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Abstract
Most wastewater removal and recovery processes primarily target dissolved inorganic nitrogen (DIN) species, leaving the untreated non-reactive dissolved organic nitrogen (DON) in the effluent. This DON fraction can account for a substantial part of the total nitrogen (N) load. We analyzed large datasets of N species and concentrations (with a focus on quantifying the fraction of DON) in surface water, ground water, and wastewater effluent across the United States. We then reviewed strategies to remove and recover DON based
on results of a range of treatment technologies reported in the literature, including laboratory-scale up to full-scale operation in wastewater treatment plants. Our meta-analysis showed that DON concentrations are greatest in wastewater effluent followed by surface water and groundwater. The concentration of DON in wastewater effluent varied from 0.01 to 10.9 mg N/L (number of data points, n = 163), where the range in surface water was 0.002 to 14.3 mg N/L (n = 11,803). Organic N accounted for the majority of total N in 12.3% of wastewater effluent samples and 49.1% of surface waters. Our literature review showed that currently available wastewater treatment processes do not efficiently target DON removal nor recovery of the DON as a valuable product. One potential DON removal and recovery strategy is transforming DON into DIN, which is generally more easily removed and recovered. Transformation strategies reported in the literature include ozonation, UV/H₂O₂, and electrooxidation. However, as advanced oxidation processes are often energy- and cost-intensive, further research is needed to improve DON removal and recovery.

Graphical abstract

Abbreviations
BEC - bio-electrochemical cell
BNR - biological nutrient removal
DEMON - deammonification
DIN - dissolved inorganic nitrogen
DON - dissolved organic nitrogen
DUFC - direct urea fuel cell
ECHO - Enforcement and Compliance History Online
ED - electrodialysis
EO - electro-oxidation
EPA - United States Environmental Protection Agency
GW - groundwater
HAA - haloacetic acid
LDH - layered double hydroxide
MIEX - magnetic ion exchange
MOF - metal organic framework
N - nitrogen
NDMA - N-nitrosodimethylamine
NIH - National Institutes of Health
NWQMC - National Water Quality Monitoring Council
P - phosphorus
PAC - powdered activated carbon
Keywords
Advanced oxidation process (AOP), Eutrophication, Nutrients, Sustainability, Resource recovery, Transformation

1. Nitrogen forms and their behavior in aquatic ecosystems and wastewater treatment plants

1.1. The importance of nitrogen removal and recovery from wastewater
Nitrogen (N) is one of the key nutrients needed to sustain all living beings. However, excess inputs of nutrients, i.e., N and phosphorus (P) lead to eutrophication and greenhouse gas emissions (Beaulieu et al., 2019). In nutrient management, the emphasis is often on P discharge regulations as P is considered the limiting nutrient in many ecosystems. However, freshwater and coastal waters may be limited by N or co-limited by both N and P under certain conditions, including seasonal and spatial variation (Conley, 1999). Thus, excess N can lead to eutrophication and hypoxic conditions in a range of surface waters (Seitzinger et al., 2002).

Future projections suggest that anthropogenic N inputs to freshwater systems will increase due to urban or agricultural run-off or wastewater sources (Seitzinger et al., 2002; Xie and Ringler, 2017). Wastewater-derived N inputs can account for a large fraction of N flows to natural waters. For instance, approximately 19% of the total nitrogen (TN) in the Chesapeake Bay is derived from wastewater (Mesfioui et al., 2012). Hence, it is crucial to monitor and regulate anthropogenic N inputs such as wastewater. Additionally, N can increase the formation potential of harmful disinfection by-products (DBPs), e.g., N-nitrosodimethylamine (NDMA) (Krasner et al., 2005).

Another aspect of N management is the potential for recovery of N from wastewater as N is imperative for modern agriculture. The use of N fertilizer (primarily in the ammonium, ammonia, or urea form) increased more than 9-fold between 1961 and 2019 to accommodate the food demands of the world's growing population (International Fertilizer Association, 2019). Unfortunately, the industrial Haber-Bosch process traditionally used for synthesis of ammonium from atmospheric N\textsubscript{2} is expensive and energy intensive (van der Hoek et al., 2018). Recovery of N from wastewater can help reduce dependence on the Haber-Bosch process while advancing the circular N economy by reusing N from wastewaters as fertilizer/soil amendments or other products such as biofuel feed stock.
1.2. Forms of nitrogen and the importance of the dissolved organic nitrogen fraction

While N removal and recovery from wastewater can contribute to sustainable nutrient management, thereby advancing solutions to one of the National Academy of Engineering’s Grand Challenges (2019), existing treatment processes may not effectively target all types of N.

Common N species in aquatic systems occur in both oxidized and reduced inorganic forms (e.g., \( \text{NO}_3^- \), \( \text{NO}_2^- \), \( \text{NH}_4^+ \), and \( \text{NH}_3 \)), as organic molecules, and in dissolved and particulate forms. The fraction smaller than 0.20 μm is classified as dissolved N, whereas the larger size fraction is particulate N (Jørgensen, 2009) (Fig. 1). In conventional wastewater treatment facilities, particulate N is generally well removed during primary treatment, with subsequent biological treatment removing the remaining particulate N (Sattayatewa et al., 2020). Among the dissolved species, dissolved inorganic N (DIN) is most effectively removed in wastewater treatment facilities. Owing to the lesser extent of dissolved organic nitrogen (DON) reactivity, recovery processes also generally target DIN. However, as DON is more poorly removed/recovered, it may pass through treatment systems, and can constitute a substantial fraction of effluent TN.

Fig. 1. Forms of nitrogen (N) in water, modified from APHA (2012). Dissolved inorganic nitrogen (DIN) and particulate N (shaded in green) can be treated effectively using conventional methods, while dissolved organic nitrogen (DON, shaded in red) is not effectively treated with current technologies. Treatment technologies targeting transformation of DON to the more readily removable/recoverable DIN can be employed to achieve effective DON removal and recovery.

Wastewater DON includes proteins, nucleic acids, amino acids, urea, and micropollutants coming from pharmaceuticals (e.g., flushed medications or release of pharma compounds through excretion) or agriculture (e.g., pesticides, herbicides, insecticides, and fertilizer run-off). Examples of wastewater DON compounds are shown in Fig. 2.
Fig. 2. Examples of representative dissolved organic nitrogen (DON) compounds in wastewater. The natural organic matter image was taken from the National Center for Biotechnology Information (2022). Protein and nucleic acid images were taken from the National Institutes of Health (Madej et al., 2014) and RSCB (Berman et al., 2000) databases, respectively, specifically: insulin, PDB ID 1ZNI (Bentley et al., 1976); phosphate binding protein, PDB ID 40MB (Neznansky et al., 2014); ammonia transporter protein, PDB ID 2B2J (Andrade et al., 2005); DNA, PDB ID 1BNA (Drew et al., 1981); RNA, PDB ID 1CQ5 (Schmitz et al., 1999). All other images were taken from Chemspider.

Anthropogenic sources including wastewater discharges are estimated to contribute 30% of global DON discharge to the environment (Jickells et al., 2017). Thus, treatment processes facilitating wastewater DON removal and recovery can help reduce TN discharge to streams and achieve sustainable nutrient management. The objective of this study was to quantify the occurrence of DON in different water matrices and critically assess currently available N treatment processes in terms of their DON removal and recovery potential.

2. Meta-analysis of DON in environmental waters and wastewaters

2.1. Occurrence of DON

Understanding the occurrence of DON in environmental waters and wastewater effluents is important for elucidating the potential effects of DON on natural ecosystems. We assessed the occurrence of DON and TDN in groundwater, surface water, and wastewater effluent. Water quality data for groundwaters and surface waters in 2019 were downloaded from the Water Quality Portal (https://www.waterqualitydata.us/portal/; sponsored by the United States Geological Survey [USGS], United States Environmental Protection Agency [EPA], and the National Water Quality Monitoring Council [NWQMC]). This data set includes water quality data collected from more than 400 sites across the United States. The initial search returned more than 630,000 N data points, which were then filtered to include only data for sites reporting both DON and DIN for the sampling event. Most sites did not directly report DON measurements, but for sites reporting dissolved inorganic species ($\text{NO}_3^-$, $\text{NO}_2^-$, and $\text{NH}_4^+$ or DIN) and TDN, DON was calculated as the difference. A full description of the data analysis is available in Section S1 of the Supplementary Materials (SM).

For municipal wastewater effluent, discharge data for 2019 was retrieved from the EPA’s Enforcement and Compliance History Online (ECHO) website (https://echo.epa.gov/). The initial search returned 72,468 N data
points. Like the environmental water data, wastewater effluent data were filtered to include only those with geographic/temporally matched inorganic and organic N measurements, resulting in a total of 168 data points. The ECHO data did not explicitly differentiate between dissolved and particulate species. One-way ANOVA and Tukey post-hoc analyses were performed to determine statistical significance in the datasets using GraphPad Prism 9.3.1 (GraphPad Software, Inc., San Diego, CA).

The variability in TDN and DON in different water matrices is presented in Fig. 3. The concentration of TDN was significantly higher in wastewater effluent than in groundwater \((p < 0.0001)\), which in turn exceeded surface water TDN \((p < 0.0001)\). Wastewater effluent TDN was between 0.79 mg N/L and 22.7 mg N/L \((median = 4.4 \text{ mg N/L, } n = 163)\). Groundwater ranged from 0.1 to 13.7 mg N/L \((median = 1.2 \text{ mg N/L, } n = 106)\). The concentration of TDN in surface water ranged from 0.011 to 22.8 mg N/L \((median = 0.9 \text{ mg N/L, } n = 11,803)\). According to the EPA (2013), TDN less than 6 mg N/L does not disrupt environmental ecosystems, although state or regional agencies may impose lower regulations depending on the water quality in local reservoirs. The majority of surface waters assessed here \((97\%)\) were below the suggested maximum of 6 mg N/L TDN.

![Fig. 3. Variability of (a) total dissolved nitrogen (TDN) and (b) dissolved organic nitrogen (DON) concentrations in groundwater (GW), surface water (SW), and wastewater (WW) effluent. Data for groundwater \(n = 106\) from 75 sites), surface water \(n = 11,803\) from 1599 sites), and wastewater effluent \(n = 163\) from 163 sites) is from the US in 2019. Environmental and wastewater effluent data for these analyses were downloaded from the Water Quality Portal and Enforcement and Compliance History Online (ECHO) websites, respectively. The whiskers represent the minimum and maximum values in the data set, the boxes represent the 25th and 75th percentile values with a median line inside the box, and the mean is shown as a “+” sign.](image)

The concentration of DON also varied greatly among the different water matrices, with significantly more DON in wastewater effluent than surface water and groundwater \((Fig. 3b; p < 0.0001)\). Wastewater effluent DON varied from 0.01 to 10.9 mg N/L \((median = 1.1 \text{ mg N/L, } n = 163)\). Surface water DON ranged from 0.002 to 14.3 mg N/L \((median = 0.3 \text{ mg N/L, } n = 11,803)\), while groundwater DON ranged from 0.005 to 3.24 mg N/L \((median = 0.07 \text{ mg N/L, } n = 106)\).

The ratio of DON to TDN illustrates the prevalence of DON in different water matrices, where increasing values indicate higher levels of DON relative to DIN. Generally, in oligotrophic systems where N enrichment is low, DON is the dominant species, and it may also be an important secondary constituent in enriched hypertrophic systems (Durand et al., 2011). As shown in Fig. 4a, the ratio of DON to TDN varied from 0.3 to 86.7% in groundwater \((median = 8.7\%, n = 106)\), 0.1 to 99.7% in surface water \((median = 48.2\%, n = 11,803)\), and 0.07 to 99.7% in wastewater effluent \((median = 25.7\%, n = 163)\). The DON to TDN ratio was significantly higher in surface water than in wastewater effluent \((p < 0.0001)\), which was in turn greater than groundwater \((p = 0.0047)\). The majority of the N was in the DON form for 7.5% of groundwaters, 49.1% of surface waters, and 12.3% of wastewater effluents \(Fig. 4b\).
2.2. Spatial variation in the occurrence of DON in surface waters in the US

The concentration of TDN, DON, and ratio of DON to TDN in surface water samples varied spatially across the US. Similar analysis was not conducted for groundwater and wastewater, as the datasets had groundwater and wastewater data from only 13 and 8 states, respectively. The TDN and DON analyses are shown in Figs. S1 and S2 of the SM, respectively. Nebraska had significantly higher TDN than all other states (p ≤ 0.0001) except Iowa (p = 0.0712). The highest DON levels, however, were reported in North Dakota (p ≤ 0.0268). Notably, comparison of DON data among different states is limited as the number of sites with temporally matched DIN, DON, and TDN data varied widely among the states, with some states reporting very few values and others reporting large amounts of data (Fig. S3). Given that organic N is introduced into aquatic and soil ecosystems from terrestrial run-off, leaching, sediment release, active and passive release from phytoplankton, algae, zooplankton, etc. (Berman and Deborah, 2003; Joye and Anderson, 2008), a combination of factors could potentially impact DON prevalence.

The ratio of DON:TDN in surface water for each state is shown in Fig. 5. Florida reported significantly higher DON:TDN (n = 3171) than all other states (p ≤ 0.0467) except for Alaska and Wyoming (which were statistically similar, albeit with much smaller datasets, with 4 and 2 datapoints, respectively). Based on the DON to TDN ratio in the samples, DON accounted for more than 25% of TDN in more than half of the states, while DON constituted the majority of N in almost 20% of the states. Thus, DON can constitute a substantial fraction of TDN in environmental waters and efforts to reduce DON discharges could help to reduce TDN concentrations in environmental waters.
3. Significance of DON treatment

3.1. DON removal

As shown in Fig. 4, the majority of the N was present as DON in nearly half of the surface waters analyzed here. Similarly, 60–69% of TDN in rivers, estuaries, and open ocean waters was previously reported to be DON (Shetye et al., 2019; Sipler and Bronk, 2015). Since DON can bio-assimilate or transform to more bioavailable DIN species over time, it contributes to eutrophication in receiving waters. Moreover, waters with high levels of DON can increase the potential for NDMA or other harmful disinfection by-product formation if the water is used as influent for drinking water treatment purposes. Therefore, DON treatment strategies are important in achieving advanced N management goals.

The degree of eutrophication in an N-limited aquatic system depends on the bioavailability of the N species or the composition of the TN pool. Although DIN is more bioavailable (Ryther and Dunstan, 1971), when DON is present in abundance, it can also be bio-assimilated through several different pathways. For instance, both microbial activity and photochemical reactions (Vähätalo, 2009) can transform DON to bioavailable NH₄⁺ and other DIN species. Direct bio-assimilation of DON (without transforming DON to DIN species) is also possible in DIN-scarce aquatic systems, with an estimated 18–61% of effluent DON being bioavailable (Urgun-Demirtas et al., 2008). Urgun-Demirtas et al. (2008) observed successful biomass growth utilizing DON as the N source. Additionally, 28–61% of effluent DON was assimilated by algae over a 14-day growth period (Qin et al., 2015). Low molecular weight DON compounds like urea and amino acids can also be bio-assimilated by phytoplankton (Bradley et al., 2010).
Wastewater effluent discharge can be one of the major anthropogenic sources of DON release into streams (Hu et al., 2016). Tertiary effluent DON concentrations typically range from 0.4 to 2.2 mg N/L, often accounting for 65–80% of the effluent TDN (Fan et al., 2017) (0.1 to 99.7% in our meta-analysis). Effluent DON contains influent DON that passes through the treatment system as well as microbiologically-generated DON from microbial growth and biodegradation of organic matter. Microbiologically-derived DON is released during metabolic processes as well as microbial lysis (Zheng et al., 2021). Differentiating untreated influent DON and microbiologically-derived DON is difficult, but Hu et al. (2020) recently modeled DON in wastewater and reported that microbiologically-derived DON theoretically accounts for approximately 50% of total effluent DON.

The bioavailability of N species varies depending on the structure of the compounds. Effluent DON characterization is therefore helpful for understanding bioavailability, and thus eutrophication potential, which is relevant to selection of effective N treatment strategies (Lee and Westerhoff, 2006). However, effluent DON characterization is challenging, with approximately 70% of it being unidentifiable; thus, effluent DON is often characterized based on size distribution and hydrophobicity (Hu et al., 2016; Yu, 2012). The majority of effluent DON is low molecular weight (67% < 1 kDa), and 93% is hydrophilic (Pehlivanoglu-Mantas and Sedlak, 2006). This low molecular weight, hydrophilic fraction of DON is more bioavailable, and can cause eutrophication (Feng et al., 2019).

In addition to its potential to contribute to eutrophication in receiving waterbodies, DON can also lead to nitrogenous DBP formation, e.g., halonitromethanes, haloacetonitriles, haloacetamides, and N-nitrosamines (Kristiana et al., 2017; Peters et al., 1990). In particular, low molecular weight DON can cause higher NDMA formation (Feng et al., 2019). Speciation of other by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs), both of which are regulated in drinking water in the US, can also be affected by DON. For instance, if the source water contains high levels of DON, HAAs might exceed THMs, and levels of the HAA dihaloacetic acid may increase (Westerhoff and Mash, 2002). Some studies show that HAAs can be more harmful for fetal growth than THMs and dihaloacetic acid may be associated with higher risk for genotoxicity than trihaloacetic acid (Plewa et al., 2010; Porter et al., 2005). Accordingly, wastewater treatment processes capable of removing DON in addition to DIN can help reduce eutrophication and DBP formation potential.

3.2. DON recovery
In addition to its potential to contribute to eutrophication in receiving waterbodies, DON can also lead to nitrogenous DBP formation, e.g., halonitromethanes, haloacetonitriles, haloacetamides, and N-nitrosamines (Kristiana et al., 2017; Peters et al., 1990). In particular, low molecular weight DON can cause higher NDMA formation (Feng et al., 2019). Speciation of other by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs), both of which are regulated in drinking water in the US, can also be affected by DON. For instance, if the source water contains high levels of DON, HAAs might exceed THMs, and levels of the HAA dihaloacetic acid may increase (Westerhoff and Mash, 2002). Some studies show that HAAs can be more harmful for fetal growth than THMs and dihaloacetic acid may be associated with higher risk for genotoxicity than trihaloacetic acid (Plewa et al., 2010; Porter et al., 2005). Accordingly, wastewater treatment processes capable of removing DON in addition to DIN can help reduce eutrophication and DBP formation potential.

4. N treatment processes
Although DON removal and recovery can contribute to sustainable N management goals, typical wastewater N treatment processes (discussed in the following sections) cannot effectively treat DON due to its relative recalcitrance. Table 1 summarizes the available N treatment processes and helps shed light on which N species are typically targeted by each process. As shown, no existing processes explicitly target DON removal/recovery, although DON is treated to some extent using several of the technologies.
Table 1. Currently available nitrogen (N) treatment technologies and susceptibility of dissolved organic nitrogen (DON) to removal/recovery using these technologies.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Typically targeted N species</th>
<th>Dissolved organic N removal</th>
<th>Current scale of testing</th>
<th>References</th>
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<tr>
<td><strong>Biological processes</strong></td>
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<tr>
<td>Biological N removal (BNR)</td>
<td>NH$_4^+$, NO$_3^-$</td>
<td>Not targeted, partial removal through hydrolysis</td>
<td>Full-scale</td>
<td>(Eom and Park, 2021)</td>
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<tr>
<td>Anammox, SHARON-Anammox, DEMON-Anammox</td>
<td>NH$_4^+$, NO$_3^-$</td>
<td>Not targeted, partial removal through hydrolysis</td>
<td>Full-scale</td>
<td>(Zuo et al., 2020)</td>
</tr>
<tr>
<td>Microalgal uptake</td>
<td>NH$_4^+$, NO$_3^-$</td>
<td>Not targeted, partial removal through hydrolysis</td>
<td>Full-scale</td>
<td>(Díez-Montero et al., 2020; Nagarajan et al., 2020)</td>
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<tr>
<td><strong>Physicochemical processes</strong></td>
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<tr>
<td>Adsorption:</td>
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<tr>
<td>Layered double hydroxides (LDH)</td>
<td>NH$_4^+$, NO$_3^-$, NO$_2^-$</td>
<td>Up to approximately 1.2 mg DON/g LDH from biochemical leachate tailings</td>
<td>Bench</td>
<td>(Xu et al., 2020)</td>
</tr>
<tr>
<td>Nanomaterials (iron, copper, platinum, manganese, carbon nanotube, nanofibers, nanocomposites such as polymers, graphene-based nanocomposites, Co-Fe$_3$O$_4$ activated on peroxymonosulfate)</td>
<td>NH$_4^+$, NO$_3^-$</td>
<td>Up to approximately 0.75 mg DON (histidine) / (0.1 g Co-Fe$_3$O$_4$ activated on 228 mg peroxymonosulfate)</td>
<td>Bench</td>
<td>(Abdollahbeigi and Asgari, 2020; Han et al., 2021; Luo et al., 2021)</td>
</tr>
<tr>
<td>Biochar</td>
<td>NH$_4^+$, NO$_3^-$</td>
<td>Significant removal of DON was not reported</td>
<td>Bench</td>
<td>(Clough et al., 2013; Saarela et al., 2020; Zhang et al., 2020)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>NH$_4^+$, NO$_3^-$</td>
<td>Up to 72% wastewater effluent DON removal using powdered activated carbon</td>
<td>Full-scale</td>
<td>(Han et al., 2021; Hu et al., 2020; Parkin and McCarty, 1981)</td>
</tr>
<tr>
<td>Zeolite, bentonite, natural clay</td>
<td>NH$_4^+$, NO$_3^-$</td>
<td>Not reported</td>
<td>Pilot-scale</td>
<td>(Han et al., 2021; Lazaratou et al., 2020)</td>
</tr>
<tr>
<td>Metal organic framework (MOF)</td>
<td>NH$_4^+$, NO$_3^-$</td>
<td>Up to 95.1 mg DON (bovine serum albumin) / g of MOF-loaded ultrafiltration membrane. Efficiency of ultrafiltration alone was not reported</td>
<td>Bench</td>
<td>(Han et al., 2021; Pishnamazi et al., 2020)</td>
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<tr>
<td>Process Type</td>
<td>Chemicals</td>
<td>Removal Efficiency</td>
<td>Scale</td>
<td>References</td>
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<tr>
<td>Ion exchange:</td>
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<tr>
<td>Ion exchange resin</td>
<td>NH$_4^+$, NO$_3^-$</td>
<td>10–56% DON removal from wastewater effluent</td>
<td>Full-scale</td>
<td>(Czerwionka and Makinia, 2014; Li et al., 2020; Parkin and McCarty, 1981)</td>
</tr>
<tr>
<td>Magnetic ion exchange (MIEX)</td>
<td>NH$_4^+$, NO$_3^-$</td>
<td>Up to 0.8 mg DON removal /mL MIEX from wastewater effluent</td>
<td>Bench</td>
<td>(Tang et al., 2021)</td>
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<td>Membrane:</td>
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<tr>
<td>Reverse osmosis (RO)</td>
<td>NH$_4^+$, NO$_3^-$, organic</td>
<td>&gt; 90% DON removal from wastewater effluent</td>
<td>Full-scale</td>
<td>(Merlo et al., 2012; Wang et al., 2020; Zheng et al., 2021)</td>
</tr>
<tr>
<td>Micro/ultra/nano filtration</td>
<td>NH$_4^+$, NO$_3^-$</td>
<td>Limited, as most wastewater DON compounds are less than 1 kDa in molecular weight</td>
<td>Full-scale</td>
<td>(Huang et al., 2021)</td>
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<tr>
<td>Electrochemical:</td>
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<tr>
<td>Electro-dialysis (ED)</td>
<td>NH$_4^+$, NO$_3^-$</td>
<td>Not reported</td>
<td>Pilot-scale</td>
<td>(Mohammadi et al., 2021)</td>
</tr>
<tr>
<td>Bio-electrochemical cell (BEC)</td>
<td>NH$_4^+$, NO$_3^-$</td>
<td>Up to 37.8 g N/m$^2$-d urea removal from synthetic wastewater in the absence of competing ions</td>
<td>Pilot-scale</td>
<td>(Rodríguez Arredondo et al., 2015; Sun et al., 2020)</td>
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<tr>
<td>Direct urea fuel cell (DUFC)</td>
<td>Organic N</td>
<td>&gt;90% urea removal</td>
<td>Bench</td>
<td>(Nangan et al., 2021; Schranck and Doudrick, 2020)</td>
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<tr>
<td>Urea-nitrate fuel cell (UNFC)</td>
<td>Organic N, NO$_3^-$</td>
<td>Urea removal was reported but not quantified</td>
<td>Bench</td>
<td>(Nangan et al., 2021)</td>
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<tr>
<td>Other physicochemical processes</td>
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<tr>
<td>Air stripping</td>
<td>NH$_4^+$</td>
<td>Up to 7% removal</td>
<td>Full-scale</td>
<td>(Gunes et al., 2020)</td>
</tr>
<tr>
<td>Struvite precipitation</td>
<td>NH$_4^+$</td>
<td>Not removed as struvite is formed using NH$_4^+$</td>
<td>Full-scale</td>
<td>(Saerens et al., 2021)</td>
</tr>
<tr>
<td>Coagulation</td>
<td>DIN species</td>
<td>Up to 48% removal from river water with 0.25–0.35 mg N/L DON initially</td>
<td>Full-scale</td>
<td>(Lee and Westerhoff, 2006)</td>
</tr>
<tr>
<td>Photo-catalysis</td>
<td>NH$_4^+$, NO$_3^-$, organic</td>
<td>&gt; 90% removal of nitrobenzene using iron-doped TiO$_2$</td>
<td>Full-scale</td>
<td>(Feng et al., 2021; Li et al., 2021; Nitoi et al., 2015; Wang et al., 2021)</td>
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</table>
As shown in Table 1, and described in further detail in the following sections, existing full-scale technologies offer limited DON removal, with the exception of reverse osmosis (RO) and activated carbon. Notably, neither RO nor activated carbon is operated to target DON treatment; thus, limited DON removal may be observed as a byproduct of operation. Bench-scale studies of layered double hydroxides (LDH), ion exchange resin, metal organic frameworks (MOFs), and electrochemical treatments indicate some extent of DON removal, but future research is needed at larger scales in more realistic wastewater matrices.

4.1. Biological treatment
In general, the biological processes have limited effectiveness for DON treatment. Some DON is hydrolyzed to NH$_4^+$ in biological nitrogen removal (BNR) and anammox-based processes (Qian et al., 2017). In typical BNR processes, effluent DON concentrations can range from 1 to 2 mg N/L (Henze, 1991). A survey of four full-scale treatment plants reported that DON decreased from 1–3 mg N/L to 0.69–1.42 mg N/L during BNR (Sattayatewa et al., 2010). Chen et al. (2011) showed that biodegradation removed up to 39% of DON from wastewater containing an initial concentration of 0.69–1.56 mg N/L DON. While biodegradation of DON is possible, it would take place in the absence of DIN as the DIN species are more easily accessible to microbes. Likewise, removal and recovery of N through microalgal uptake also targets NH$_4^+$ or NO$_3^-$ in the feedstock as the inorganic N species are more easily bio-assimilated. Microbial uptake of DON is limited to scenarios in which NH$_4^+$ or NO$_3^-$ are scarce (Díez-Montero et al., 2020; Nagarajan et al., 2020).

4.2. Adsorption and ion exchange
Among the different physicochemical processes for N treatment, adsorption is very effective. Parkin and McCarty (1981) reported up to 72% removal of tertiary effluent DON using powdered activated carbon (PAC); however, studies reporting DON recovery using activated carbon are lacking. Moreover, recent reports suggest that wastewater DON is mostly hydrophilic, hence, removal of wastewater DON using activated carbon adsorption might not be effective (Arnaldos and Pagilla, 2010; Pehlivanoglu-Mantas and Sedlak, 2008). Among the various adsorbents, LDHs and nanomaterials reportedly offer potential for organic N adsorption, although no distinction between DON versus PON was reported (Luo et al., 2021; Saarela et al., 2020; Xu et al., 2020; Zhang et al., 2020).

To our knowledge, the only study reporting the use of the emerging MOF adsorbent for DON removal showed 98.1% removal of DON (bovine serum albumin) using UiO-66 NH$_2$ and ZIF-8 MOFs loaded onto polyvinylidene fluoride/chitosan ultrafiltration membranes (Pishnamazi et al., 2020). Although high removal was achieved using MOF adsorption, the process was coupled with ultrafiltration. As bovine serum albumin is a large molecule (approximately 66.5 kDa), it may be readily removed by ultrafiltration alone, whereas removal of low molecular weight DON compounds using coupled MOF-ultrafiltration is yet to be tested.

Cation and anion exchange resins can reportedly remove wastewater effluent DON. However, removal efficiency varies depending on the resin's functional groups and ion selectivity as well as the electron density, aromaticity, and hydrophobicity of the target DON compounds (Jorgensen and Weatherley, 2003). Substantial DON removal using adsorbents or ion exchange resins might be possible by more selectively targeting different functional groups of DON compounds (e.g., NH$_4^+$ selective resins may remove DON compounds with primary amine groups). However, DON would be outcompeted by NH$_4^+$ if the water matrix has a high NH$_4^+$ content (e.g., wastewater influent).

4.3. Filtration
There are some reports of effective DON removal using RO or micro-, ultra-, or nanofiltration (Huang et al., 2021; Zheng et al., 2021). However, as most wastewater DON is low molecular weight, micro- and ultrafiltration tend to be less effective compared to RO. Additionally, membrane fouling is one of the major concerns for any
membrane treatment processes, making DON removal very challenging because the membranes are more prone to fouling in the presence of low molecular weight DON compounds (Zheng et al., 2021). In addition to membrane fouling, valence of the DON compounds, which varies as a function of pH due to deprotonation, might play a role in the effectiveness of membrane treatment for DON removal. For instance, RO generally offers selective retention of divalent cations compared to monovalent cations (Biesheuvel et al., 2019). Thus, it is possible that di- or multivalent DON may be retained while the monovalent forms of DON pass into the permeate depending on the molecular weight distribution of the DON compounds.

4.4. Electrochemical treatment
Emerging technologies like electro-dialysis (ED) and bio-electrochemical cells (BECs) have limited DON removal. In ED and BEC, DIN species outcompete DON due the higher electrostatic interaction between electrodes and the comparatively more electron-dense DIN species (Rabaey et al., 2010; Ward et al., 2018).

Among the various electrochemical cell configurations, direct urea fuel cell (DUFC) and urea-nitrate fuel cell (UNFC) remove the most common wastewater DON compound, urea, and the concentrate can be used as urea fertilizer (with co-recovery of energy from the wastewater). In DUFC, electrocatalysis is used to oxidize urea, with nickel serving as the most common catalyst (Sayed et al., 2019). Indirect oxidation of urea by the intermediate Ni(OH)₂ or direct oxidation on the electrode can contribute to DON removal (Sayed et al., 2019). A modification for DUFC is a coupled cell UNFC where urea is oxidized in alkaline media and NO₃⁻ is reduced in acid media. In both DUFC and UNFC, electricity is generated while wastewater N is lost as N₂ in the atmosphere, negating the potential for recovery of wastewater-derived DON. Both DUFC and UNFC are at the early stages of development, and only bench-scale studies using urea have thus far been reported (Nangan et al., 2021). Large-scale implementation of DUFC and UNFC is currently limited by deficiencies in electron transfer caused by loss of activity in the nickel electrodes over time. Alloying electrodes with materials with greater adsorption affinity for urea, including metals (manganese, cobalt, molybdenum, zinc, and chromium), nickel-phosphite nanoparticles, and sulfur-coated nickel hydroxide nanosheets may improve performance (Nangan et al., 2021; Sayed et al., 2019).

4.5. Other physicochemical processes
Alum coagulation with a polydiallyldimethyl-ammonium chloride (polyDADMAC) coagulant aid preferentially removed higher molecular weight DON compounds (>10 kDa) (Lee and Westerhoff, 2006). However, given that the major fraction of wastewater DON is low molecular weight (< 1 kDa), coagulation may offer limited opportunity for DON removal.

Among the different options for photocatalysis, use of Pd-In, Pd-Cu, Pd-Sn, or TiO₂ doped with Mg²⁺ and Zn²⁺ can reduce NO₃⁻ and/or oxidize NH₄⁺ and DON (Chaplin et al., 2007; Wang et al., 2021). However, studies of photocatalysis for DON removal used synthetic matrices containing only DON compounds (amino acid solution containing histidine or phenylalanine) (Nitoi et al., 2015). Thus, research is needed to assess feasibility of photocatalysis for wastewater DON removal.

4.6. Transformation for enhanced recovery
Among the DON treatment technologies, adsorption-based approaches can be useful for enhanced N recovery by enabling subsequent desorption of DON, ideally in a pure, concentrated form. However, only activated carbon shows effective DON adsorption, and DON recovery efficacy from activated carbon is yet to be explored. One possible route for DON recovery may be first transforming DON to the more readily removable and recoverable DIN species, which can then be further treated using conventional or emerging processes targeting enhanced N removal and recovery. For instance, once transformed to DIN, the N can be recovered using ion exchange and reused as mineral fertilizer or biofuel feedstock (Kim et al., 2020). Successful transformation of
non-reactive species to reactive species, e.g., soluble non-reactive phosphorus to soluble reactive phosphorus, has been demonstrated using UV/H\textsubscript{2}O\textsubscript{2} and electrooxidation (Mallick et al., 2021; Sindelar et al., 2016; Venkiteshwaran et al., 2021). Similarly, transformation of DON to DIN can be achieved via oxidation or hydrolysis.

Currently, there are limited studies of transformation of DON to DIN species. Ahmadi’s (2017) thesis reported up to 48% transformation of tertiary effluent DON to DIN with 120 min of ozonation at a dose of 3 mg/L. This study, however, did not explore the transformation mechanism nor optimized conditions for DON to DIN transformation.

Mallick et al. (2021) explored the feasibility of DON to DIN transformation using UV/H\textsubscript{2}O\textsubscript{2} compared to electro-oxidation (EO). This study analyzed four DON compounds representing four types of wastewater DON (protein, amino acid, micropollutant, and urea) in different size categories (less than or greater than 1 kDa). Effective DON to DIN transformation was not achieved using UV/H\textsubscript{2}O\textsubscript{2}, while transformation of urea was 11.7 ± 0.09% with 30 min of EO treatment (under these treatment conditions, 6.41 ± 1.49% of wastewater effluent DON was transformed to DIN). Greater transformation was achieved using extended treatment times. Notably, EO-based transformation was higher for the low molecular weight DON compounds, which constitute the major fraction of wastewater DON. This study also showed that susceptibility to EO-based transformation depends on the type of bonds in the DON molecule and their susceptibility to cleavage during oxidation. Oxidation was ostensibly achieved through direct electron transfer, rather than via reactive oxidant species.

Although EO-based DON to DIN transformation was more efficient than UV/H\textsubscript{2}O\textsubscript{2} in terms of the degree of transformation and energy consumption, large-scale implementation of EO remains challenging due to high capital cost and maintenance, including electrode replacement over time. Accordingly, transformation of DON to DIN might be more practical as a process byproduct at utilities with existing UV/H\textsubscript{2}O\textsubscript{2} advanced oxidation processes targeting trace organic contaminants. For large-scale implementation, future transformation studies should focus on the efficacy of the process, effective treatment conditions, and the susceptibility of different type of DON compounds.

5. Conclusions
Release of DON into natural streams has consequences including eutrophication and formation of NDMA or other by-products if the water is subsequently disinfected. Hence, DON discharge into receiving waterbodies should be accounted for when setting treatment targets. Refractory DON can be bio-assimilated over long periods of time or transformed to bioavailable DIN species, eventually causing eutrophication in natural steams. The meta-analysis presented here demonstrates that DON can account for a large fraction of TDN in wastewater effluent as well as environmental waters. Specifically, DON accounted for the majority of dissolved N in nearly half of the 11,803 surface waters evaluated here. Wastewater effluent had higher DON content compared to environmental waters, but the relative DON fraction was often lower (DON accounted for the majority of dissolved N in less than 15% of wastewater effluents, although 90% of effluents contained more than 10% DON). Removal of DON from wastewater can thus help reduce TN discharges while enabling DON recovery.

Conventional wastewater treatment processes target DIN removal to satisfy location-specific DIN and TN regulations. Thus, DON removal is often low, which precludes its subsequent recovery potential. Activated carbon and RO are currently the only full-scale technologies with effective DON removal capacity. However, further evaluations of the adsorption-desorption mechanisms are needed to support development of effective DON removal and recovery strategies. Several other treatment technologies, e.g., MOF, DUF\textsubscript{C}, and UN\textsubscript{F}C, can target DON removal, but have only been tested at the bench-scale using synthetic water matrices. While DUF\textsubscript{C}
and UNFC can be useful for removing DON, they do not offer DON recovery, as these processes release DON as N$_2$ into the atmosphere.

One strategy to increase DON treatability is transforming DON compounds to the more readily removable and recoverable DIN species using advanced oxidation processes. After transformation to DIN, the N can either be directly reused (e.g., as biofuel feed stock or mineral fertilizer), or further treated with other processes to recover the N (e.g., struvite formation). While EO-based transformation has been demonstrated, evaluations of the efficacy of DON transformation to DIN and the energy required to do so are needed.

Accordingly, assessments of the efficiency and cost effectiveness of treatment processes, both with and without advanced pretreatment to transform DON, are needed. Additionally, the susceptibility of DON compounds in different treatment technologies can vary depending on characteristics such as size, functional groups, and polarity. For instance, DON removal during coagulation depends on molecular size, while functional groups influence DON removal using ion exchange. Hence, deeper understanding of the mechanisms and optimum treatment conditions of different DON treatment technologies is needed to inform the development of full-scale technologies that can help advance progress on the grand challenge of N management.

CRediT authorship contribution statement

Synthia P Mallick: Conceptualization, Methodology, Formal analysis, Investigation, Data Curation, Writing – Original draft, Writing – Review and editing, Visualization. Zayed Mallick: Formal analysis, Investigation, Data curation, Writing – Review and editing. Brooke K Mayer: Conceptualization, Resources, Writing – Review and editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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