

# Feasibility of Recycling Excess Agricultural Nitrate with Electrodialysis

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## Abstract

One of the most serious environmental problems associated with agriculture is excessive nitrate N in waters leaving fields. It is a health hazard in drinking water and a primary cause of hypoxia in ocean waters receiving drainage from agricultural regions. Recent mitigation efforts have focused on techniques that promote denitrification—conversion of excess agricultural nitrate to  $N_2$ . This seems inherently wasteful since industrial production of nitrate fertilizer from  $N_2$  requires a substantial input of energy and is a major source of greenhouse gas emissions. Thus, it is desirable to develop methods to recycle nitrate, keeping it in a form suitable for reuse as fertilizer. One possibility is electrodialysis, in which direct current is passed through alternating cation- and anion-permeable membranes, creating separate streams of dilute and concentrated water. We tested the concept under controlled conditions in a greenhouse and in a field setting on a contaminated trout stream with nitrate N concentrations consistently above  $20 \text{ mg L}^{-1}$ . The solar-powered field system removed 42% of the nitrate from water passing through it and concentrated it in a tank for subsequent application as fertilizer. The upper limit of concentration was approximately  $520 \text{ mg L}^{-1}$ , above which precipitation of calcite limited operation. Economic analysis indicates that in comparison to denitrification methods such as bioreactors, electrodialysis is likely to be more expensive per unit of nitrate removed. The approach will be most feasible for situations in which nitrate concentrations are well above environmental standards for extended periods, to maximize operating time and nitrate removal rate.

## Core Ideas

- Nitrate can be extracted from contaminated water and concentrated by electrodialysis.
- The concentrated nitrate can be reused as fertilizer.
- The degree to which nitrate can be concentrated is limited by mineral precipitation.
- The method is promising, but research is needed to reduce costs.

THE DEVELOPMENT of a process to transform atmospheric nitrogen ( $N_2$ ) and hydrogen to ammonia fundamentally altered the course of human history (Erisman et al., 2008). This new capability of making N fertilizer from ubiquitous  $N_2$  allowed crop yields to explode in the 20th century, enabling agriculture to more than keep pace with a rapidly increasing population (Smil, 1999). But the injection of so much ammonia into the biosphere has a number of decidedly negative consequences, particularly after it has been nitrified, either by fertilizer manufacturers or by soil microbes. The hypoxic zone that forms annually in the Gulf of Mexico is directly attributable to nitrate loading of the Mississippi River, much of it from the midwestern Corn Belt (Rabalais et al., 2007). Additionally, recent evidence has shown that nitrate lost to streams may be a much larger source than previously believed of indirect, or beyond the field, emission of nitrous oxide, a greenhouse gas nearly 300 times more potent per molecule than carbon dioxide (Turner et al., 2015).

Offsite loss of nitrate from agricultural fields is a pervasive and stubborn problem that has resisted solution, despite decades of research. Numerous adjustments in management practices have been tested with minimal success, leading many to the conclusion that only a major shift in land use (e.g., more perennial crops, more complex rotations) will significantly move the needle with respect to nitrate loading of streams in the upper Mississippi basin (David et al., 2010). However, changes of this sort are unlikely in the near term, given the substantial production and processing infrastructure that exists for corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.].

It is not surprising that the corn–soybean system is leaky with respect to nitrogen. Corn requires approximately 17 kg of N for every megagram of grain produced, and while it can actively take up ammonium ( $NH_4^+$ ) if it is present, ubiquitous soil microbes rapidly convert available  $NH_4^+$  to nitrate (Hageman, 1984) so that in practice nearly all of the crop's N, roughly  $200 \text{ kg ha}^{-1}$  on the most productive fields, is absorbed passively as nitrate N ( $NO_3^-$ -N) in the transpiration stream, and it occurs during an approximately 6- to 7-wk period commencing about 40 d after planting (Watts and Hanks, 1978). Eddy covariance data

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**Abbreviations:** CRF, cost reduction factor; EAC, equal annual cost; EDR, electrodialysis reversal system; ICP, inductively coupled plasma; TPVC, total present value of the cost of the practice; VDC, volt direct current.

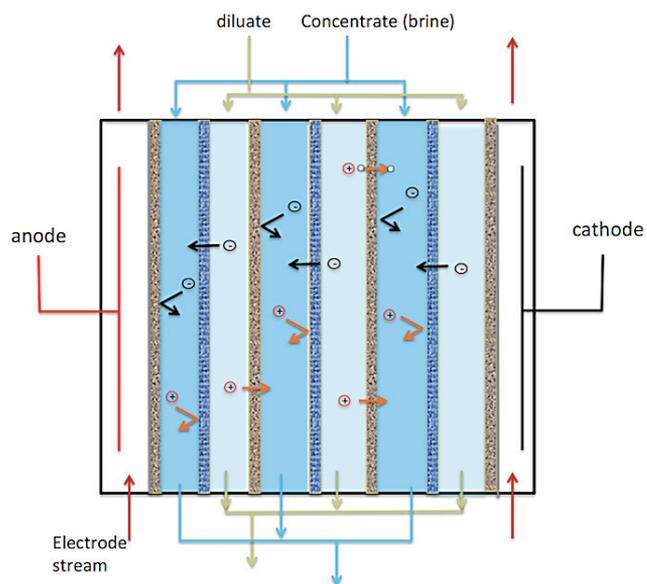
(Baker et al., 2012; Lagos et al., 2013) indicate that evapotranspiration from a corn field during this period in the midwestern United States is typically on the order of 200 mm, so that the transpiration stream, and thus soil water, must have a  $\text{NO}_3\text{-N}$  concentration during this period on the order of  $100 \text{ mg L}^{-1}$ . Unfortunately, this period coincides with the highest likelihood of heavy rain events in this region, so transport of nitrate out of the root zone is a frequent, almost inevitable occurrence.

For small rural communities that must remove nitrate from contaminated wells, the costs can be quite high—recent figures indicate a cost of between  $\$0.25$  and  $\$1.50 \text{ m}^{-3}$  (Minnesota Department of Agriculture, n.d.). The costs can be equally shocking for larger communities, which led the city of Des Moines, IA, to sue several agricultural watersheds in an attempt to recover expenses of nitrate removal. The suit was dismissed on procedural grounds, and the city now plans to spend  $\$15$  million for expansion of nitrate removal capacity (Elmer, 2017). These high costs have encouraged the search for approaches to solve the problem upstream, where nitrate-laden water exits farm fields. In the absence of recycling options, the primary solution is to encourage microbial denitrification, essentially converting fertilizer back to  $\text{N}_2$ . This is done by routing drainage water through bioreactors, natural or artificial wetlands, or saturated vegetative buffers (Jaynes and Isenhardt, 2014). In fields that are not tile-drained, these artificial denitrifying approaches are generally not an option, and much of the nitrate that leaves the root zone eventually finds its way to streams or groundwater.

## Recycling Alternatives

The perversity of devoting so much money and energy to turn manufactured reactive N back into  $\text{N}_2$  naturally inspires thoughts of conservation. Efforts to recycle excess nitrate have focused primarily on the use of winter cover crops to scavenge nitrate not taken up by the primary grain crop and then release it via decomposition during the subsequent growing season. This is appealing because cover crops provide other benefits, reducing wind and water erosion (Brandi-Dohrn et al., 1997; Bergström and Jokela, 2001; Krueger et al., 2011). However, it can be challenging to establish winter cover crops in regions with shorter growing seasons (Wilson et al., 2013), and it is also difficult to predict how much of the N taken up will be available to the following crop. More significantly, at least for the US Corn Belt, winter cover crops provide little or no benefit during a time of high likelihood for nitrate loss, late spring–early summer. Given these challenges, we propose exploring a method for both capturing excess nitrate and concentrating it for reuse.

Electrodialysis is a process that uses selectively permeable membranes to segregate charged species (Strathmann, 2010). Membranes that are permeable to either cations or anions can be manufactured by affixing either negatively or positively charged groups to a polymer substrate. When cation- and anion-permeable membranes are alternately stacked and separated by water-filled spacers, with an electrode at either end of the stack, a voltage difference between the electrodes will cause cations to move toward the cathode and anions to move toward the anode (Fig. 1). Because the cation-permeable membranes are impermeable to anions, and the opposite is true for the anion-permeable membranes, ions will only cross one membrane, resulting in alternating channels of concentrated and dilute solution. Electrolysis



**Fig. 1. Schematic of the electrodiagnosis process.** A stack consists of multiple cells, each containing a cation-permeable membrane and an anion-permeable membrane. When a direct current voltage is applied across the stack, anions move toward the anode but are repelled by the first cation-permeable membrane that they encounter, while the opposite occurs for cations. The result is alternating channels of dilute and concentrated water. The electrodes are bathed in a separate stream, typically a dilute acid, that carries away gases produced by hydrolysis reactions.

reactions at the two electrodes produce gases, primarily oxygen and hydrogen, which are carried off in a recirculating stream and released to the atmosphere.

Electrodialysis is widely used to desalinate sea water and to recover reagents in a variety of manufacturing processes. In a few cases, it has been tested to purify well water contaminated with nitrate (Hell et al., 1998; Elmidaoui et al., 2001; Bi et al., 2011), leading us to believe that it might be a practical means for simultaneously removing excess nitrate from agricultural drainage waters near the source and concentrating it for reuse in fertigation. Our objective in this project was to explore that proposition by evaluating the energy requirements, economic feasibility, and potential challenges associated with the method.

## Materials and Methods

Two electrodiagnosis reversal systems (EDRs) were used for the tests. The first was built around a small benchtop unit (EDR-200, PCCell GMBH) that contained 10 membrane pairs with a total active membrane area of  $0.4 \text{ m}^2$ , rated for nominal flow of  $1 \text{ L min}^{-1}$  through each of the two flow paths, designated as brine and diluate. Peristaltic pumps were used to circulate flows through each path and to circulate a  $0.2 \text{ M}$  sulfamic acid solution past the electrodes. The EDR and the pumps were powered by separate 12 volt direct current (VDC) power supplies. This system was installed on a greenhouse bench, and testing was conducted to explore the factors affecting the efficiency of  $\text{NO}_3\text{-N}$  removal, using 380-L tanks of water obtained from Trout Brook, a nitrate-contaminated stream approximately 50 km south of St. Paul, MN, that drains into the Cannon River 30 km upstream of its juncture with the Mississippi River.

In this test, the brine tank was initially filled with 5 L of water from Trout Brook, which had a  $\text{NO}_3\text{-N}$  concentration of

20.3 mg L<sup>-1</sup>. This water was recirculated through the concentrate channels of the EDR during the entirety of the test, with periodic samples taken for subsequent analysis. The remaining stream water in the 380-L supply tanks was passed through the diluate channels of the EDR, after which it was routed through an optical nitrate analyzer (Nitratex Plus sc, 0.1–50 mg L<sup>-1</sup> range; Hach Co.) and then exhausted to a floor drain. The sensor was checked against NO<sub>3</sub>-N laboratory standards before and after the test. Diluate and concentrate water flows were matched at 0.8 L min<sup>-1</sup>, and initial EDR voltage was set at 12.0 VDC. After a stable concentration was reached in the outlet stream, voltage, current, and outlet NO<sub>3</sub>-N concentrations were recorded. Then voltage was set to a new level in stepwise fashion and the process repeated.

A second, larger system was constructed to evaluate the challenges associated with the use of an EDR system for nitrate removal under field conditions, without access to alternate current power. The location for the test was on the west branch of Trout Brook. As its name implies, the stream is popular with fishermen, but it has been increasingly plagued in recent decades with excessive nitrate concentrations that are causing algal blooms and degrading fish habitat, while also contributing to the nitrate load carried to the Gulf of Mexico by the Mississippi River. Land use in the watershed of approximately 3000 ha is entirely agricultural. It is primarily devoted to corn and soybean production, along with several animal operations and a limited amount of pasture. Much of the cropland is under center pivot irrigation, and the underlying stratigraphy is karst. The stream is fed by numerous springs, all of which exhibited NO<sub>3</sub>-N concentrations exceeding the drinking water standard of 10 mg L<sup>-1</sup> when sampled in 2014 by personnel from the local Soil & Water Conservation District. Our periodic sampling in 2016 to 2017 throughout the nonfrozen portion of the year revealed in-stream concentrations consistently in excess of 20 mg L<sup>-1</sup>, with a mean value of 23.6 ± 2.3 mg L<sup>-1</sup> ( $n = 27$ ), and no discernible seasonal trend.

The core of the field system was an EDR 1100 electro dialyzer (PCCell GMBH, Germany) containing 25 cell pairs with a total membrane area of 5.5 m<sup>2</sup>, capable of sustaining flow rates of 15 L min<sup>-1</sup> through each path. A 380-L polyethylene tank on a trailer was used to hold the brine solution, which initially consisted of water pumped from the stream. We used 24-VDC pumps designed for solar power use (Dankoff Solar Pumps) to circulate the brine and to pump water from the stream through the diluate side of the EDR. A third, smaller 24-VDC pump (Shurflo model 2088-474-144, Northern Arizona Wind & Sun) was used to circulate a 0.4 M sulfamic acid solution past the electrodes. The EDR and the pumps were powered from a bank of six 12-V marine batteries for which charge was maintained with a set of four 256-W solar panels. Rotameters were plumbed into the brine and diluate circuits to match flows. An ammeter measured current through the EDR, and an optical nitrate sensor was installed in the output hose leading from the EDR back to the stream. Water samples were taken periodically during the 31-h test from the stream, the brine tank, and the outflow line and were frozen for subsequent analysis.

Water analyses from both the greenhouse and field tests were conducted by the University of Minnesota Research Analytical Laboratory. Concentrations of a suite of 15 dissolved elements

were measured by inductively coupled plasma (ICP) atomic emission spectroscopy, and seven anion concentrations were determined with ion chromatography (ICP analytes: Al, B, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Zn; ion chromatography analytes: F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>). Concentration data were subsequently used in the publicly available software Visual Minteq (<https://vminteq.lwr.kth.se>) to estimate chemical speciation and degree of saturation of various compounds of interest.

## Economic Analysis

The potential costs associated with nitrate removal by EDR were analyzed following methodology used to compare the costs of different approaches for nitrate mitigation (Christianson et al., 2013). Briefly, it allows comparison of practices that may differ in up-front costs, periodic maintenance costs, and system lifetimes by computing an equal annual cost (EAC) for each that is the product of the total present value of the cost of the practice (TPVC) multiplied by a cost reduction factor (CRF) that depends on the annual real discount rate ( $i$ ) and the number of years in the analysis ( $n$ ). The TPVC is in turn composed of the initial establishment cost of the practice ( $C_i$ ) and the periodic maintenance costs over the lifetime of the practice ( $C_m$ ), discounted over the lifetime of the analysis ( $n$ ):

$$TPVC = C_i + C_m$$

$$CRF = \frac{i(1+i)^n}{(1+i)^n - 1}$$

$$EAC = TPVC \times CRF$$

The initial costs of several commercially available EDR units of varying sizes were included in the analysis, and the costs and intervals of maintenance were based on information provided by the manufacturers. The cost of money was set at 4% per annum (Christianson et al., 2013). The lifetime of an EDR unit was assumed to be 40 yr, similar to the assumed lifetimes of bioreactors and controlled drainage structures used by Christianson et al. (2013), and considered reasonable by the EDR manufacturers (personal communications, 2017). Calculations were based on each EDR unit running at full capacity (rated flow rate) when in operation and were repeated for a range of incoming nitrate concentrations and duty cycles (fraction of time in operation). Electrical use was calculated on the basis of pumping rate, assuming 60% efficiency, and desired output NO<sub>3</sub>-N concentration, arbitrarily taken as 7 mg L<sup>-1</sup>. The difference between the calculated energy use and the energy value of the conserved NO<sub>3</sub>-N (taken as \$1.10 kg<sup>-1</sup>) was factored into the EAC calculations, assuming an electrical cost of \$0.11 kWh<sup>-1</sup>.

The power required to pump water is given by the following:

$$P = \frac{Q dp}{60 \epsilon_p}$$

where  $P$  = pumping power requirement (W);  $Q$  = pumping rate (L min<sup>-1</sup>);  $dp$  = pressure change across pump (kPa); and  $\epsilon_p$  = fractional pump efficiency (unitless; 0–1).

# Results and Discussion

## Greenhouse Test

The outgoing  $\text{NO}_3\text{-N}$  concentrations of the diluate (means of three to five readings) at various imposed EDR voltages are shown in Table 1. The entering water had a concentration of  $20.3 \text{ mg L}^{-1}$  and a steady flow of  $0.8 \text{ L min}^{-1}$ , and as step changes in voltage to the EDR were imposed, the outlet concentration correspondingly changed, showing how the system can be tuned to produce a desired product concentration. The response was quite linear over this voltage range, with a correlation coefficient of 0.9994 ( $p < 0.0001$ ).

Data from the stepwise voltage changes were used to calculate (i) the energy required to move nitrate from the diluate to the brine and (ii) the electrical efficiency of the process for this specific water source. In Fig. 2 on the left axis, the  $\text{NO}_3\text{-N}$  concentration reduction in the diluate path ( $C_{\text{in}} - C_{\text{out}}$ ) is plotted against the electrical current through the dialyzer at each applied voltage. Plotted on the right axis is the corresponding energy efficiency of the dialysis process, expressed as milligrams of  $\text{NO}_3\text{-N}$  removed per joule. Ion transport increased linearly with current, as theory predicts. However, this monotonic increase was accompanied by a monotonic decrease in dialyzing efficiency. Others have noted that dialyzer electrical efficiency decreases with increasing voltage (Elmidaoui et al., 2001). This is apparently due to the fact that current leakage around the edges of the membranes increases with voltage. It is important to note that dialyzing efficiency will be different for each water source. In general, it will increase with increasing nitrate concentration of the source water and with the ratio of nitrate to total anion concentration in the water.

Figure 3 shows overall energy efficiency for the same data set, for two different hypothetical pump efficiencies, 0.3 and 0.6 (30 and 60%), and demonstrates that whole system efficiency is less variable and, unlike dialyzing efficiency, is not a monotonic function of  $\text{NO}_3\text{-N}$  removal rate. It declines at low removal rates due to the fixed electrical cost of pumping and at high rates due to the decreasing efficiency of the dialyzing process.

## Field Test

The field test was conducted over the period of a week in mid-September 2016 at Trout Brook, approximately 45 km southeast of St. Paul, MN. Chemical analysis of the stream water at this time is given in Table 2. Five cations and three anions were present at detectable levels, and total organic carbon concentrations were  $0.58 \pm 0.28 \text{ mg L}^{-1}$ . Electrical conductivity and pH were not measured on these samples, but measurements on subsequent stream samples have averaged  $0.56 \text{ dS m}^{-1}$  and 7.6, respectively. Actual system operating time during the week of testing was approximately 31 h. Flows in the diluate and concentrate lines were initially set at  $12.4 \text{ L min}^{-1}$ , although

Table 1. Outgoing diluate  $\text{NO}_3\text{-N}$  concentration as a function of voltage applied to the electro dialyzer (EDR 200, PCCell GMBH, Germany). Incoming concentration was  $20.3 \text{ mg L}^{-1}$ .

Voltage	[ $\text{NO}_3\text{-N}$ ] $\text{mg L}^{-1}$
4	$10.60 \pm 0.029$
6	$9.518 \pm 0.018$
8	$8.585 \pm 0.030$
10	$7.708 \pm 0.027$
12	$6.743 \pm 0.013$

flow declined somewhat over the course of the experiment for reasons discussed later. Mean flow over the entire period averaged  $11.4 \text{ L min}^{-1}$ , so the total amount of water processed was approximately 21,200 L. As described earlier, the system was run entirely on 24 VDC power provided from a battery bank charged by a solar panel, with no attempt to adjust voltage to the EDR. Mean stream concentration of  $\text{NO}_3\text{-N}$  during the period of data collection was  $22.6 \pm 0.4 \text{ mg L}^{-1}$ , and the mean outflow concentration of the diluate was  $13.2 \pm 3.1 \text{ mg L}^{-1}$ . A  $t$  test confirmed that the difference between the two means was significant ( $p < 0.001$ ). The  $\text{NO}_3\text{-N}$  concentration in the brine tank reached  $523 \text{ mg L}^{-1}$  by the conclusion of the test, indicative of the potential to concentrate N for reuse. Multiplying the total diluate flow by the difference in mean  $\text{NO}_3\text{-N}$  concentration between inflow and outflow yields a total of 199,317 mg extracted from the stream. As a check, multiplying the volume of the brine tank by the difference between its initial and final concentrations gives a value of 189,401 mg captured for reuse, about 5% less, but a reasonable mass balance.

System efficiency was evaluated at five points during the field test, yielding a mean value of  $0.01 \pm 0.0006 \text{ kg N MJ}^{-1}$ . The pumps in this system were not operating in their optimal range, with efficiencies of approximately 0.2 (20%); pump efficiencies of 50% or better would lower the energy required to separate and

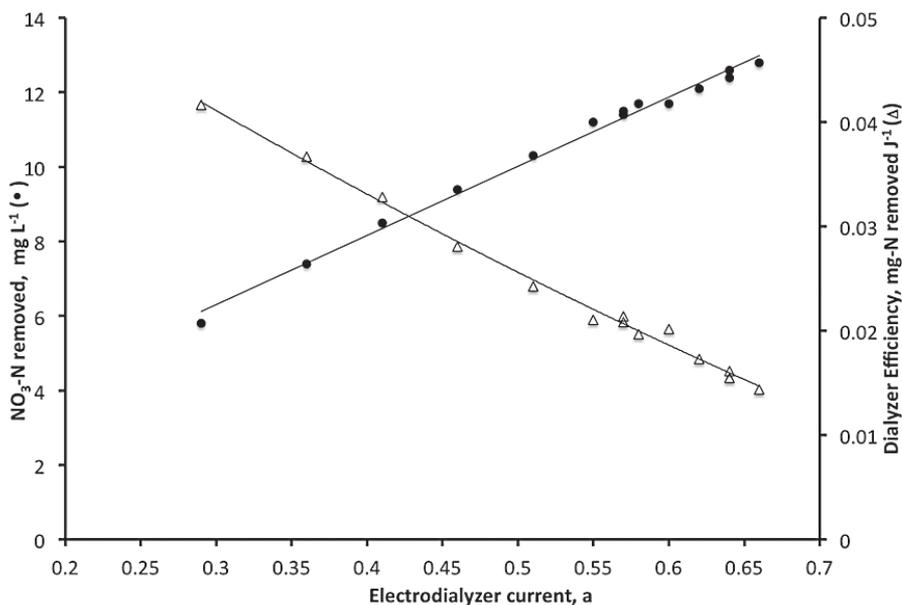


Fig. 2. Electrical testing of small benchtop electro dialyzer for removing  $\text{NO}_3\text{-N}$  from source water with a concentration of  $20.3 \text{ mg L}^{-1}$ . On the left axis,  $\text{NO}_3\text{-N}$  removal from the diluate (inflow concentration-outflow concentration) is plotted against electrical current through the dialyzer (closed circles). Electrical efficiency of N removal is plotted on the right axis (open triangles).

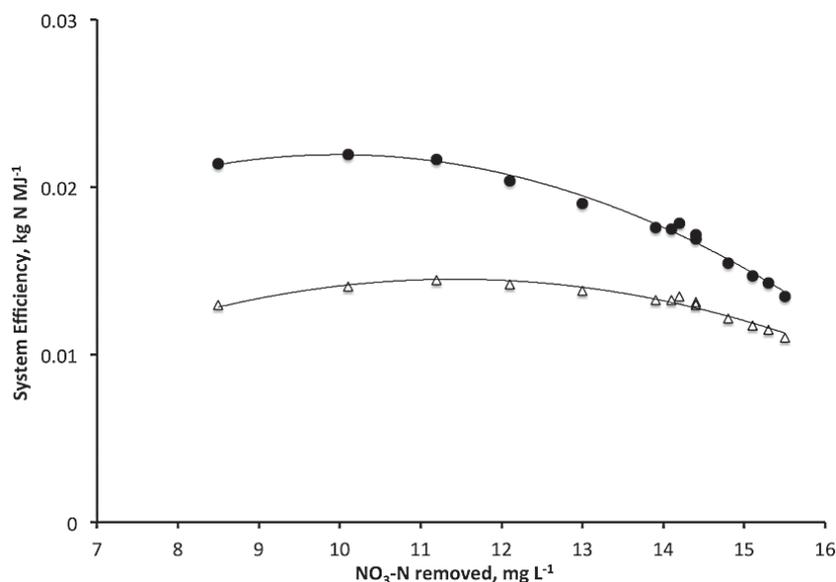


Fig. 3. Overall system efficiency (including pumping power) for the same test as in Fig. 2, plotted for two different pump efficiencies: 0.3 (open triangles) and 0.6 (closed circles).

concentrate NO<sub>3</sub>-N from this particular water source to something on the order of 40 MJ kg<sup>-1</sup>, coincidentally similar to the energy required to manufacture it.

Two serious issues arose during the field test: sediment accumulation and mineral precipitation. The EDR manufacturer recommended a 10- $\mu$ m sediment filter, whereas the pumps that were used had a more stringent requirement of 5  $\mu$ m. The mean sediment load (5  $\mu$ m or greater) in the stream at the intake point was 19.7 mg L<sup>-1</sup>; thus, at the mean flow rate of 11.4 L min<sup>-1</sup>, the filter was trapping nearly 110 g during an 8-h run, requiring daily replacement to maintain acceptable flow. For long-term operation, it would be necessary to develop a strategy or system to address this. Measures could include use of more sediment-tolerant pumps, automated periodic backwashing of the filter, and design of intake systems that allow sediment to settle out, thus reducing dependence on filtration.

The problem that actually ended the field test was mineral precipitation in the system, which reduced flow and NO<sub>3</sub>-N removal, ultimately limiting the maximum achievable brine NO<sub>3</sub>-N concentration to approximately 520 mg L<sup>-1</sup>. Both cations and anions are concentrated in the brine during the dialysis process, and due to the karst topography in the watershed, the stream has particularly high levels of calcium and magnesium (Table 2). Figure 4 shows a time series of brine concentration during the test run (expressed in mmol kg<sup>-1</sup>) of the four dominant ions. There is an obvious discontinuity in dissolved calcium at 19 h. Visual Minteq was run with measured brine concentrations at that point, and it indicated that a number of minerals were substantially oversaturated, with saturation indices greater than 1, including aragonite (1.48), calcite (1.62), dolomite

(3.26), and huntite (2.19). Oversaturation does not always result in precipitation—in fact, the water in Trout Brook itself has somewhat positive saturation indices for several of these minerals—but the drop in calcium concentration from 19 h onward (with no corresponding drop in magnesium concentration), coupled with decreased flow in the EDR and observed scale formation within the brine tank, is evidence that calcium carbonate precipitation occurred. This was confirmed following the experiment when the EDR membranes were soaked in deionized water. They released a fine, powdery material that was submitted for X-ray diffraction analysis and found to be calcite, with a high degree of confidence (B.M. Toner, personal communication, 2017). Subsequent testing showed that calcite precipitation in the system at this site can be delayed by reducing the pH of the brine tank; bubbling CO<sub>2</sub> through it allowed the NO<sub>3</sub>-N concentration to exceed 1000 mg L<sup>-1</sup> before precipitation occurred.

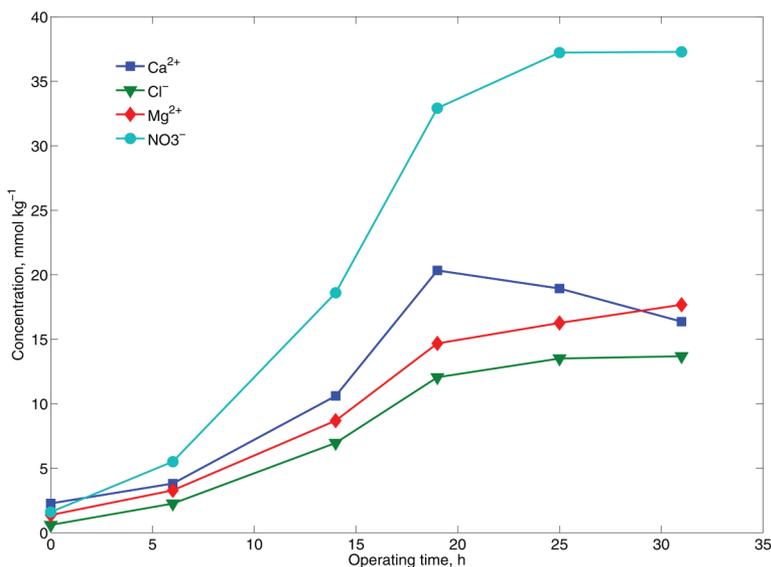
### Economic Analysis

The viability of EDR for nitrate recycling depends on the interrelated questions of scalability and cost. For this exercise, equipment costs and treatment capacities of four different units of widely varying capacity were analyzed. Relevant information is summarized in Table 3. The financial model that was used is described in detail in Christianson et al. (2013).

The four commercial EDR units that were considered range in cost from \$10,000 to \$550,000, with corresponding flow rates of 20 to 1500 L min<sup>-1</sup>. For the analysis, each was assumed to have a lifetime of 40 yr, with membrane replacement every 10 yr. Results (Table 3) indicate that the estimated EAC for each liter per minute of capacity ranges between \$20 and \$46, with the lowest EAC associated with the largest capacity. A sensitivity analysis, in which each input variable (initial cost, membrane replacement interval, expected lifetime) was varied by  $\pm 10\%$  showed that EAC was most sensitive to initial cost of the unit and least sensitive to membrane replacement interval. Translation to dollars per kilogram of NO<sub>3</sub>-N removal requires two operational variables: the duty cycle (operating time per annum) of the system, and the N removal rate, i.e., concentration difference between the source water and the outflow. We varied both over reasonable expected ranges to create response surfaces in dollars per kilogram that could be used to determine the feasibility of the method, given a specified target cost per unit of N removed. Results for two of the units are shown in Fig. 5. In each case, they show a tremendous range, with the lowest cost associated with maximizing the duty cycle

Table 2. Mean elemental and anion concentrations in water sampled from Trout Brook six times during the week of the field test, with standard deviations in parentheses. Elements that were included in the inductively coupled plasma analysis, but below detection limit included Al, B, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. Anions that were below detection limit included NO<sub>2</sub><sup>-</sup>-N, Br<sup>-</sup>, F<sup>-</sup>, and PO<sub>4</sub><sup>2-</sup>-P.

Dissolved cationic species					Anions		
Al	Ca	K	Mg	Na	Cl	NO <sub>3</sub> -N	SO <sub>4</sub> -S
mg L <sup>-1</sup>							
0.010 (0.010)	90.83 (0.82)	2.61 (0.089)	33.39 (0.18)	7.08 (0.29)	23.89 (5.9)	22.53 (0.34)	7.49 (0.49)



**Fig. 4.** Brine tank concentrations of the major ions during the field test. The decrease in dissolved Ca after 19 h was coincident with the appearance of precipitate in the tank.

and having a consistently high concentration of NO<sub>3</sub>-N in the source water. For instance, for the smaller of the two units, the EDR 4000H (PcCell GMBH), the analysis indicates that the dollar cost per kilogram of nitrate recovered can be kept below \$5 only if the system is operated more than 6 mo of the year and the N removal rate exceeds 20 mg L<sup>-1</sup> (the dark blue area in the upper right of the left graph in Fig. 5). For the larger unit (GE2020), the same \$5 target cost can be achieved with a much broader combination of duty cycles and N removal rates. However, the larger unit has a rated flow rate that is 10 times as great, so it may not be appropriate for some situations where the flow of contaminated water is lower than the rated capacity of the EDR.

For comparison, Christianson et al. (2013) estimated the median cost of NO<sub>3</sub>-N removal for a variety of agronomic practices, ranging from \$1.70 kg<sup>-1</sup> for controlled drainage, \$2.00 kg<sup>-1</sup> for bioreactors, and \$2.80 kg<sup>-1</sup> for constructed wetlands (all denitrification strategies), up to nearly \$40.00 kg<sup>-1</sup> for cropping system modifications like cover crops and rotational systems that rely on plants to scavenge excess NO<sub>3</sub>-N. The general conclusion from that work is that there is a clear divide—practices encouraging microbial conversion of nitrate to N<sub>2</sub> can remove NO<sub>3</sub>-N for less than \$3 kg<sup>-1</sup>, whereas

agronomic practices that scavenge NO<sub>3</sub>-N can cost more than \$30 kg<sup>-1</sup> (although the latter provide additional valuable benefits, such as erosion prevention). We conclude from our analysis that it is possible for electro dialysis systems to operate in the broad space that lies between these extremes. One final point worth mention is that nitrate recycling with electro dialysis is well suited to alternative energy sources such as solar and wind, a potentially fortuitous match since wind turbines are scattered across the landscape of the midwestern United States, and so, increasingly, are solar farms.

### Limitations and Challenges

In general, this approach will be most applicable for water sources that have relatively high nitrate concentrations for much of the year, such as contaminated wells and streams like Trout Brook; on the other hand, the costs will probably be prohibitive for situations in which nitrate loads are ephemeral, with extremely high flows or concentrations for short periods of time, such as tile-drained systems that may only flow for a month or two in the spring, as well as for cases in which the source concentration is too low to sustain high NO<sub>3</sub>-N removal rates.

The limitations imposed by mineral precipitation in calcium-rich waters are also a significant problem for economical N recycling because the transport cost per unit of fertilizer N is inversely proportional to its concentration. Typical liquid N fertilizer solutions are 28 to 32% N, while a 1000 ppm EDR-generated solution is only 0.1% N. For source waters that are lower in calcium, it should be possible to reach higher nitrate concentrations, but the presence of high levels of other cations, particularly sodium, may be problematic. Finally, the broad-spectrum reduction of ion concentrations in the treated water that is returned to the stream or water body may have unintended effects on aquatic life—such potential impacts have not been studied.

### Conclusions

Nitrate contamination is largely a diffuse, or nonpoint source, problem, so the appropriate scale for remediation technology is something that can be widely deployed and that is ideally not dependent on significant infrastructure. Electrodialytic recycling is potentially feasible for some applications of this sort. It is compatible with rural alternative energy production systems, and

**Table 3.** Cost estimates for commercially available electro dialyzers. Maintenance cost estimates are based on information provided by the manufacturers. Calculations of total present value (TPV) and equal annual cost (EAC) follow the approach outlined by Christianson et al. (2013).

Manufacturer	Model	Flow rate L min <sup>-1</sup>	Initial cost	Maintenance costs	TPV	EAC	EAC/Q†
				\$			
PC Cell GMBH	EDR1100	15–60	\$10,000–\$23,000	Replace membranes every 10 yr (PV‡ = \$2484–\$9936)	\$13,660–\$34,990	\$690–\$1,767	\$46–\$29.45
PC Cell GMBH	EDR 4000H	167	\$85,000	Replace membranes every 10 yr (PV = \$23,040)	\$108,040	\$5,456	\$32.67
GE	Aquamite	568	\$375,000	Estimated annual cost = \$2000 (PV = \$39,590)	\$414,590	\$20,937	\$36.86
GE	2020	1514	\$550,000	Estimated annual cost = \$3000 (PV = \$59,390)	\$609,390	\$30,774	\$20.33

† Q = pumping rate.

‡ PV, present value.

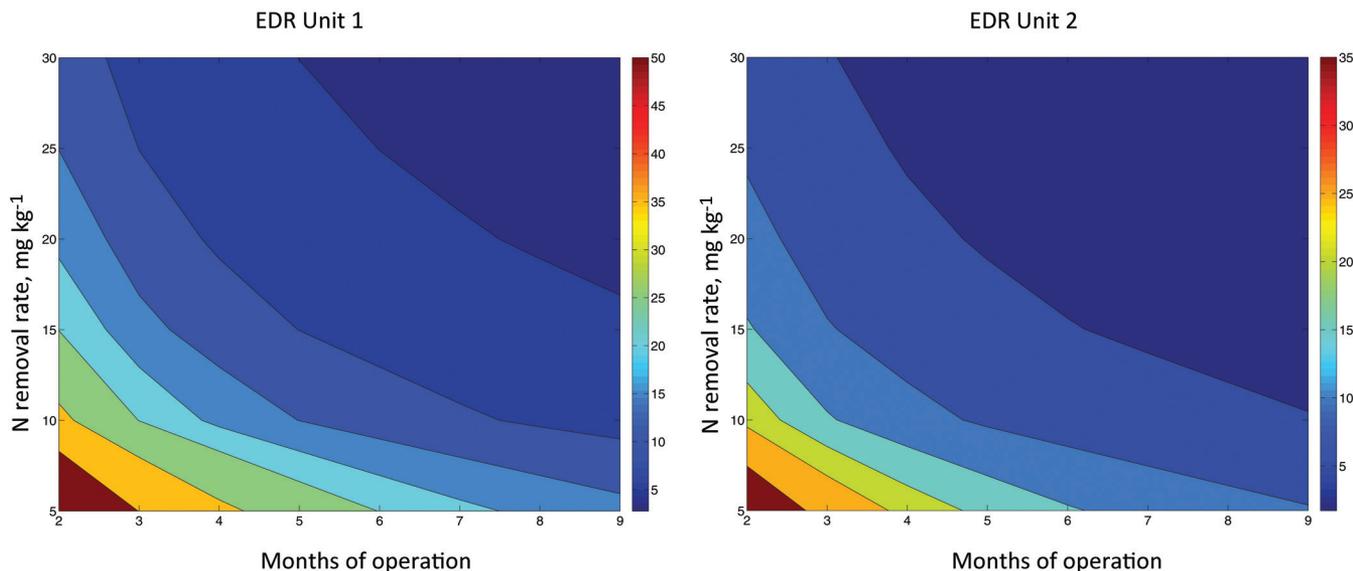


Fig. 5. The estimated cost (\$) per kilogram of N removed as a function of the duty cycle (months of operation per year) and the N removal rate,  $\text{mg L}^{-1}$ , for two dialyzers, one of moderate size (ED 4000H, PC Cell GMBH) on the left and a much larger unit (Model 2020, GE) on the right. Color bars to the right of each plot denote the scales. For comparison, the dark blue area in the upper right of each plot represents the region where estimated costs are below  $\$5 \text{ kg}^{-1}$ .

under some circumstances it can conserve excess reactive N for costs that are not too far removed from those of denitrifying practices that return N to the atmosphere. There are, however, problems and challenges that must be addressed, among them mineral precipitation and sediment loading that can foul membranes, the possible necessity of further processing of the brine before it can be used for irrigation, and high initial equipment costs that must be amortized over many years. Research and development devoted to systems specifically designed for agricultural applications may solve these challenges and increase the effectiveness of electro dialysis as a mitigation and conservation tool.

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