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Fate of organic contaminants in electrochemical nitrogen recovery from urine

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Abstract

This study compared the fate of pharmaceuticals and disinfection byproducts across three electrochemical nitrogen recovery processes treating urine: electrochemical stripping (ECS), electrodialysis (ED), and bipolar electrodialysis (BPED). ECS achieved greater TAN recovery efficiencies than ED and BPED and was the only process that recovered a urine-derived ammonium sulfate product rather than a mixed concentrate (containing TAN, sodium, and potassium). Enrichment and removal ratios based on target pharmaceutical quantification and suspect screening were used to evaluate the fate of organic compounds relative to nitrogen recovery. These metrics suggested that ECS prevented organic contamination of the product more effectively than the other two processes and that both ECS and BPED achieved greater organic removal than ED. No disinfection byproducts were detected in the product for any process, but formation in other chambers may require mitigation. Our findings inform pre- and post-treatment for electrochemical nitrogen recovery, as well as modifications to reactor configuration and operating conditions. With future work using suspect screening and identification of additional compounds to build greater mechanistic understanding of compound fate and characterize the toxicity of contaminants detected in treated urine and recovered products, our work will advance electrochemical technologies that recover high-purity, safely applied products and enable a circular nitrogen economy.

Environmental Significance Statement

Nitrogen recovery from wastewater can reduce the environmental impacts and cost of wastewater treatment and ammonia production. Electrochemical processes are an emerging technology that



can enable nitrogen recovery in a modular, scalable, and automatable way using high-nitrogen waste streams like urine. However, pharmaceutical prevalence in urine poses a risk to recovered nitrogen product purity and could contribute to the already common occurrence of pharmaceuticals in the environment. Non-target analysis is needed to broadly understand transformation and fate of organic contaminants and ensure that electrochemically recovered nitrogen products and treated waste streams are safe. Addressing concerns about organic micropollutants would eliminate a barrier to using recovered nitrogen products among farmers and consumers to facilitate environmentally responsible implementation.

1 Introduction

Nitrogen in wastewater has negative environmental, human health, and economic impacts, including impairing drinking water quality and causing widespread eutrophication that leads to tens to hundreds of billions of dollars in annual economic losses in the U.S. alone.¹ To reduce nitrogen discharges to the environment, wastewater treatment currently uses substantial chemical and energy inputs to remove nitrogen.^{2,3} Meanwhile, nitrogen is a critical component of fertilizers and other industrial chemicals,⁴ and ammonia synthesis via the Haber-Bosch process accounts for about 1% of global fossil fuel energy consumption⁵ and 1.4% of global carbon dioxide emissions.⁶ Recovering nitrogen from wastewater for beneficial reuse in a circular economy can reduce environmental impacts and costs of wastewater treatment and chemical production. Because 80% of nitrogen in wastewater comes from urine that accounts for only 1% of wastewater volume,⁷ nitrogen can be removed more efficiently from urine than combined wastewater.⁸ Multiple studies have demonstrated acceptance of urine-derived fertilizers among farmers and food consumers, indicating a potential market and supporting viability of urine-derived fertilizers.⁹⁻¹⁵ Urine's high conductivity (16-35 mS/cm for urine¹⁶⁻¹⁹ compared to 1 mS/cm for domestic wastewater²⁰⁻²²) also



facilitates electrochemical treatment with minimal energy consumption because of low solution resistance. Electrochemical urine treatment processes have achieved nitrogen removal, pharmaceutical degradation or separation, energy recovery (e.g., via hydrogen generation), and selective nitrogen recovery.²³ Electrochemical nitrogen recovery technologies may be particularly promising for distributed urine treatment (e.g., toilet-scale, building scale) due to their modularity, process stability, reduced chemical inputs, automation, and ease of maintenance and operation.^{23–}

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However, on average 65% of pharmaceuticals are excreted via urine,²⁶ and concerns about environmental contamination with urine-derived pharmaceuticals and the purity of urine-derived products pose a major barrier to implementing nitrogen recovery from urine. Many pharmaceuticals are poorly removed in conventional wastewater treatment trains.^{27,28} Furthermore, residual contaminants and their transformation products are becoming prevalent in the environment (e.g., pharmaceuticals detected in 80% of U.S. streams²⁹), threatening humans and aquatic species.^{29–31} Farmers and the general public mention micropollutants, especially pharmaceuticals, among the most important risks associated with urine-derived fertilizers.^{9–11,13–15} To be widely implemented, nitrogen recovery processes must prevent further environmental contamination and effectively separate pharmaceuticals from recovered products. Thus, it is critical to understand the fate of pharmaceuticals in electrochemical nutrient recovery systems to enable development of mitigation strategies.

To date, research on pharmaceutical fate in electrochemical and other urine treatment processes has largely focused on specific pharmaceuticals via target analysis. Targeted studies have documented the extent of removal of particular pharmaceuticals in processes designed for micropollutant removal from urine, such as granular activated carbon adsorption,³²



nanofiltration,³³ electrochemical oxidation,³⁴ and UV-based advanced oxidation processes.³⁵ Researchers have also evaluated the fate of pharmaceuticals in urine treatment processes focusing on volume reduction (e.g., evaporation³⁶) and nutrient recovery (e.g., ion exchange,³⁷ electrochemical stripping,¹⁹ struvite precipitation³⁸). Similar evaluations have been conducted for processes that simultaneously recover nutrients and remove micropollutants from urine.^{36,39} Electrochemical urine treatment is still nascent and at lower technology readiness levels than most other urine treatment technologies;²³ thus studies of pharmaceutical fate during electrochemical treatment of other wastewaters (e.g., anaerobic digestate, reverse osmosis concentrate, secondary effluent) could supplement understanding of urine treatment. These studies also typically use target analysis to evaluate pharmaceutical removal in direct and indirect electrochemical oxidation,^{40–46} electrodialysis,^{47,48} and electrochemical membrane biofilm reactors⁴⁹ and to evaluate pharmaceutical fate in electrodialysis for nutrient recovery.^{50–52} Target analysis facilitates evaluation of fate and treatment performance for a limited number of species but leaves many compounds, including transformation products that may be more toxic and persistent than parent compounds, unidentified and unquantified.^{25,39,53}

Analyzing larger data sets via nontarget analysis of trace organic compounds enables more comprehensive understanding of the electrochemical fate of pharmaceuticals and transformation products. Whereas true nontarget analysis makes no assumptions about the likelihood of detecting any compound, suspect screening (one type of nontarget analysis) uses a list of compounds (i.e., suspects) that are likely present based on the sample matrix (e.g., urine).⁵⁴ Both approaches facilitate detection of pharmaceuticals, metabolites formed in humans, and transformation products using mass spectral data for tentative compound identification without reference standards and without *a priori* selection criteria for compounds of interest. These techniques can



semi-quantitatively relate effluent and influent samples and enable retrospective analysis of compounds identified or synthesized in the future.^{53,55–62} By expanding the set of identifiable compounds beyond target analysis, non-target analysis and suspect screening can more broadly elucidate the fate of pharmaceuticals and other organic contaminants in electrochemical urine treatment, but such studies remain limited. Suspect screening and non-target analysis have been preliminarily conducted for electrochemical oxidation processes^{43,63,64} that do not specifically target nutrient removal or recovery from urine to identify transformation products and elucidate degradation pathways for a select few pharmaceuticals (e.g., carbamazepine^{43,63}). Suspect screening and non-target analysis are needed to identify risks associated with a broad array of pharmaceutical and pharmaceutical-derived contaminants. This knowledge can inform strategies for mitigation in electrochemical nitrogen recovery processes treating urine and support the establishment of urine treatment standards⁶⁵ that can facilitate widespread implementation of urine diversion, treatment, and resource recovery for sustainable nitrogen and wastewater management.

In addition to pharmaceuticals, disinfection byproducts (DBPs) pose an obstacle to electrochemical water and urine treatment^{23,25,66,67} because they are reported as a barrier or knowledge gap for 40% of electrochemical nutrient removal or recovery technologies.⁶⁸ Many DBPs are cytotoxic, neurotoxic, mutagenic, or genotoxic^{69–71} and are associated with increased cancer risk and other detrimental health impacts (e.g., birth defects).^{71–74} Some DBPs, including trihalomethanes (THMs), haloacetic acids (HAAs), and dichloroacetonitrile (DCAN), are regulated drinking water contaminants.⁷⁵ DBPs are increasingly prevalent throughout the environment^{76,77} and have negative impacts on aquatic organisms,^{78,79} such as endocrine disruption in shrimp⁸⁰ and toxicity in various species.^{81–83} Electrochemical processes often expose chloride-rich urine (1,600 – 7,700 mg/L chloride^{23,84}) to an oxidizing environment, which can lead to DBP



formation. For example, during electrochemical oxidation of latrine wastewater, two regulated DBPs (chloroform and haloacetic acids) were observed at concentrations 10 to 1,000 times the EPA drinking water maximum contaminant levels.⁸⁵ Characterizing DBP formation and fate in electrochemical nutrient recovery systems is essential to developing mitigation strategies that reduce effluent toxicity and enhance product purity, enabling these technologies to up-concentrate nutrients without concomitant accumulation of harmful byproducts.

This study evaluates potential risks of electrochemical technologies for nitrogen recovery from urine by characterizing the fate of pharmaceuticals and DBPs in electrochemical stripping (ECS), electrodialysis (ED), and bipolar electrodialysis (BPED). These three technologies were selected because they rely on similar mechanisms for nitrogen removal/recovery (i.e., electromigration across ion exchange membranes), which enables evaluation of the impacts of reactor architecture and different types of membranes on nitrogen removal/recovery and byproduct fate. Moreover, ECS is representative of an emerging nitrogen recovery technique combining electrodialysis with membrane stripping;^{19,86} ED is a more established electrochemical treatment process that can be useful for benchmarking newer processes like ECS;^{23,87} and BPED utilizes bipolar membranes, which are increasingly studied due to their lower energy consumption.^{88,89} For urine treatment using these three technologies, the specific objectives of this study were to (1) compare pharmaceutical concentrations in treated effluent to existing regulatory standards, (2) evaluate recovered product purity and safety based on the fate of pharmaceuticals and their transformation products within the reactors, and (3) elucidate mechanisms that govern organic compound fate during electrochemical nitrogen treatment. Our results inform pre- and post-treatment strategies and motivate concrete objectives for optimizing reactor configuration and operating conditions, which are among the most common knowledge gaps facing nutrient technologies at large.⁶⁸ Based



on elucidating and addressing these barriers, outcomes of this study will advance electrochemical nutrient recovery technologies toward implementation.

2 Methods

2.1 Urine Collection, Storage, and Treatment

All processes evaluated in this study treated hydrolyzed human urine collected in the Shriram Center for Chemical Engineering and Bioengineering at Stanford University. Urine was collected from July 3 to October 8, 2021 with approximately equal contributions from male and female donors over age 18 (Internal Review Board Protocol 60601). Urine was stored in a closed container at room temperature (25°C) and 0.6 mg/L urease (41,050 units/g solid, Sigma-Aldrich, St. Louis, MO) was added to accelerate urea hydrolysis. Due to low natural pharmaceutical levels, collected urine was spiked with 20 µg/L of acetaminophen, emtricitabine, iopromide, atenolol (ATE), sulfamethoxazole, N-acetyl-sulfamethoxazole, trimethoprim (TMP), metoprolol (MET), naproxen, bezafibrate (BZF), propranolol (PRO), carbamazepine (CBZ), and diclofenac (DIC); this concentration is approximately representative of realistic urine.²⁶ This set of compounds enabled quantification of target pharmaceuticals for validation of the non-target analysis workflow. Urine was characterized comprehensively (including total ammonia nitrogen (TAN), ions, and pH (Section **S****Error! Reference source not found.**), as well as pharmaceuticals (Section 2.3)) prior to each experiment to verify that composition remained consistent over time (**Error! Reference source not found.**).

Electrochemical stripping (ECS) and bipolar electro dialysis (BPED) (Figure 1) were evaluated using 12-hour batch experiments in which solutions within each chamber were recirculated internally. Electrodialysis (ED) was evaluated using 4-hour batch experiments due to potentiostat



limits (**Error! Reference source not found.**). We chose batch over continuous operation to facilitate comparison of our results for electrochemical processes to prior non-target analyses and suspect screens conducted for other urine treatment processes.⁹⁰ Batch experiments also facilitated collection of sufficient sample volume at each time point to characterize both pharmaceuticals and disinfection byproducts. For each reactor, a constant current density of 100 A/m² was applied using a VMP-300 potentiostat (Biologic, Seyssinet-Pariset, France) with a leakless eDAQ Ag/AgCl reference electrode placed in the chamber containing the anode (eDAQ, Colorado Springs, CO). Solutions (prepared as described in Section **Error! Reference source not found.**) were recirculated within each reactor chamber at a flowrate of 75 mL/min for 4 (ED) or 12 (ECS and BPED) hours. Additional details about reactor setup and operation and sample collection (**Error! Reference source not found.**) are provided in Section **Error! Reference source not found.**



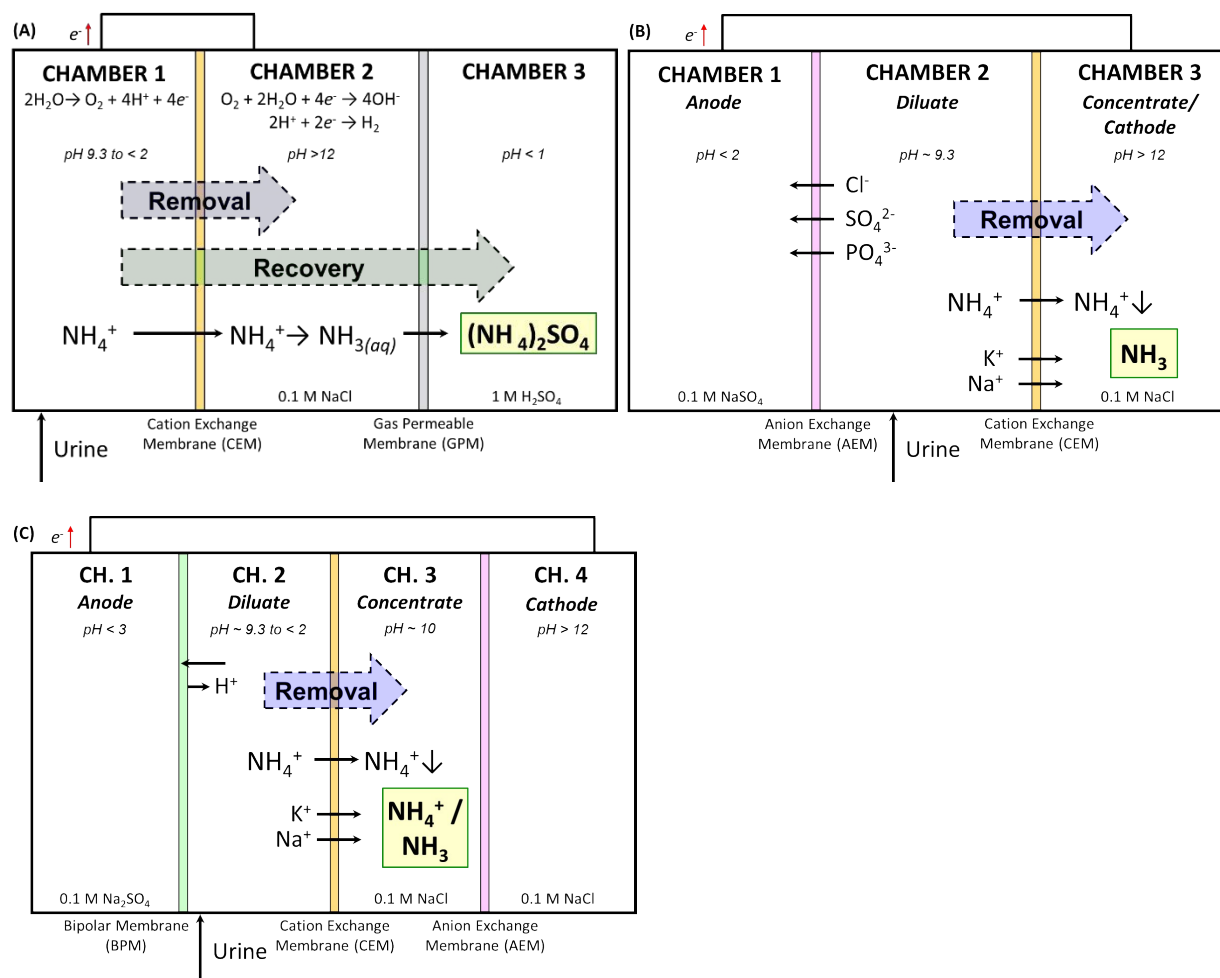


Figure 1. Schematics of electrochemical nitrogen treatment processes: electrochemical stripping (ECS, A), electrodialysis (ED, B), and bipolar electrodialysis (BPED, C). (A) For ECS, in Chamber 1, current applied to electrodes in Chambers 1 and 2 catalyzes the oxygen evolution reaction, lowering the pH of influent wastewater and converting NH_3 to NH_4^+ . NH_4^+ ions migrate across the cation exchange membrane (CEM) from Chamber 1 to 2. In Chamber 2, applied current catalyzes the hydrogen evolution reaction, raising the pH and converting NH_4^+ ions into NH_3 . NH_3 is volatile and can diffuse across the gas permeable membrane (GPM) from Chamber 2 to 3, separating TAN from cations extracted from the wastewater (e.g., Na^+ , K^+ , Mg^{2+} , Ca^{2+}). In Chamber 3, sulfuric acid converts NH_3 to NH_4^+ , allowing recovery of ammonium sulfate solution. (B) For ED, urine is introduced into Chamber 2 (diluate chamber). Electric current applied to an anode in Chamber 1 and a cathode in Chamber 3 drives cations, including NH_4^+ , across the CEM from Chamber 2 to 3 (concentrate) while driving anions across the anion exchange membrane (AEM) from Chamber 2 to 1 (anode). Water splitting at the cathode elevates Chamber 3 pH. The product from ED is a mixture of cations and NH_3 . (C) For BPED, urine is introduced into Chamber 2. Electric current is applied to an anode in Chamber 1 and a cathode in Chamber 4, driving water splitting in the bipolar membrane (BPM) separating Chambers 1 and 2. The BPM releases protons into Chamber 2, converting NH_3 in urine to NH_4^+ , which electromigrates across the CEM into Chamber 3 along with other cations. An



AEM separating Chambers 3 and 4 allows hydroxide ions generated by water splitting in Chamber 4 to pass to Chamber 3. BPED, therefore, generates a product mixture containing $\text{NH}_3/\text{NH}_4^+$ and cations. The pH evolution in each reactor chamber over time is shown in Figure S2-1.

2.2 Evaluation of Nitrogen Recovery Performance

Total ammonia nitrogen (TAN) concentrations were measured via segmented flow analysis (SEAL Analytical, Mequon, WI) using a phenol-based colorimetric method (Section **SError! Reference source not found.**). The fold change in TAN concentration from influent to product, FC_{TAN} , was calculated as follows:

$$FC_{TAN} = \frac{[TAN]_{product,final}}{[TAN]_{influent,initial}}$$

We expected FC_{TAN} to be approximately one because experiments were designed to achieve complete TAN recovery.

2.3 Pharmaceutical Analysis

Samples for pharmaceutical analysis were prepared by solid phase extraction (SPE) as described in Section **SError! Reference source not found.** Extracts were stored at -20°C until analysis via liquid chromatography-mass spectrometry (LC-MS) for target analysis and liquid chromatography-high resolution mass spectrometry (LC-HRMS) for suspect screening.

2.3.1 Target Analysis

Seven pharmaceutical compounds (atenolol (ATE), trimethoprim (TMP), metoprolol (MET), bezafibrate (BZF), propranolol (PRO), carbamazepine (CBZ), and diclofenac (DIC)) were quantified using standard curves ($0.01 - 50 \mu\text{g/L}$) and deuterated internal standards ($200 \mu\text{g/L}$) (**Error! Reference source not found.**). Samples were analyzed on an Agilent 1260 HPLC with an Agilent 6460 Triple Quadrupole MS using an Agilent Poroshell 120 EC-C18 $2.7 \mu\text{m}$, 3.0×50



mm column (Agilent, Santa Clara, CA). Additional LC-MS method details are provided in Section **S**Error! Reference source not found. (Error! Reference source not found. and Error! Reference source not found.).

2.3.2 Suspect Screening

For non-target analysis, samples were analyzed on a Thermo Scientific Orbitrap Exploris 240 mass spectrometer (Thermo Scientific, Waltham, MA) using an Agilent Poroshell 120 EC-C18 2.7 μm , 3.0 x 50 mm column (Agilent, Santa Clara, CA) for ECS and a Kinetex Core-Shell C18 2.6 μm , 2.1 x 150 mm column (Phenomenex, Torrance, CA) for ED and BPED. Additional LC-HRMS method details are provided in Section **S**Error! Reference source not found. (Error! Reference source not found.). Suspect screening was performed in R (version 4.3.0) using an open-source package, patRoon (version 2.2.0).^{91,92} A step-by-step illustration of the workflow is provided in **Error! Reference source not found.**, and parameters for each step are provided in **Error! Reference source not found.** through **Error! Reference source not found.** (Section **S**Error! Reference source not found.). The suspect screening workflow was validated using the compounds quantified via target analysis.^{56,93}

2.3.3 Metrics for Pharmaceutical Behavior

For target compounds, measured concentrations of pharmaceuticals were compared to existing water reuse guidelines (**Error! Reference source not found.**). For target compounds and compounds identified via non-target analysis, we calculated two types of fold change (FC) in pharmaceutical concentrations as follows:

$$FC_{enrichment} = \frac{[pharmaceutical]_{product}}{[pharmaceutical]_{influent}}$$



$$FC_{removal} = \frac{[pharmaceutical]_{effluent}}{[pharmaceutical]_{influent}}$$

where $[pharmaceutical]$ is the concentration or peak intensity for a single compound at a particular time in one of the reactor chambers. The specific samples for each reactor denoted by the subscripts in the formulas above are shown in **Error! Reference source not found.** and **Error! Reference source not found.**

Pharmaceutical fate relative to nutrient recovery was quantified according to enrichment and removal ratios:

$$Enrichment\ Ratio = \frac{FC_{enrichment}}{FC_{TAN}}$$

$$Removal\ Ratio = \frac{FC_{removal}}{FC_{TAN}}$$

Optimal performance would achieve a low enrichment ratio (i.e., high TAN recovery and low pharmaceutical contamination in product). The removal ratio captures the extent of pharmaceutical removal achieved (relative to ammonia recovery) via chemical transformation and physical migration across ion exchange membranes. With a focus on maximizing nutrient recovery, a low removal ratio would be optimal. However, if pharmaceuticals are transformed to less toxic and less persistent compounds, higher removal ratios would be desirable. Fold changes and ratios were calculated for target compounds and features found via suspect screening to facilitate comparison of the two ratios and evaluate how representative target compounds are of the broader array of pharmaceuticals and organic compounds found in urine.⁹⁴



2.3.4 Statistical Analysis

Experimental triplicates with analytical duplicates or triplicates (i.e., each experiment was performed in triplicate and each sample was extracted in duplicate at final time and in triplicate at initial time) were averaged and compared using bidirectional t-tests ($\alpha=0.05$). Statistical analysis was conducted using R (Version 4.3.0). All replicates (i.e., six measurements at final time, nine measurements at initial time) in all sample pairings (i.e., influent and effluent, influent and product) were used to be as conservative as possible in compound identifications and comparisons between unit processes. For suspect screening, features that were detected in more than zero and less than 5 of 6 or 7 of 9 replicate samples were discarded. The results of these statistical analyses were used to create volcano plots that visualize changes that are both large in magnitude and statistically significant by showing the p-values for comparisons of two groups of pharmaceutical concentrations versus the associated ratio (i.e., enrichment or removal).⁹⁵

2.4 Disinfection Byproduct Analysis

DBPs in seven classes (trihalomethanes or THMs, haloacetic acids or HAAs, haloacetonitriles or HANs, haloacetaldehydes or HALs, haloketones or HKs, halonitromethanes or HNMs, and haloacetamides or HAMS, **Error! Reference source not found.**) were extracted using modified EPA methods 551.1 and 552.3 and analyzed via gas chromatography-mass spectrometry (GC-MS, Agilent, Santa Clara, CA). Details on analytes and methods are included in Section **Error! Reference source not found.** (detection limits in **Error! Reference source not found.**). Both regulated and unregulated DBPs were evaluated because previous work suggested that regulated DBP concentrations may not adequately indicate overall DBP exposure⁹⁶ and unregulated DBPs, such as HAMS and HALs, exhibit higher cytotoxicity than regulated DBP classes.⁹⁷ Iodinated trihalomethanes (I-THMs) were excluded from analysis because initial screening experiments



showed no I-THM formation. We chose to report only presence/absence of DBPs, rather than measured concentrations. Concentration variability between experiments was high, but presence/absence of compounds was consistent. Presence was defined as detection in at least 5 of 6 replicate samples.

3 Results and Discussion

3.1 Nitrogen Removal and Recovery Performance

The three electrochemical processes – ECS, ED, and BPED – rely on electrochemically generated pH changes, electromigration, and diffusion to remove and recover nitrogen from urine. For ECS, current applied between Chambers 1 and 2 lowers the pH of influent urine in Chamber 1 and converts NH_3 to NH_4^+ . NH_4^+ ions migrate across the CEM from Chamber 1 to 2. In Chamber 2, applied current raises the pH, converting NH_4^+ ions into NH_3 . NH_3 volatilizes and diffuses across the GPM from Chamber 2 to 3. Sulfuric acid in Chamber 3 converts NH_3 to NH_4^+ , allowing recovery of ammonium sulfate solution. For ED, urine is introduced into Chamber 2 (diluate chamber). Electric current applied between Chambers 1 and 3 drives NH_4^+ across the CEM from Chamber 2 to 3 (concentrate) while driving anions across the anion exchange membrane (AEM) from Chamber 2 to 1 (anode). The pH in Chamber 3 rises, while the pH in Chamber 1 decreases and the pH in Chamber 2 remains approximately constant at the wastewater's initial pH. For BPED, urine is also introduced into Chamber 2. Electric current applied between Chambers 1 and 4 drives water splitting in the BPM separating Chambers 1 and 2. The BPM releases protons into Chamber 2, lowering the pH of the urine and converting NH_3 to NH_4^+ . NH_4^+ ions electromigrate across the CEM into Chamber 3 along with other cations. An AEM separating Chambers 3 and 4 allows hydroxide ions generated in Chamber 4 to pass to Chamber 3, raising the pH in Chambers



3 and 4. Electric current and associated pH changes (Figure S2-1) determine the fate of TAN and organic compounds in the system.

Before investigating the fate of organic compounds, we characterized TAN removal and recovery performance (**Error! Reference source not found.**, Figure S2-2, **Error! Reference source not found.**). ECS and BPED achieved nearly complete TAN removal within 12 hours ($96.9 \pm 0.5\%$ and $88.9 \pm 1.1\%$, respectively), while ED achieved $56.6 \pm 4.0\%$ removal. ECS achieved more complete recovery ($97.2 \pm 11\%$ or fold change of 0.972 ± 0.11) than ED ($64.3 \pm 5.9\%$ or fold change of 0.643 ± 0.059) and BPED ($79.0 \pm 6.2\%$ or fold change of 0.790 ± 0.062). The lower removal and recovery efficiencies of ED were caused by shorter operation and higher pH in the diluate chamber (Figure S2-1). At higher pH, more TAN in the diluate was present as NH_3 , which limited removal and recovery with only ion exchange membranes present in ED. Neutral NH_3 , unlike cationic NH_4^+ , cannot be removed by electro-migration, only by diffusion from the diluate to the concentrate. However, TAN accumulation in the concentrate and the fact that NH_3 was the dominant TAN species at the concentrate's high pH (11.4 ± 0.04 to 12.7 ± 0.03) reduced the driving force for diffusion. BPED's lower recovery efficiency was likely caused by its less closed TAN mass balance compared to ECS and ED (**Error! Reference source not found.**). In BPED, TAN loss was more likely than in ED and ECS: the concentrate compartment (Chamber 3) pH was alkaline while Chamber 3 in ECS was acidic and BPED was operated for 12 hours compared to 4 hours for ED, allowing NH_3 volatilization. Given these performance metrics and the fact that ED and BPED recovered a mixed concentrate (containing all cations removed from urine, including Na^+ , K^+ , and NH_4^+) while ECS recovered ammonium sulfate, ECS was a more effective nitrogen recovery process than ED and BPED.



3.2 Fate of Organic Contaminants

The fate of organic contaminants was evaluated using both a target analysis of seven pharmaceuticals and a suspect screen relying on the Pubchemlite database and validated using the target analysis. Identification of detected features by the suspect screening workflow was validated by verifying detection of target compounds (**Error! Reference source not found.**). For ECS and BPED, 7 of 7 target formulas and compounds were annotated, while 6 of 7 targets were annotated for ED. These statistics help validate the suspect screening workflow although having a larger set of target compounds for validation would further improve confidence.

No maximum allowed concentrations have been defined for our target compounds in recycled water policies in the U.S. but such levels have been set in Australia's recycled drinking water guideline (**Error! Reference source not found.**). For all target compounds except diclofenac, initial pharmaceutical concentrations in urine were below Australian guidelines (Table S1-1). Diclofenac concentrations were reduced to below the guideline in ECS and BPED, but not in ED (**Error! Reference source not found.**). Therefore, pharmaceutical degradation under acidic conditions may be important for enabling reuse of urine after electrochemical nutrient recovery.

Mass balances on target pharmaceuticals (i.e., totaling to less than 100% of initial mass present) indicate that the selected pharmaceuticals were transformed to varying degrees in the investigated electrochemical processes (**Error! Reference source not found.**). For example, trimethoprim, propranolol, and diclofenac were largely transformed during ECS, and metoprolol and carbamazepine to a lesser extent. Previous studies suggested that reaction with surface-bound reactive chlorine species significantly contribute to transformation of several of these compounds.⁴³ ED less completely transformed compounds with only propranolol and diclofenac being removed to some extent. In BPED, propranolol and diclofenac were largely transformed,



while trimethoprim, metoprolol, bezafibrate, and carbamazepine were partially transformed. For the compounds that were only partially transformed, most compounds remaining at the end of treatment were found in urine (i.e., influent), but some compounds migrated to other chambers. For example, atenolol crossed the CEM into the cathode or concentrate chambers in all three processes. Trimethoprim, propranolol, and diclofenac crossed the AEM toward the anode chamber in ED.

Compound properties explain observed target compound fates (Figure S2-4, Table S2-4). Diclofenac and bezafibrate are the only compounds with pKa below 5, but bezafibrate is mostly conserved (especially in ECS and ED) while diclofenac is largely removed from solution (especially in ECS and BPED). Both compounds are neutral at pH values observed in urine during ECS and the later part of BPED, preventing electromigration. Both are negatively charged at pH values observed in urine during ED, facilitating some electromigration across the AEM to the anode chamber. Diclofenac has been reported to adsorb to ion exchange membranes due to its high molecular volume and hydrophobicity when in neutral form, facilitating greater removal from solution during ECS and BPED than ED.⁹⁸ Trimethoprim has a near-neutral pKa. Therefore, it is neutral at pH values observed in urine during ED, causing it to be mostly conserved. By contrast, trimethoprim becomes positively charged at low pH occurring in urine in ECS and BPED, enabling electromigration to Chamber 2 in ECS and Chamber 3 in BPED, where high pH converts the molecule to its neutral, adsorption-prone form and could lead to base-catalyzed hydrolysis. Trimethoprim's low Henry's constant makes it unlikely that volatilization would contribute to removal. More complete removal during ECS than BPED could result from urine pH decreasing more quickly during ECS than BPED, allowing more time for migration.



Atenolol, metoprolol, and propranolol have pKa values between 9.1 and 9.6. These compounds exist as a mixture of cationic and neutral forms in urine in ED but are mostly cationic at low pH occurring in urine in ECS and BPED. Greater electromigration in ECS and BPED than ED could enhance adsorption to CEMs and enable degradation under alkaline conditions occurring in Chamber 2 of ECS and Chamber 3 of BPED. Notably, the extent of removal of these three compounds matches the order of hydrophobicity with atenolol being least hydrophobic and least removed and propranolol being most hydrophobic and most removed. Greater hydrophobicity likely increases adsorption onto ion exchange membranes,⁹⁹ and propranolol has been shown to adsorb to mixed metal anodes due to hydrophobicity.⁴³ Carbamazepine is the target compound with the highest pKa (13.9). It is conserved in ED and BPED, and its fate in ECS is somewhat uncertain, suggesting some removal. Carbamazepine remains neutral across the pH range observed in all three processes, limiting electromigration. Removal during ECS could be due to degradation via indirect electrochemical oxidation in the presence of active chlorine species formed during ECS, with more effective degradation at lower pH.¹⁰⁰ Adsorption to mixed metal anodes due to organic compound hydrophobicity⁴³ can also contribute to removal in ECS, which is the only process studied that places urine in direct contact with the electrode. Carbamazepine is the most volatile of the target compounds with a Henry's constant 1 to 7 orders of magnitude greater than other compounds. The oxygen evolution reaction occurring at the anode in ECS could enhance removal via volatilization due to bubble formation, which does not occur in urine in the other processes. These patterns illustrate that pKa, hydrophobicity, and volatility are important properties affecting the fate of organic contaminants in electrochemical nitrogen recovery processes.



Based on suspect screening, volcano plots indicate a wide range of enrichment and removal ratios for all processes (Figure 2A, **Error! Reference source not found., Error! Reference source not found.**, Table S2-5). ERs were shifted slightly leftward for ECS compared to those for ED and BPED, suggesting that having two barriers between influent urine and the product chamber (i.e., CEM and GPM) more effectively prevented organic contaminants from reaching the product than a single barrier (i.e., CEM). Differences were statistically significant except for the ER calculated from suspect data for ECS and BPED (Table S2-5). Average ER was less than 1 when considering only target compounds, indicating that TAN recovery was preferred over organic transport to the product (Figure 2B, C and **Error! Reference source not found.**). The higher initial TAN concentration compared to that of pharmaceuticals leads to a higher concentration gradient, increasing the driving force for diffusion. TAN transport by diffusion in addition to electromigration would contribute to greater TAN recovery compared to pharmaceutical accumulation in the product. Average RRs were greater than ERs, and RRs for ED were shifted rightward compared to those for ECS and BPED. This difference was likely caused by lower TAN recovery achieved by ED than ECS and BPED. Differences in urine pH for ED compared to ECS and BPED could also have affected transformation and migration of contaminants, leading to different RRs. RR differences were statistically significant except for the RR calculated from target intensities for ECS and BPED (Table S2-5). Average RRs were also often less than 1, except for ED, indicating that the processes more effectively performed their intended function (i.e., TAN recovery) than a potential additional function (i.e., organic contaminant removal) and that organic compounds generally tended to be removed rather than accumulated in the treated urine. ERs and RRs for the same features detected during suspect screening did not appear to be strongly correlated (**Error! Reference source not found. Error! Reference source not found.**).



Average enrichment and removal ratios calculated for all suspect compounds differed from those calculated for suspects identified as target compounds with some statistically significant but perhaps not practically significant differences between calculation methods and datasets (Figure 2B, C, Table S2-6, and Table S2-7). Average ERs for target features were statistically significantly lower than those determined for all features found during suspect screening. Average RRs were also statistically significantly lower for target features than for all features, but the values overlapped more than ERs did (Table S2-6). Average ERs calculated based on target analysis were generally similar to ER calculated for features identified as target compounds based on suspect screening (**Error! Reference source not found.A**, Table S2-7). For ECS and ED, average ER for all features from suspect screening overlapped with ERs for target compounds calculated in at least one way. However, for BPED, the ER based on all features from suspect screening was greater than the values for target compounds regardless of calculation method. Average RRs showed more overlap for target compounds and the complete dataset compared to ERs (**Error! Reference source not found.B**, Table S2-7). Generally, target data showed higher variability than suspect data, which is expected because of the large difference in the number of target vs. suspect screened compounds. These differences between target and suspect data indicate that selecting additional standards could allow the fate of target compounds to more completely reflect the range of behavior of all suspect compounds.



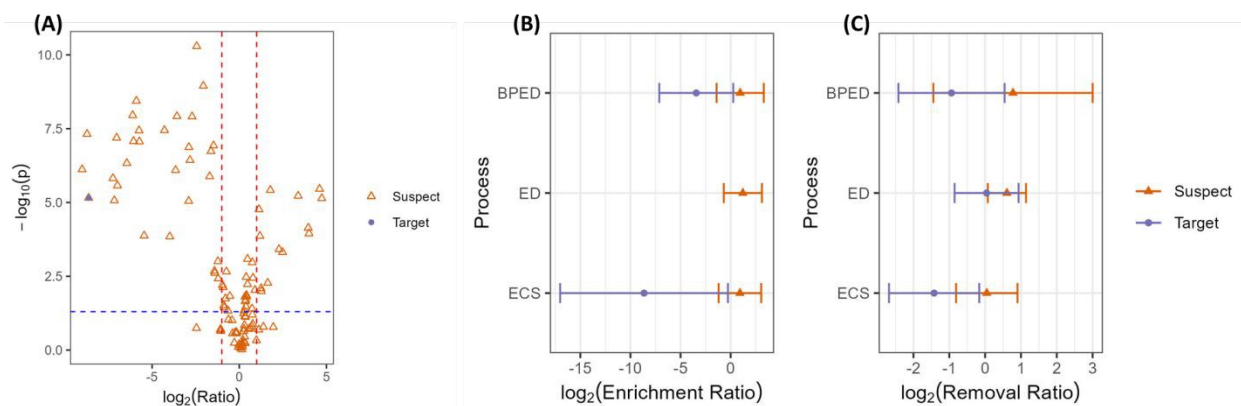


Figure 2. Enrichment and removal ratios based on target pharmaceutical analysis and suspect screening. (a) Volcano plot for enrichment ratio for ECS as calculated for each of the target pharmaceuticals and all features detected during suspect screening. Analogous plots for enrichment ratio for ED and BPED and for removal ratio for all processes are shown in **Error! Reference source not found.** and **Error! Reference source not found.**. (b) Average enrichment ratio for each process for all target pharmaceuticals and all features detected during suspect screening. (c) Average removal ratio for each process for all target pharmaceuticals and all features detected during suspect screening. No average enrichment ratio for targets is shown for ED because none of the features detected in the product chamber were identified as target compounds during suspect screening. Results of statistical analysis are shown in Table S2-5 through Table S2-7.

3.3 Product Purity

Product purity is a crucial consideration for implementation of electrochemical nutrient recovery processes.^{9–11,13–15} We evaluated product purity based on detection of three groups of species: target pharmaceuticals, target disinfection byproducts, and suspect features (Figure 3). No target pharmaceuticals were detected in the ammonium sulfate product recovered by ECS, while a few target pharmaceuticals were detected in ED and BPED products. These results suggest that two barriers with different separation mechanisms between urine and the product – a cation exchange membrane and a hydrophobic gas permeable membrane in ECS – facilitated more effective separation of contaminants from nutrients than a single barrier – a cation exchange membrane for ED and BPED. However, the number of suspect features detected in the product did not illustrate such an advantage for ECS.



Notably, no DBPs were detected in the product chambers for all processes despite formation of multiple DBPs in the anode chambers (**Error! Reference source not found.**). DBPs were detected in treated urine and the anode chambers for all processes, suggesting that DBPs might be a concern for effluent quality and overall safety (**Error! Reference source not found. to Error! Reference source not found.**, Section S**Error! Reference source not found.**). On the time scales of operation evaluated in this study, DBPs posed a minimal risk to product purity and safety for all processes, even at extended treatment times due to batch operation. Nevertheless, we recommend studies with longer treatment and larger volumes of urine to confirm these findings.

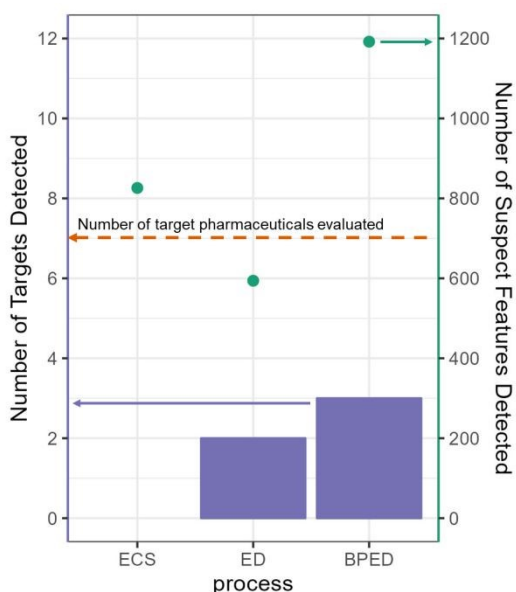


Figure 3. Number of detected species in products, including target pharmaceuticals (7 quantified) and features detected during suspect screening. Note that no disinfection byproducts characterized via target analysis (20 quantified) were detected in the products.

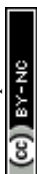
3.4 Identification of Priority Compounds

Identifying undesired compounds in recovered products is important from a product safety perspective. Identifying priority compounds based on their degree of removal or formation in treated urine could show co-removal of organics with nitrogen recovery processes and help



evaluate the safety of treated effluent. We selected priority features that exhibit both (1) significant differences in enrichment or removal ratios between the process influent and effluent samples ($p < 0.05$ with two-sided t-test) and (2) extreme enrichment or removal of the compounds compared to nutrient recovery (ER or $RR > 2$, ER or $RR < 0.5$). Table 1 and **Error! Reference source not found.** through **Error! Reference source not found.** summarize the distribution of features among priority and other categories, as well as compound identification rates. For all processes, more features were detected only in the influent than only in the effluent or product, indicating that more compounds were removed than formed. For ECS and BPED, more features had $ER < 0.5$ than $ER > 2$, while ED showed the opposite relationship. Therefore, ECS and BPED may be more effective at separating nitrogen from organic contaminants. ECS facilitated more removal of organic contaminants than ED and BPED simultaneously with nitrogen recovery because more feature groups were removed to a larger extent (i.e., $RR < 0.5$) and fewer feature groups were up-concentrated (i.e., $RR > 2$). This difference is likely due to urine being in direct contact with the anode in ECS, but not in ED and BPED. Across processes, priority features accounted for small fractions of total detected features. Focusing on this relatively small set of features that show significant and large changes between influent and effluent or product yields a manageable dataset and centers analysis on the most important contaminants and potential indicator compounds. However, loosening the definition of priority compounds to include more features could broaden analysis and associated insights.

Table 1. Breakdown of features detected during suspect screening and identification rates. The values in the “Feature Breakdown” section are percentages of all detected features with the corresponding number of features indicated in brackets. The values in the “Identification Rates” section are the percentage of features in that group that were tentatively identified with the corresponding number of features indicated in brackets. The denominators for reported identification rates are the total number of features in each category (i.e., the number in brackets in the “Feature Breakdown” section). Note that feature groups retained based on ER or RR include all feature groups that were detected in either no replicate samples or in more than 7 of 9 or 5 of 6 replicate samples.



Process	ECS	ED	BPED
Feature Breakdown			
Features retained based on ER	17.4 [2,268]	8.8 [1,604]	12.9 [2,167]
Priority features based on ER	0.42 [55]	0.24 [44]	1.3 [213]
ER < 0.5	0.29 [38]	0.09 [17]	0.83 [139]
ER > 2	0.13 [17]	0.15 [27]	0.44 [74]
Features retained based on RR	16.9 [2,199]	6.6 [1,204]	10.9 [1,838]
Priority features based on RR	1.2 [150]	0.55 [101]	0.78 [131]
RR < 0.5	0.86 [112]	0.04 [8]	0.41 [69]
RR > 2	0.29 [38]	0.51 [93]	0.37 [62]
Identification Rates			
All features retained based on ER	73.9 [1,677]	74.9 [1,202]	71.2 [1,543]
Priority features based on ER	65.9 [29]	57.1 [16]	82.8 [140]
Priority features with ER < 0.5	61.3 [19]	70.6 [12]	91.0 [122]
Priority features with ER > 2	76.9 [10]	36.4 [4]	51.4 [18]
All features retained based on RR	74.8 [1,645]	75.2 [906]	76.3 [1,402]
Priority features based on RR	74.6 [85]	69.2 [0]	77.9 [53]
Priority features with RR < 0.5	70.8 [68]	62.5 [5]	73.8 [31]
Priority features with RR > 2	94.4 [17]	80.0 [4]	84.6 [22]

Identification rates were generally similar across processes and across different groups of compounds. This similarity is expected because all processes treated the same influent urine (i.e., started with the same contaminants present); in addition, similar reactor materials, separation mechanisms, and reactions are involved in the three electrochemical processes. In some cases, identification rates differed more between processes as the groups of compounds considered became smaller (e.g., ER > 2 vs. all priority features based on ER). Given that data quality should be similar across all groups of features, lower or higher identification rates for smaller groups likely resulted from less averaging of probabilities of matching to a compound when working with a smaller sample size. Some priority compounds were matched to two features (14 out of 91 features that were annotated with compounds). Typically, the features had similar ER or RR values, except for 6 features. In most cases, the features that were annotated as the same compound had the same masses and similar retention times, suggesting that the features should have been grouped throughout analysis. Additional discussion about some priority compounds based on ER



is provided next, while such discussion about priority compounds based on RR is included in Section S**Error! Reference source not found.**

Of identified priority compounds (Table S2-8), no compounds had $ER > 2$ or $ER < 0.5$ in all three processes. The absence of such a group of compounds likely resulted from the ER being a complex metric dependent on multiple variables, such as the type(s) of membrane(s) separating influent urine from product solutions and pH conditions over time in the influent, intermediate, and product chambers. Nevertheless, we observed similar behavior of some compounds in two of the three processes (Table S2-9, Table S2-10). For example, features identified as linoleic acid, ricinoleic acid, and methyl ricinoleate all had $ER > 2$ in ED and BPED but were not identified as priority compounds in ECS. Linoleic acid and ricinoleic acid have pKa values of 4.7-4.8. At acidic pH values occurring in urine during BPED, the species would be mostly neutral and able to diffuse across the CEM to the product. The higher pH in urine during ED would lead to deprotonation of the compounds, but the neutral fraction could still diffuse across the CEM. The compounds would largely be deprotonated in the concentrate chambers for ED and BPED and in Chamber 2 of ECS, effectively trapping the compounds in these chambers. The compounds are non-volatile with Henry's constant values on the order of 10^{-7} atm-m³/mol, making it difficult for them to cross the GPM into the product in ECS. Features identified as carbamazepine and bakuchiol had $ER < 0.5$ in ED and BPED. Aromatic rings in these compounds and their largely neutral nature across a large pH range could lead to adsorption onto ion exchange membranes and reduced transport to product chambers.^{98,99}

For ECS and BPED, Ne-Boc-L-lysine was the only identified priority compound with $ER > 2$. This compound has a pKa of 2.53 for the carboxyl group and likely between 9 and 10 for the amino group, putting its isoelectric point around pH 6.^{101,102} Therefore, at low pH occurring in urine in



ECS and BPED, this compound can electromigrate across the CEM but would not do so at the higher pH observed during ED. Although the alkaline conditions in Chamber 2 of ECS would lead to an overall negative charge on the molecule, the low-molecular weight, neutral fraction in equilibrium could diffuse across the GPM. Several priority compounds with $ER < 0.5$ in both ECS and BPED were identified: (2E,6Z)-N-ethylnona-2,6-dienamide; benzylideneacetone; and beta-damascenone. Benzylideneacetone and beta-damascenone are both small, neutral molecules that could diffuse across CEMs and possibly GPMs. They both contain aromatic rings that could lead to adsorption onto CEMs, reducing accumulation in the product chambers. (2E,6Z)-N-ethylnona-2,6-dienamide contains an amino group that could be protonated in acidified urine during ECS and BPED, facilitating migration across CEMs. In alkaline conditions like those in Chamber 2 of ECS, the molecule would be neutral, potentially enabling diffusion across the GPM. One priority compound, pinonic acid ($pK_a = 4.82$), had $ER > 2$ for ECS and $ER < 0.5$ for BPED. Pinonic acid would be protonated and neutral at low pH's occurring in urine during ECS and BPED, enabling diffusion across CEMs. However, urine pH remained elevated in BPED for part of the treatment time, causing deprotonation and a negative charge that enhances retention in the urine (as also occurs in ED). For ECS and ED, 1,4-dimethyl-2,3,4,5,6,7-hexahydro-1h-1,6-methano-4-benzazonin-10-ol was the only priority compound identified with $ER > 2$ and bicyclo(2.2.2)octane was the only priority compound identified with $ER < 0.5$. Both of these molecules could diffuse across CEMs and GPMs; bicyclo(2.2.2)octane is more hydrophobic, which could increase adsorption to the organic components of CEMs and therefore reduce its ER. These priority compounds included cosmetic ingredients, flavoring agents, drugs for specific conditions or purposes (e.g., seizures, contraception), and compounds used in manufacturing of preparation drugs (Table S2-11). With molecular properties, such as pK_a , molecular weight, and



hydrophobicity, affecting compound fate, different temporal trends in pH across processes explain differences in compound fate and may guide future process design setpoints for pH during operation.

Useful indicator compounds would have very high or very low ERs or RRs (**Error! Reference source not found.**). For example, for ECS, beta-damascenone had an ER of ~ 0.008 while (2S)-2-amino-6-(((tert-butoxy)carbonyl)amino)hexanoic acid had an ER of ~ 5.6 . Galanthamine had an ER of ~ 0.02 , while 1-ethylpiperidine had an ER of ~ 6 . These two compounds with the most extreme RRs essentially cover the entire range of RRs observed for ECS (**Error! Reference source not found.**), but identification of additional compounds could provide better indicator compounds for the variation of ERs observed (Figure 2).

3.5 Mechanistic Understanding of Compound Fate

Our dataset did not illustrate strong correlations between compound properties and fate, making it difficult to mechanistically understand compound fate (Figure 4, **Error! Reference source not found.** through **Error! Reference source not found.**, Table S2-12 through Table S2-17). Only a few correlations between ER or RR and 27 properties obtained from PubChem were statistically significant. For example, for ECS, ER was weakly negatively correlated with hydrogen bond donor count and weakly positively correlated with anion count. The presence of more hydrogen bond donors increases polarity, which could hinder molecules from crossing the hydrophobic membrane into the product. Anionic functional groups should hinder compounds from migrating across the CEM and GPM, reducing enrichment, so the observed relationship between anion count and ER indicates insufficient narrowing of priority compounds, incorrect identification of compounds, or paired transport with cations. For ECS, RR and charge were weakly negatively correlated, suggesting that more negatively charged species were removed to a greater extent. While



electromigration would not contribute significantly to removal of negatively charged molecules because they generally cannot cross the CEM between Chambers 1 and 2, electrochemical transformations within Chamber 1 could explain the removal observed. Negatively charged species would remain in Chamber 1 and be attracted to the anode, increasing exposure to reactive species (e.g., HOCl). Extent of removal would likely be affected by residence time in continuous operation of the process, potentially changing how compound properties impact fate.

Looking at priority compounds for ED and BPED, a few statistically significant correlations between fate and property were identified. For ED, ER positively correlated with logP, bond stereo count, and defined bond stereo count. More lipophilic molecules (i.e., higher logP) could cross the CEM from the urine to concentrate by interacting with the CEM's polymer matrix. The association between ER and the presence of stereocenters is difficult to explain but the correlation is weak. No significant correlations between RR and compound properties were identified for ED. For BPED, we observed negative correlations between ER and several properties: exact mass, complexity, heavy atom count, volume, Z steric quadrupole, feature count, and feature ring count. Larger molecules (e.g., higher mass, higher heavy atom count (total number of non-hydrogen atoms), greater complexity, higher volume, more features and feature rings, higher Z steric quadrupole (analogous to molecule height)) less readily pass through the CEM separating urine and concentrate, reducing their accumulation in the product. We observed a positive correlation between RR and atom stereo count and feature count for BPED. The presence of more stereocenters could reduce conformational flexibility, making it more difficult for molecules to pass through the CEM. A higher feature count (i.e., higher total number of hydrogen bond acceptors, hydrogen bond donors, anions, cations, hydrophobes, and rings) could indicate larger molecules that pass less easily through the CEM. Differences in correlations between compound



fate and properties for the three processes indicate that differences in reactor architecture and solution conditions affect compound fate.

Extending the compounds considered in the correlation analysis often increased the number of statistically significant correlations observed but correlations remained weak (**Error! Reference source not found.****Error! Reference source not found.** through **Error! Reference source not found.**, Table S2-14 through Table S2-17). For example, when considering all identified compounds for ECS, no significant correlations between ER and compound properties were observed, but RR was weakly positively correlated with topological polar surface area (TPSA), hydrogen bond donor count, hydrogen bond acceptor count, and feature count. There was no overlap between significant correlations for priority compounds and all compounds. Considering all compounds that showed significant change in intensity between influent and effluent or product ($p < 0.05$), results were somewhat similar to those for all compounds though with fewer significant correlations. No significant correlations were observed for ER, but RR was weakly positively correlated with TPSA and hydrogen bond acceptor count. As for ECS, expanding the dataset beyond priority compounds for ED and BPED did not reveal any correlations that were significant in all three cases. Increasing confidence in compound identification could improve mechanistic understanding of compound fate.



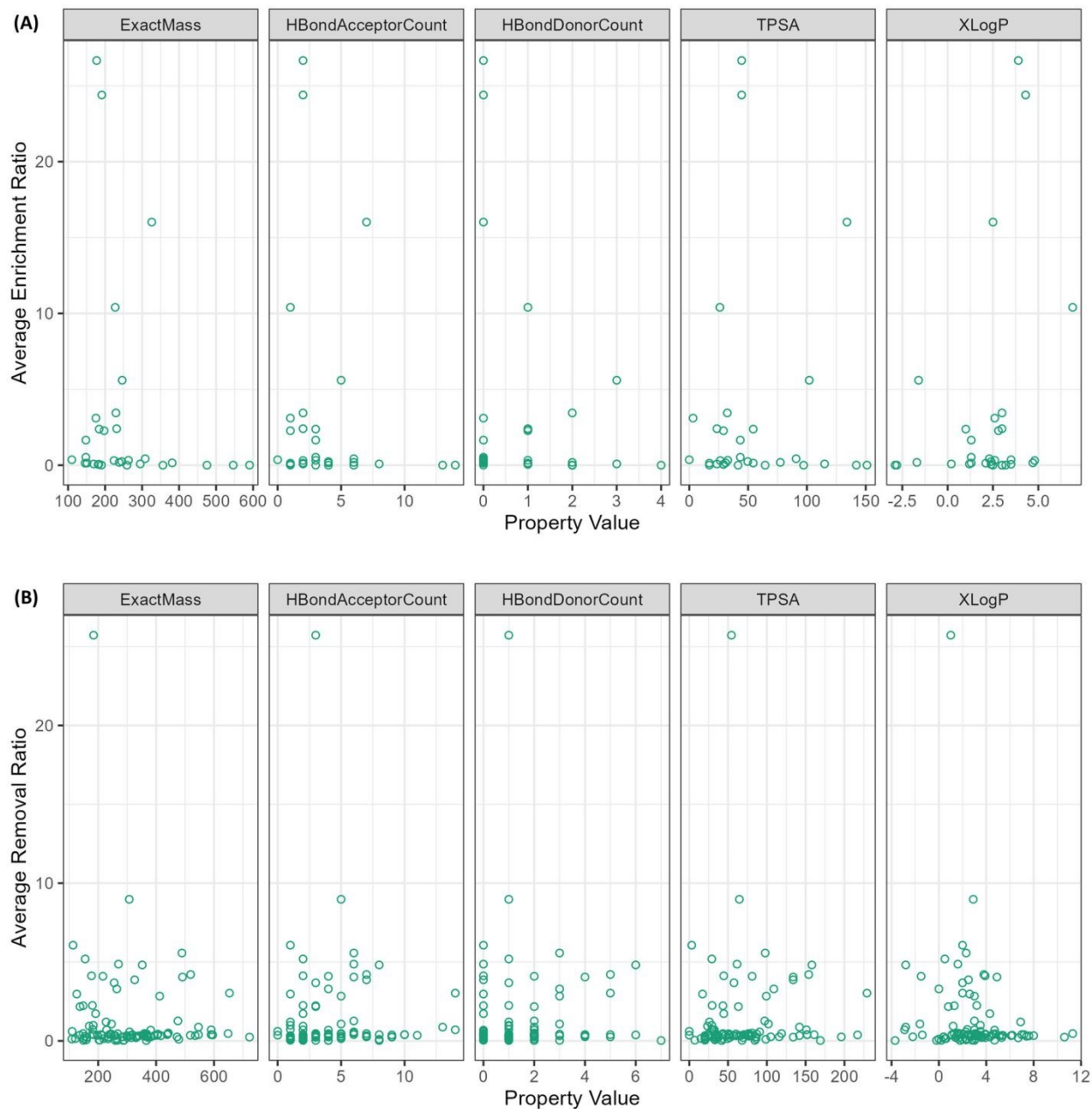


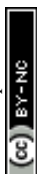
Figure 4. Relationships between compound properties and fates as illustrated by enrichment ratio (a) and removal ratio (b) for priority compounds in ECS. Analysis of the relationships between compound fate and additional properties for all three processes are shown in **Error! Reference source not found.** through **Error! Reference source not found.****Error! Reference source not found.**. Correlation strength (ρ) and significance (p -value) based on Spearman correlation are summarized in Table S2-12. Linear fit results are summarized in Table S2-13.



4 Conclusion

This study compared the fate of pharmaceuticals and disinfection byproducts across three electrochemical nitrogen recovery processes: electrochemical stripping, electrodialysis, and bipolar electrodialysis. ECS achieved greater TAN recovery efficiencies than ED and BPED and was the only process that recovered an ammonium sulfate product rather than a mixed concentrate, containing TAN, sodium, and potassium extracted from urine. Products from ED and BPED would require additional separation (e.g., sodium removal) to improve product efficacy (e.g., as a fertilizer) and prevent negative side effects of application (e.g., increasing soil salinity). Target pharmaceuticals and organic contaminants detected during suspect screening were removed and/or transported to product chambers to varying extents. Enrichment ratios were generally lower for ECS than ED and BPED, suggesting that having two barriers between influent urine and the product chamber (i.e., CEM and GPM) more effectively prevented organic contaminants from reaching the product than a single barrier (i.e., CEM). Removal ratios were generally higher for ED than ECS and BPED due to lower TAN recovery in ED and the impact of pH on compound transformation and migration. The products recovered by all processes had little to no contamination with DBPs, suggesting that the membranes in the reactors were effective barriers to the transfer of these contaminants. However, DBP formation in other reactor chambers was a significant concern, especially in the anode chambers for ECS and ED.

Our study highlighted the importance of selecting broader sets of target compounds to be more representative of the range of behaviors observed for organic contaminants. Through suspect screening, we tentatively identified other compounds with very high or low ERs or RRs, which could be useful indicator compounds. Identification of additional compounds could provide better indicator compounds. Our data did not show strong correlations between compound fate and



properties. Therefore, future work utilizing suspect screening is needed to facilitate mechanistic understanding of compound fate and characterization of the potential toxicity of treated urine, recovered products, and other process solutions. Such investigations will enable mitigation of potential negative side effects (e.g., integrating BPMs to reduce overall DBP formation) and build confidence in the safety of products recovered from urine. These advances will support deployment of electrochemical nitrogen recovery from urine, which could replace about one-quarter of current nitrogen fertilizers worldwide,¹⁰³ enabling a circular nitrogen economy.

Data Availability Statement

Data for this study are available in an online data repository (<https://doi.org/10.25740/ps371sj4433>).

Author Contributions

Anna Kogler: conceptualization, data curation, formal analysis, investigation, methodology, resources, software, validation, visualization, writing – original draft, writing – review & editing.

William A. Tarpeh: conceptualization, funding acquisition, methodology, validation, resources, writing – review & editing

Conflict of Interest

The authors have no conflicts of interest to declare.

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Data Availability Statement

Data for this study will be made available in a data repository at the revision stage with the URL provided here.

