane, cyanogen chloride, dichloroacetonitrile, and trichloronitromethane with the TDIROF anode.

**Influence of the Current Density.** Figure 4 shows that chloride was oxidized with increased current efficiency on BDD



**Figure 4.** Concentration profiles of chloride and chlorate in urine during the electrolysis on BDD and TDIROF at three different current densities (Symbols black:  $20 \text{ mA}\cdot\text{cm}^{-2}$ , gray:  $15 \text{ mA}\cdot\text{cm}^{-2}$ , white:  $10 \text{ mA}\cdot\text{cm}^{-2}$ ).

when the applied current density was increased. Therefore, also chlorate was produced more efficiently. This was not the case



**Figure 3.** AOX concentrations in urine and the explainable fractions (due to chlorate and perchlorate interference and the amount of OCBPs measured by GC/MS) during the electrolysis of stored urine at  $20 \text{ mA}\cdot\text{cm}^{-2}$ . Temperature:  $16.5^\circ\text{C}$ , electrode gap BDD: 9 mm, TDIROF: 10 mm.



Table 1. Totally Produced OCBPs after the Electrolysis of Stored Urine up to 9 Ah of Transferred Charge

current density	(mA·cm <sup>-2</sup> )	BDD			TDIROF		
		20	15	10	20	15	10
dichloromethane	(mg)	1.44	2.51	0.22	0.44	0.33	0.30
trichloromethane	(mg)	0.64	1.12	0.24	0.42	0.31	0.29
tetrachloromethane	(mg)	0.07	0.16	0.03	0.00	0.00	0.00
1,2-dichloroethane	(mg)	0.02	0.03	0.00	0.15	0.15	0.16
1,2-dichloropropane	(mg)	0.00	0.00	0.00	0.08	0.09	0.10
chlorobenzene	(mg)	0.00	0.00	0.00	0.04	0.05	0.07
total OCBPs	(mmolCl·L <sup>-1</sup> )	0.15	0.26	0.03	0.07	0.06	0.06

on the TDIROF anode. Chloride was removed equally efficient at all current densities, and chlorate was formed accordingly.

OCBPs were formed at all current densities with both anode materials. The sum of all the quantified OCBPs revealed that BDD produced more of the targeted OCBPs than TDIROF when high current densities were applied (Table 1). However, at the lowest current density of 10 mA·cm<sup>-2</sup> the TDIROF anode produced more of the targeted OCBPs. With both anodes, the sum of targeted OCBPs did not clearly depend on the current density. With BDD, the strongest formation was observed with a medium current density of 15 mA·cm<sup>-2</sup>, whereas with TDIROF the production was similar at all three current densities.

## DISCUSSION

**Experimental Setup for OCBP Measurement.** In this paper, we present a novel method for the measurement of volatile OCBPs evolving from an electrolysis cell. The setup is simple and flexible and does not require sophisticated instrumentation. The cutoff in detectability of OCBPs, which is due to the boiling point of dodecane, can be circumvented by using other absorbents to extract OCBPs from urine and by combining different absorbents in the wash bottles connected in series or in parallel. Another advantage is that the dodecane samples can be stored easily and the analysis can be done with standard GC/MS equipment independently of the experiment itself.

The method allowed us to quantify OCBPs at a relatively high timely resolution compared to other methods. Johnson et al. used solid sorbent column traps which yielded a measurement point only after replacement every 8 h.<sup>24</sup> Comminellis and Nerini probably analyzed directly the gas in the headspace of a recirculation vessel – but details for sampling and quantification remain unclear.<sup>22</sup>

It is important to choose the right materials (i.e., glass, metal, or Teflon) for the tubing and the wash bottles to prevent OCBPs from adsorbing at the surfaces or diffusing through them. Furthermore, condensation of OCBPs at the walls of tubes and wash bottles has to be prevented by ensuring a lower temperature inside of the system compared to the ambient temperature. The wash bottles need to be tall, and the gas diffusers need to produce fine bubbles such that equilibrium between the gas phase and the absorbent phase is established. Representative samples are guaranteed due to the intense mixing of the absorbent by the rising gas bubbles.

**Reaction Schemes on BDD and TDIROF.** Before entering the discussion of our results we consider it useful to briefly review the current knowledge about the most relevant electrochemical oxidation processes on BDD and TDIROF. Chemical chlorate formation was briefly reviewed in section F

of the SI, and schemes summarizing these processes are given in the SI, Figure S.4.

On TDIROF, there is a consensus that chloride is oxidized by a direct electron transfer yielding adsorbed chloride radicals. In a subsequent step, two of the latter recombine to form active chlorine in a heterogeneous reaction.<sup>28,31</sup> The products of chloride oxidation are assumed to be mainly active chlorine species<sup>28</sup> although some studies also proposed direct oxidation of chloride to chlorate.<sup>32,33</sup> Organic substances can either be oxidized by a direct electron transfer at the electrode surface or by active chlorine species. The products can be smaller chained organic substances (intermediates), OCBPs, or CO<sub>2</sub>. The latter one is an end-product, while the other substances can undergo further oxidation. Active chlorine species can be oxidized to chlorate by direct oxidation on the electrode surface via chlorite as a possible intermediate.<sup>34</sup>

The discussion on chlorine formation on BDD is controversial in the literature. Some studies proposed a similar direct oxidation mechanism as observed on active type electrodes resulting in chlorine evolution being a competitive reaction to hydroxyl radical formation.<sup>18,35</sup> Other studies concluded that the oxidation by hydroxyl radicals led to the formation of active chlorine on BDD.<sup>28,36</sup> In the latter case, chloride is oxidized through indirect oxidation by hydroxyl radicals in a homogeneous reaction close to the anode.<sup>36</sup> The products are again likely to be active chlorine species.<sup>28</sup> Organic substances were shown to be oxidized by hydroxyl radicals,<sup>37,38</sup> but they can also be oxidized by active chlorine species.<sup>11</sup> Similar to TDIROF, the products can be smaller chained organic substances (intermediates), OCBPs, or CO<sub>2</sub>, and the first two might be further oxidized. Chlorate was reported to be formed by hydroxyl radical oxidation of active chlorine species.<sup>36</sup> Perchlorate formation was argued to require a direct electron transfer followed by a homogeneous reaction with hydroxyl radicals.<sup>20</sup>

**Efficiency of Chloride Oxidation.** The higher current efficiency for chloride oxidation on BDD compared to TDIROF could result from the distinct oxidation mechanisms. On TDIROF, chloride oxidation was probably limited by the availability of active sites at high chloride concentrations. This would explain why the current efficiency for chloride oxidation is not depending on the bulk concentration of chloride and why chloride oxidation does not increase with current density. On the BDD anode, the chloride oxidation rates were constant in each experiment. Either because of limiting active sites<sup>18</sup> or because the probability of a chloride ion meeting a hydroxyl radical<sup>28</sup> remained constant. This could be because the concentration of hydroxyl radicals in the reaction zone close to the anode increased with transferred charge, while the one of chloride and COD decreased. The higher concentration of

hydroxyl radicals then also resulted in stronger oxidation of chlorate to perchlorate and stronger oxygen evolution.

The higher current efficiency of chloride oxidation on BDD with increasing current density likely resulted from more strongly accelerated kinetics of direct chloride oxidation<sup>17,34</sup> compared to the kinetics of other anodic processes. Jeong et al.<sup>28</sup> reported a linear sweep voltammogram (LSV) on BDD which showed that the presence of chloride led to additional currents compared to a LSV in only supporting electrolyte indicating the faster acceleration of direct chloride oxidation with increasing anode potential. In our case, an increased current density led to an increased anode potential (SI, Figure S.5). If direct chloride oxidation on BDD happened at a lower on-set potential than other significant reactions, the increasing anode potential had a stronger effect on chloride oxidation due to the exponential character of the Butler–Volmer relationship.<sup>39</sup> Nevertheless, also chloride oxidation by hydroxyl radicals might have proceeded simultaneously.<sup>28,36</sup>

**Consequences for OCBP Formation.** On BDD, the stronger breakdown of organic substances in the reaction with hydroxyl radicals<sup>22</sup> led to more short chained intermediates which coexisted with higher concentrations of active chlorine. Consequently, more short chained OCBPs were produced especially in the beginning when the reaction rates were high. The lower production of the targeted OCBPs at  $20 \text{ mA}\cdot\text{cm}^{-2}$  (Table 1) may be explained with the more complete mineralization of organics to  $\text{CO}_2$  or by stronger formation and immediate stripping of chloromethane (not quantified) which could not be further chlorinated to dichloromethane or trichloromethane. With TDIROF on the other hand, the oxidative breakdown of organic molecules was less complete due to the weaker oxidizing environment (no hydroxyl radicals). The precursors for OCBP formation were therefore longer chained resulting in longer chained OCBPs.

The production of longer chained OCBPs also partially explains the higher amount of unknown AOX with the TDIROF anode. The GC/MS measurements showed that TDIROF was prone to form longer chained OCBPs. This indicated that on TDIROF OCBPs might have formed which were undetectable with our GC/MS method but which appear in the AOX measurements. Another explanation for unknown AOX are chloramines. On BDD, the stronger oxidation of chloride may have resulted in conditions also found in breakpoint chlorination.<sup>40</sup> Consequently, ammonia would have been oxidized all the way to  $\text{N}_2$  leaving little chloramines in solution. It is less probable that such conditions were reached on TDIROF due to less chloride oxidation which may led to more chloramines showing up in the AOX measurements.

**Fate of OCBPs.** The fate of the measured OCBPs was considerably different on the two electrodes. On TDIROF, they were entirely removed from urine by electrochemical stripping. This is easily seen at the end of the experiment where OCBPs were transferred completely into the gas phase (Figure 2). In contrast to the BDD anode, there was no evidence for another process that would remove OCBPs. The fact that tetrachloromethane was not found on TDIROF indicates that it was not formed: if it had been formed, it would have been stripped into the wash bottles due to the low solubility in water, and it would have been trapped in the wash bottles due to the high absorbability in dodecane (SI, Table S.1).

On BDD, the elimination of dichloromethane and trichloromethane may have resulted from further oxidation, to a small extent by chlorination to tetrachloromethane, or by complete

mineralization<sup>41</sup> to  $\text{CO}_2$  which was indicated by the smaller production of OCBPs at  $20 \text{ mA}\cdot\text{cm}^{-2}$  compared to  $15 \text{ mA}\cdot\text{cm}^{-2}$  (Table 1). Another possibility is that they got reduced at the cathode.<sup>42</sup> However, we used a steel cathode for which, to our knowledge, electro-reductive properties of OCBPs have not been reported yet. Additional experiments are needed to clarify this aspect because reductive dehalogenation of trichloromethane was observed and found to be strongly dependent on the cathode material.<sup>43,44</sup>

**Relative Importance of CBPs.** Chlorate was formed much more strongly than OCBPs with both anodes. Since OCBPs and chlorate are supposed to be formed in reactions involving active chlorine, the two processes are in competition. The much weaker formation of OCBP could result from small amounts of organic precursors for OCBP formation or from slow reaction kinetics of these reactions compared to chlorate formation. The strong chlorate formation likely resulted from simultaneous direct oxidation of chloride and active chlorine (TDIROF)<sup>32</sup> or the oxidation of active chlorine via hydroxyl radicals (BDD)<sup>36</sup> and chemical reactions of active chlorine species.<sup>45</sup> Thereby, chemical chlorate formation could have been favored by an ideal pH range (between 6 and 9)<sup>45,46</sup> due to the good buffer capacity of urine.

Perchlorate formation was low on both electrodes as long as chlorate was present at much lower concentrations than chloride and COD. This indicates that chloride, active chlorine, and COD were preferentially oxidized over chlorate. In contrast to earlier results,<sup>17</sup> strong production of perchlorate was observed on TDIROF toward the end of the experiments. This may be explained with chemical perchlorate formation due to ideal pH conditions in the diffusion layer (3.5–7.5)<sup>46,47</sup> resulting from the moderate current densities applied and the good buffer capacity in real urine (detailed discussion in SI, section H). On the BDD anode, not only a competition of chloride and chlorate for active sites on the electrode was already suggested<sup>18</sup> but also a competition for hydroxyl radicals could be an explanation. Thus, high concentrations of chloride and COD could prevent perchlorate formation. However, if COD and chloride are completely eliminated after the same amount of transferred charge as in our experiments, there is a risk of strong perchlorate formation.

According to our results three risks exist with the chlorine mediated electro-oxidation of urine concerning CBPs: The first is the potentially massive formation of dissolved chlorate and especially perchlorate. These can be minimized by working at low current densities (BDD) and by respecting a maximum specific charge (residual chloride should be left). Second, targeted OCBPs and unidentified AOX can be left in solution at lower specific charges. Their toxicity remains unknown. However, in preliminary experiments (SI, section I) a nonspecific chlorophyll fluorescence test<sup>48</sup> indicated a positive effect of electrolysis (BDD,  $10 \text{ mA}\cdot\text{cm}^{-2}$ ) on the baseline toxicity of urine, which means that the overall reduction of toxicity was higher than the increase by producing toxic OCBPs. Finally, we conclude that it is not sufficient to look at byproducts in the liquid phase. The gas phase is equally important. In this work, the stripping of OCBPs into the gas phase accounted for 40% to 100% of the targeted OCBPs on BDD and for 95% to 100% on TDIROF. Accordingly, electrolysis units which produce OCBPs should be equipped with an off-gas treatment especially if they are placed in a closed room.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b01675.

Details on experimental setup and calculations on aspects mentioned in the Discussion (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Phone: 41 58 765 5360. Fax: 41 58 765 5802. E-mail: [kai.udert@eawag.ch](mailto:kai.udert@eawag.ch).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank the Bill and Melinda Gates Foundation for financing this study within the VUNA project ([www.vuna.ch](http://www.vuna.ch), Grant No. OPP1011603). We thank Karin Rottermann and Claudia Bänninger-Werffeli for the chemical analysis and Thomas Hofstetter and Jakov Bolotin for their advice for the experimental setup and the OCBP measurements.

## ■ REFERENCES

- (1) Kerwick, M. I.; Reddy, S. M.; Chamberlain, A. H. L.; Holt, D. M. Electrochemical disinfection, an environmentally acceptable method of drinking water disinfection? *Electrochim. Acta* **2005**, *50* (25–26), 5270–5277.
- (2) Ghernaout, D.; Ghernaout, B. From chemical disinfection to electrodisinfection: The obligatory itinerary? *Desalin. Water Treat.* **2010**, *16* (1–3), 156–175.
- (3) Szpyrkowicz, L.; Radaelli, M. Scale-up of an electrochemical reactor for treatment of industrial wastewater with an electrochemically generated redox mediator. *J. Appl. Electrochem.* **2006**, *36* (10), 1151–1156.
- (4) Panizza, M.; Cerisola, G. Electrochemical oxidation as a final treatment of synthetic tannery wastewater. *Environ. Sci. Technol.* **2004**, *38* (20), 5470–5475.
- (5) Anglada, A.; Urriaga, A.; Ortiz, I. Pilot scale performance of the electro-oxidation of landfill leachate at boron-doped diamond anodes. *Environ. Sci. Technol.* **2009**, *43* (6), 2035–2040.
- (6) Cho, K.; Qu, Y.; Kwon, D.; Zhang, H.; Cid, C. A.; Aryanfar, A.; Hoffmann, M. R. Effects of anodic potential and chloride ion on overall reactivity in electrochemical reactors designed for solar-powered wastewater treatment. *Environ. Sci. Technol.* **2014**, *48* (4), 2377–2384.
- (7) Anglada, A.; Urriaga, A.; Ortiz, I. Contributions of electrochemical oxidation to waste-water treatment: Fundamentals and review of applications. *J. Chem. Technol. Biotechnol.* **2009**, *84* (12), 1747–1755.
- (8) Udert, K. M.; Larsen, T. A.; Gujer, W. Fate of major compounds in source-separated urine. *Water Sci. Technol.* **2006**, *54* (11–12), 413–420.
- (9) Candido, L.; Gomes, J.; Jambo, H. C. M. Electrochemical treatment of oil refinery wastewater for NH<sub>3</sub>-N and COD removal. *Int. J. Electrochem. Sci.* **2013**, *8* (7), 9187–9200.
- (10) Bagastyo, A. Y.; Batstone, D. J.; Rabaey, K.; Radjenovic, J. Electrochemical oxidation of electrodialed reverse osmosis concentrate on Ti/Pt–IrO<sub>2</sub>, Ti/SnO<sub>2</sub>–Sb and boron-doped diamond electrodes. *Water Res.* **2013**, *47* (1), 242–250.
- (11) Anglada, A.; Urriaga, A.; Ortiz, I.; Mantzavinos, D.; Diamadopoulos, E. Boron-doped diamond anodic treatment of landfill leachate: Evaluation of operating variables and formation of oxidation by-products. *Water Res.* **2011**, *45* (2), 828–838.
- (12) Panizza, M.; Cerisola, G. Direct and mediated anodic oxidation of organic pollutants. *Chem. Rev.* **2009**, *109* (12), 6541–6569.
- (13) Cho, K.; Hoffmann, M. R. Urea degradation by electrochemically generated reactive chlorine species: Products and reaction pathways. *Environ. Sci. Technol.* **2014**, *48*, 11504–11511.
- (14) Lacasa, E.; Llanos, J.; Canizares, P.; Rodrigo, M. A. Electrochemical denitrification with chlorides using DSA and BDD anodes. *Chem. Eng. J.* **2012**, *184*, 66–71.
- (15) Li, H.; Ni, J. Electrogeneration of disinfection byproducts at a boron-doped diamond anode with resorcinol as a model substance. *Electrochim. Acta* **2012**, *69*, 268–274.
- (16) Perez, G.; Saiz, J.; Ibanez, R.; Urriaga, A. M.; Ortiz, I. Assessment of the formation of inorganic oxidation by-products during the electrocatalytic treatment of ammonium from landfill leachates. *Water Res.* **2012**, *46* (8), 2579–2590.
- (17) Li, H.; Yu, Q.; Yang, B.; Li, Z.; Lei, L. Electro-catalytic oxidation of artificial human urine by using BDD and IrO<sub>2</sub> electrodes. *J. Electroanal. Chem.* **2015**, *738*, 14–19.
- (18) Bergmann, M. E. H.; Rollin, J.; Iourtchouk, T. The occurrence of perchlorate during drinking water electrolysis using BDD anodes. *Electrochim. Acta* **2009**, *54* (7), 2102–2107.
- (19) Donaghue, A.; Chaplin, B. P. Effect of select organic compounds on perchlorate formation at boron-doped diamond film anodes. *Environ. Sci. Technol.* **2013**, *47* (21), 12391–12399.
- (20) Azizi, O.; Hubler, D.; Schrader, G.; Farrell, J.; Chaplin, B. P. Mechanism of perchlorate formation on boron-doped diamond film anodes. *Environ. Sci. Technol.* **2011**, *45* (24), 10582–10590.
- (21) Panizza, M.; Cerisola, G. Electrochemical oxidation of 2-naphthol with in situ electrogenerated active chlorine. *Electrochim. Acta* **2003**, *48* (11), 1515–1519.
- (22) Comninellis, C.; Nerini, A. Anodic oxidation of phenol in the presence of NaCl for wastewater treatment. *J. Appl. Electrochem.* **1995**, *25* (1), 23–28.
- (23) Naumczyk, J.; Szpyrkowicz, L.; ZilioGrandi, F. Electrochemical treatment of textile wastewater. *Water Sci. Technol.* **1996**, *34* (11), 17–24.
- (24) Johnson, S. K.; Houk, L. L.; Feng, J. R.; Houk, R. S.; Johnson, D. C. Electrochemical incineration of 4-chlorophenol and the identification of products and intermediates by mass spectrometry. *Environ. Sci. Technol.* **1999**, *33* (15), 2638–2644.
- (25) Zöllig, H.; Morgenroth, E.; Udert, K. M. Inhibition of direct electrolytic ammonia oxidation due to a change in local pH. *Electrochim. Acta* **2015**, *165* (0), 348–355.
- (26) Zöllig, H.; Fritzsche, C.; Morgenroth, E.; Udert, K. M. Direct electrochemical oxidation of ammonia on graphite as a treatment option for stored source-separated urine. *Water Res.* **2015**, *69* (0), 284–294.
- (27) DIN EN 1485:1996-11, *Water quality - Determination of adsorbable organically bound halogens (AOX)*; German version EN 1485:1996.
- (28) Jeong, J.; Kim, C.; Yoon, J. The effect of electrode material on the generation of oxidants and microbial inactivation in the electrochemical disinfection processes. *Water Res.* **2009**, *43* (4), 895–901.
- (29) Kraft, A.; Stadelmann, M.; Blaschke, M.; Kreysig, D.; Sandt, B.; Schröder, F.; Rennau, J. Electrochemical water disinfection. Part I: Hypochlorite production from very dilute chloride solutions. *J. Appl. Electrochem.* **1999**, *29* (7), 859–866.
- (30) Kapalka, A.; Foti, G.; Comninellis, C. Kinetic modelling of the electrochemical mineralization of organic pollutants for wastewater treatment. *J. Appl. Electrochem.* **2008**, *38* (1), 7–16.
- (31) Trasatti, S. Progress in the understanding of the mechanism of chlorine evolution at oxide electrodes. *Electrochim. Acta* **1987**, *32* (3), 369–382.
- (32) Jung, Y. J.; Baek, K. W.; Oh, B. S.; Kang, J. W. An investigation of the formation of chlorate and perchlorate during electrolysis using Pt/Ti electrodes: The effects of pH and reactive oxygen species and the results of kinetic studies. *Water Res.* **2010**, *44* (18), 5345–5355.
- (33) Czarnetzki, L. R.; Janssen, L. J. J. Formation of hypochlorite, chlorate and oxygen during NaCl electrolysis from alkaline solutions at an RuO<sub>2</sub>/TiO<sub>2</sub> anode. *J. Appl. Electrochem.* **1992**, *22* (4), 315–324.



- (34) Tasaka, A.; Tojo, T. Anodic oxidation mechanism of hypochlorite ion on platinum electrode in alkaline solution. *J. Electrochem. Soc.* **1985**, *132* (8), 1855–1859.
- (35) Polcaro, A. M.; Vacca, A.; Mascia, M.; Palmas, S.; Rodriguez Ruiz, J. Electrochemical treatment of waters with BDD anodes: Kinetics of the reactions involving chlorides. *J. Appl. Electrochem.* **2009**, *39* (11), 2083–2092.
- (36) Bergmann, M. E. H. Drinking water disinfection by in-line electrolysis: Product and inorganic by-product formation. In *Electrochemistry for the Environment*; Comninellis, C., Chen, G., Eds.; Springer: New York, London, 2010; pp 163–204.
- (37) Comninellis, C. Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for wastewater treatment. *Electrochim. Acta* **1994**, *39* (11–12), 1857–1862.
- (38) Kapalka, A.; Lanova, B.; Baltruschat, H.; Fóti, G.; Comninellis, C. Electrochemically induced mineralization of organics by molecular oxygen on boron-doped diamond electrode. *Electrochem. Commun.* **2008**, *10* (9), 1215–1218.
- (39) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; John Wiley & Sons: New York, 2001.
- (40) Kapalka, A.; Katsaounis, A.; Michels, N. L.; Leonidova, A.; Souentie, S.; Comninellis, C.; Udert, K. M. Ammonia oxidation to nitrogen mediated by electrogenerated active chlorine on Ti/PtOx-IrO<sub>2</sub>. *Electrochem. Commun.* **2010**, *12* (9), 1203–1205.
- (41) Randazzo, S.; Scialdone, O.; Brillas, E.; Sires, I. Comparative electrochemical treatments of two chlorinated aliphatic hydrocarbons. Time course of the main reaction by-products. *J. Hazard. Mater.* **2011**, *192* (3), 1555–1564.
- (42) Rondinini, S.; Vertova, A. Electroreduction of halogenated organic compounds. In *Electrochemistry for the Environment*; Comninellis, C., Chen, G., Eds.; Springer: New York, London, 2010; pp 279–306.
- (43) Sonoyama, N.; Sakata, T. Electrochemical continuous decomposition of chloroform and other volatile chlorinated hydrocarbons in water using a column type metal impregnated carbon fiber electrode. *Environ. Sci. Technol.* **1999**, *33* (19), 3438–3442.
- (44) Sonoyama, N.; Hara, K.; Sakata, T. Reductive electrochemical decomposition of chloroform on metal electrodes. *Chem. Lett.* **1997**, *2*, 131–132.
- (45) Gordon, G.; Tachiyashiki, S. Kinetics and mechanism of formation of chlorate ion from the hypochlorous acid/chlorite ion reaction at pH 6–10. *Environ. Sci. Technol.* **1991**, *25* (3), 468–474.
- (46) Landolt, D.; Ibl, N. On mechanism of anodic chlorate formation in concentrated NaCl solutions. *Electrochim. Acta* **1970**, *15* (7), 1165–1183.
- (47) D'Ans, J.; Freund, H. E. Kinetic studies 1. About the formation of chlorate from hypochlorite (German). *Z. Elektrochem., Ber. Bunsen-Ges. Phys. Chem.* **1957**, *61* (1), 10–18.
- (48) Escher, B. I.; Bramaz, N.; Maurer, M.; Richter, M.; Sutter, D.; Von Känel, C.; Zschokke, M. Screening test battery for pharmaceuticals in urine and wastewater. *Environ. Toxicol. Chem.* **2005**, *24* (3), 750–758.

#### ■ NOTE ADDED AFTER ASAP PUBLICATION

There was an error in the TOC and abstract graphic published August 28, 2015. The corrected graphic published September 1, 2015.