Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.

Tailored water treatment using enhanced primary clarification for nutrient recovery and production of water for turfgrass irrigation

Supplementary Information

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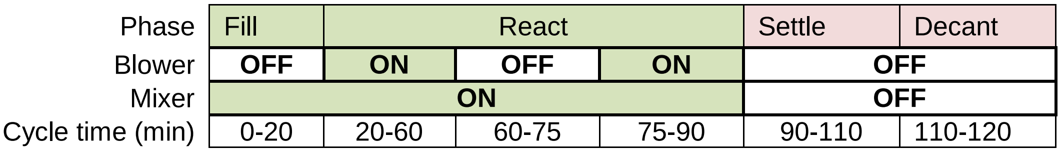
A manuscript prepared for publication in
Environmental Science: Water Research & Technology

January 2017

Table SI-1. Water characteristics for fertigation water. Nutrient values are based on the requirements of CA Title 22 for unrestricted irrigation, and values for fertilizer concentrations found in the Literature, as noted. Disinfection requirements are not included.

Parameter	Value	Notes	Ref.
COD	40 mg L^{-1}	Oxidized water had BOD_5 of 30 mg/L and BOD/COD ratio of 0.75.	1
Nitrogen	11–25 mg N L^{-1}	Based on 12-month growing season	2
	22–28 mg N L^{-1}	Based on 7-10 month growing season	2
N:P ratio	7:1–11:1	Crop uptake	3-5
($N:P_2O_5$)	0.5–4.1	Typical profile in nutrient concentrate mixtures	
Phosphorus	1–3.6 mg P_2O_5 L^{-1}	Based on N:P profile	4, 6
Phosphorus	1.3–4.8 mg PO_4 L^{-1}	Conversion	
pH	6.0–8.0	Protective of crop foliage root growth	
	6.5–8.4	protection biological treatment	1, 7



Phase	Fill	React			Settle	Decant
Blower	**OFF**	**ON**	**OFF**	**ON**	**OFF**	
Mixer	**ON**				**OFF**	
Cycle time (min)	0-20	20-60	60-75	75-90	90-110	110-120

Fig. SI-1. Typical schedule of phases and sub-phases during the bench-scale SBR testing. The phase length and aeration sub-phase lengths were controlled by the LabVIEW program.

Table SI-2. Overview of jar and small batch testing protocol. Results of jar testing were used to identify an optimal coagulant dose, polymer dose, and mixing regime. Small batch testing was conducted to establish the feasibility of chemical EPC and choose the coagulant for continuous testing.

Jar Testing	Jar testing was conducted using accepted Jar Testing protocol[8] of the three coagulants ferric chloride ($FeCl_3$) (PVS Technologies, Inc., Detroit MI), aluminum sulfate ($Al_2(SO_4)_3 \cdot 18\ H_2O$) (Sigma Aldrich, St. Louis, MO), and calcium hydroxide ($Ca(OH)_2$) (Sigma Aldrich, St. Louis, MO). Coagulant target doses were based on the typical concentrations reported in the literature,[9, 10] and doses were varied from 0.25x to 2x the typical dose, with a control (no coagulant added) included in each test set. After solids settling, the optical density of each supernatant was recorded, and the turbidity was calculated using an optical density–turbidity calibration curve developed during jar testing (see section 2.4). An optimal dose was identified for each coagulant, and additional jar tests were conducted using the optimal coagulant dose and varying polymer dose, rapid mixing method (i.e., impeller or aeration), and flocculation operating speed.
Small batch testing	Based on results from jar testing, small batch testing of EPC was conducted using the optimal dose of coagulant and polymer (60 mg $Al_2(SO_4)_3$ L^{-1}, 60 mg $FeCl_3$ L^{-1}, 200 mg $Ca(OH)_2$ L^{-1}, and 2 mg/L^{-1} polymer). Small batch tests included a series of seven tests for each coagulant using raw wastewater. For each test, 2 L of wastewater with the optimal doses of coagulant and polymer were added to six 2-L jars. Rapid mixing and flocculation were induced by the jar stirring equipment according to conditions summarized in Table SI-2 in the Supporting Information document. At the end of the settling time, a 120-ml sample of supernatant was collected from each jar and combined to make a single (composite) sample for the test. Thus, for each coagulant, a total of seven composite samples were generated, and from these, three samples were randomly chosen for analysis.
Jar and small batch test chemicals	Ferric chloride and aluminum sulfate stock solutions of 10,000 mg L^{-1} and a calcium hydroxide stock solution of 20,000 mg L^{-1} were used for jar and small batch testing. A nonionic polymer (Nalclear ® 8181, Nalco, Naperville, IL) stock solution of 10,000 mg L^{-1} was prepared and added to all jar and batch tests containers with the exception of the control.
Analyses	For jar testing, a calibration curve relating the optical density to turbidity was developed by measuring the percent absorbance of Formazin turbidity standards (Hach 2100Q Portable Turbidimeter, Loveland CO). Absorbance was measured using a single wavelength (860 nanometer), and converted to turbidity, reported as nephelometric turbidity units (NTU). The trends in turbidity were used to establish the point at which increasing the coagulant dose provided little to no reduction in turbidity. Dissolved organic carbon (DOC) concentrations were measured in small batch test samples using a carbon analyzer (Shimadzu TOC-L, Columbia, MD). DOC samples were prepared by filtering raw sample through a 0.45 µm membrane filter (Pall Corporation, Port Washington, NY, USA) into an instrument vial. Samples were acidified to pH 2 with concentrated hydrochloric acid and refrigerated at 4 °C until analyzed. Bulk analyses of supernatant included quantification of total and volatile suspended solids (TSS and VSS, respectively), COD, ortho-phosphate (PO_4^{3-}), NH_4^+, alkalinity, and pH.

Table SI-3. Coagulants and mixing/flocculation conditions for small batch testing using 2-L jars. Polymer was added to all tests at a dose of 2 mg L^{-1}, with the exception of the control test. A 10,000 mg L^{-1} stock solution of ferric chloride was made by adding 25 ml of anhydrous $FeCl_3$ concentrate to 975 ml deionized water; a 10,000 mg L^{-1} stock solution of aluminum sulfate (as $Al_2(SO_4)_3$) was made by adding 19.5 g $Al_3(SO_4)_2$•18 H_2O to 980 ml deionized water, and a 20,000 mg L^{-1} stock solution of calcium hydroxide was made by adding 20 g of $Ca(OH)_2$ to 980 ml deionized water. The polymer stock solution was made by mixing 2 ml of polymer with 98 ml of hot tap water and stirring overnight with a magnetic stirrer. Based on test results, optimum doses were determined to be 60 mg L^{-1} of ferric chloride and alum, and 200 mg L^{-1} calcium hydroxide.

Test	Coagulant	Small batch testing doses (mg L^{-1} as salt)	Conditions
Control	None		1.5 hr settle
Ferric	Ferric Chloride ($FeCl_3$)	60 mg L^{-1} as $FeCl_3$	Rapid mix 2 min @ 210 rpm; Floc 0 min @ 100 rpm, 10 min @ 60 rpm, 10 min @ 15 rpm; settle 30 min
Alum	Aluminum sulfate ($Al_2(SO_4)_3$ • 18 H_2O	60 mg L^{-1} as ($Al_2(SO_4)_3$	Rapid mix 2 min @ 210 rpm; Floc 10 min @ 80 rpm, 10 min @ 40 rpm, 10 min @ 15 rpm; settle 30 min
Lime	Calcium hydroxide ($Ca(OH)_2$)	200 mg L^{-1} as $Ca(OH)_2$	Rapid mix 3 min @ 210 rpm; Floc 10 min @ 100 rpm, 10 min @ 80 rpm, 10 min @ 25 rpm; settle 30 min

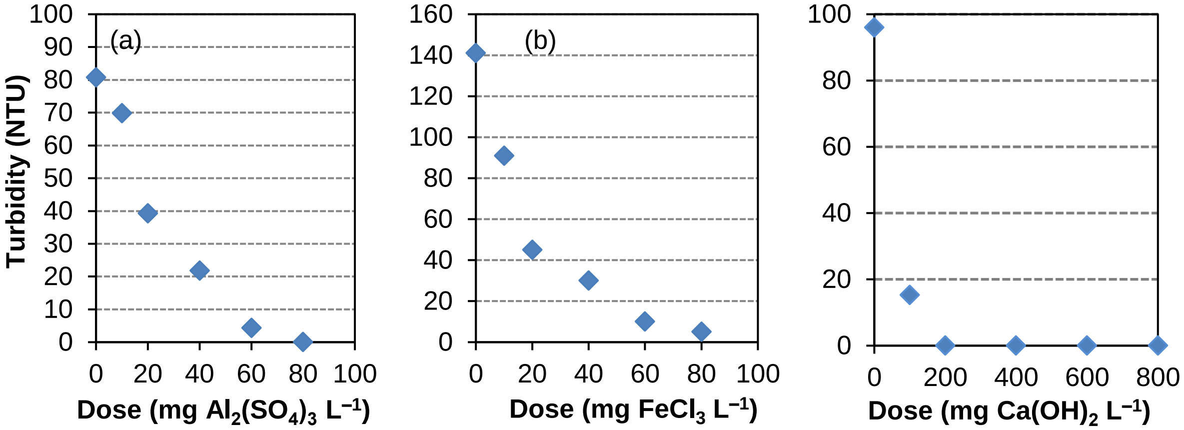


Fig. SI-2. Jar test results for coagulant screening. Turbidity was used to identify the optimal dose for (a) alum, (b) ferric chloride, and (c) calcium hydroxide. The turbidity curves show typical characteristics, and the optimal doses based on the turbidity readings were 60 mg $Al_3(SO_4)_2$ L^{-1}, 40-60 mg $FeCl_3$ L^{-1}, and 100-200 mg $Ca(OH)_2$ L^{-1}.

Table SI-4. Average effluent concentrations of small batch tests. The effluent characteristics of the wastewater subjected to EPC testing are summarized. The monthly average effluent concentrations of a full-scale EPC wastewater treatment plant (Point Loma)[11] are also provided as a reference. Each EPC treatment was more effective than CPC in reducing TSS and COD, and are within the range of monthly averages from the Point Loma plant. Ammonium (NH_4^+) effluent concentration of ferric chloride and aluminum sulfate treatments was similar to the control (CPC) and higher than the Point Loma plant; yet, calcium hydroxide was more effective in removing ammonium. Phosphorus and alkalinity concentrations of all EPC treatment effluents were lower than Point Loma.

Sample	TSS mg L^{-1}	COD mg L^{-1}	NH_4^+ mg L^{-1}	P mg PO_4 L^{-1}	Alkalinity mg $CaCO_3$ L^{-1}	pH
Influent	242±59.3	449±122	48.8±10.1	30.4±12.8	256±77	8.0
Control (CPC)	83.0±9.3	267±39.0	57.5±1.6	32.6±2.5	--	7.6
Alum	13.4±1.0	142±12.1	40.1±3.5	2.25±0.24	121±13	6.7
Ferric chloride	41.3±8.4	169±23.6	40.5±1.4	1.66±0.08	152±36	6.7
Calcium hydroxide	30.2±11.7	165±38.1	31.5±3.9	2.56±1.90	209±40	10.2
Point Loma	27-43	158-193*1	34.5	15.9*2	284	>7.1

1. COD is calculated based on BOD_5 concentration range of 95-116 mg/L and a BOD_5 to COD ratio of 0.6.
2. Point Loma effluent is reported as “P” and converted to “PO_4”

Table SI-5. Comparison of COD and DOC in the influent and supernatant of small batch tests. Primary clarification using three coagulants was performed on a common influent. As expected, the COD of the EPC tests were lower than the control (CPC). However, the EPC treatments did not reduce the DOC of the wastewater; it was unchanged in the ferric chloride EPC effluent and increased with alum and lime treatments. The lack of DOC reduction indicates that EPC alone will not produce an “oxidized” effluent per CA Title 22.

Sample	**COD** (mg L^{-1})	**DOC** (mg L^{-1})	**COD removed***1 (%)	**DOC removed***1 (%)
Influent	500	34.7		
Effluents				
Control	267	34.2	47	1.44
Ferric	134	34.4	73	0.76
Alum	110	40.2	65	-15.9
Calcium hydroxide	176	54.3	-11.1	-56.5

1. COD and DOC removal are in reference to the influent sample.

Table SI-6. Inorganic constituents in the small batch test influent and effluent. Inorganic constituents are listed by name alphabetically, with compounds listed in the US EPA in the Guidelines for water reuse[7] presented first, and other inorganic elements provided at the bottom of the table. All concentrations are below the recommended US EPA guidelines. The effluent potassium concentration provides a N:K profile of 2:1 to 4:1 mg N:mg K_2O. The SAR of all effluents is below 3, indicating that long-term irrigation with the EPC effluent will not cause structural soil damage. All EPC effluents have chloride concentrations that might produce "moderate" impact to crops.[1]

Constituent	**Ferric chloride**		**Aluminum sulfate**		**Calcium hydroxide**		**Recom-mended max**[1.]
	Influent (mg L^{-1})	Effluent (mg L^{-1})	Influent (mg L^{-1})	Effluent (mg L^{-1})	Influent (mg L^{-1})	Effluent (mg L^{-1})	(mg L^{-1})
Aluminum	0.0814	0.0497	0.0660	0.0877	0.0813	0.0506	5.0
Arsenic	<0.0042	0.0069	<0.0042	0.0076	<0.0042	<0.0042	0.10
Beryllium	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.10
Boron	0.1573	0.1518	0.1400	0.1177	0.2662	0.2172	0.75
Cadmium	<0.0003	<0.0003	0.0004	0.0004	<0.0003	<0.0003	0.01
Chloride	76.00	140.00	71.20	76.00	75.80	74.70	
Chromium	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	0.002	0.1
Cobalt	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	0.05
Copper	0.0197	0.0160	0.0171	0.0147	0.0180	0.0174	0.2
Fluoride	0.67	0.55	0.37	0.45	0.70	0.47	1.0
Iron	0.0292	0.1399	0.0257	0.0668	0.0158	0.0101	5.0
Lithium	0.0225	0.0212	0.0227	0.0230	0.0242	0.0211	2.5
Manganese	0.0199	0.1098	0.0113	0.0192	0.0114	0.0020	0.2
Nickel	0.0067	0.0091	0.0034	0.0049	0.0037	0.0032	0.2
Lead	<0.0018	0.0066	0.0038	0.0024	<0.0018	<0.0018	5.0
Selenium	<0.0061	<0.0061	<0.0061	<0.0061	<0.0061	<0.0061	0.02
Vanadium	0.0015	0.0006	0.0007	0.0008	0.0006	0.0019	0.1
Zinc	0.2162	0.1568	0.1146	0.1285	0.1082	0.0383	2.0
Molybdenum	0.0008	0.0031	0.0020	0.0015	0.0059	0.0038	0.01
Sodium	62.33	60.13	59.89	56.34	73.75	63.62	[2.]
Calcium	53.30	52.17	52.80	50.75	58.13	49.94	[2.]
Potassium (K)	12.34	11.69	13.77	12.70	13.24	12.05	
Potassium (K_2O)	14.81	14.03	16.52	15.24	15.89	14.46	[3.]
Magnesium	15.90	15.67	16.00	15.20	17.17	9.194	
Sulfur	47.52	47.10	49.94	75.3	52.35	48.10	

1. Source: [USEPA 2012 Table 3-5] unless otherwise stated
2. Water with SAR greater than 3.0 may contribute to structural deterioration of soil.
3. The optimum N:K is 1:1 to 3:1 when potassium is expressed as K_2O.[4] The ratio of potassium in the primary effluents (31.5-40 mg N L^{-1}, 9.2-15.9 mg K_2O L^{-1}) is close to the optimal range, providing a balanced N:K profile.

Table SI-7. Evaluation of trace nutrients in primary effluent of coagulants evaluated in small batch testing. Three samples of each effluent were analyzed for inorganic constituents and the average concentration reported. Hagin et al.[4] provides three examples of trace nutrient concentrates used for fertigation, and the concentrations were normalized to molybdenum. In our data, ferric chloride and alum have profiles similar to Hagin et al., with iron being present in suitable concentrations, but zinc present in excess. Calcium hydroxide effluent is markedly different, with zinc proportional to molybdenum, but iron, manganese and copper present in much lower concentrations than would be used in commercially prepared fertigation solutions.

Test Results						
	Ferric chloride		**Aluminum sulfate**		**Calcium hydroxide**	
	mg/L	Ratio	mg/L	ratio	mg/L	ratio
Iron	0.1399	45.1	0.0670	44.7	0.0101	2.7
Manganese	0.0192	6.2	0.0192	12.8	0.0020	0.5
Zinc	0.1568	50.6	0.1285	85.7	0.0383	10.1
Copper	0.0160	5.2	0.0150	10.0	0.0000	0.0
Molybdenum	0.0031	1.0	0.0015	1.0	0.0038	1.0
Literature values[4]						
	Example 1		**Example 2**		**Example 3**	
	g/L	Ratio	g/L	ratio	g/L	ratio
Iron	12.2	50.8	5.5	36.7	40.5	36.8
Manganese	5.2	21.7	2.7	18.0	20.2	18.4
Zinc	1.8	7.3	1.4	9.0	10.1	9.2
Copper	0.5	2.3	0.2	1.3	1.5	1.4
Molybdenum	0.2	1.0	0.2	1.0	1.1	1.0

Table SI-8. Molar-based ratios of carbon, nitrogen, and phosphorus in the supernatant streams during EPC batch test. The EPC effluents dramatically altered the nutrient profile in the effluent. While the concentration of phosphorus is greater than the half-saturation constant of 0.2 µmol P L^{-1} (0.006 mg P L^{-1}, 0.019 mg PO_4 L^{-1}) reported in the literature,[12] the impact of the change on the biological process is unknown.

	C	**N**	**P**
Control	20	11	1
Fe	164	203	1
Al	141	180	1
Ca	149	144	1

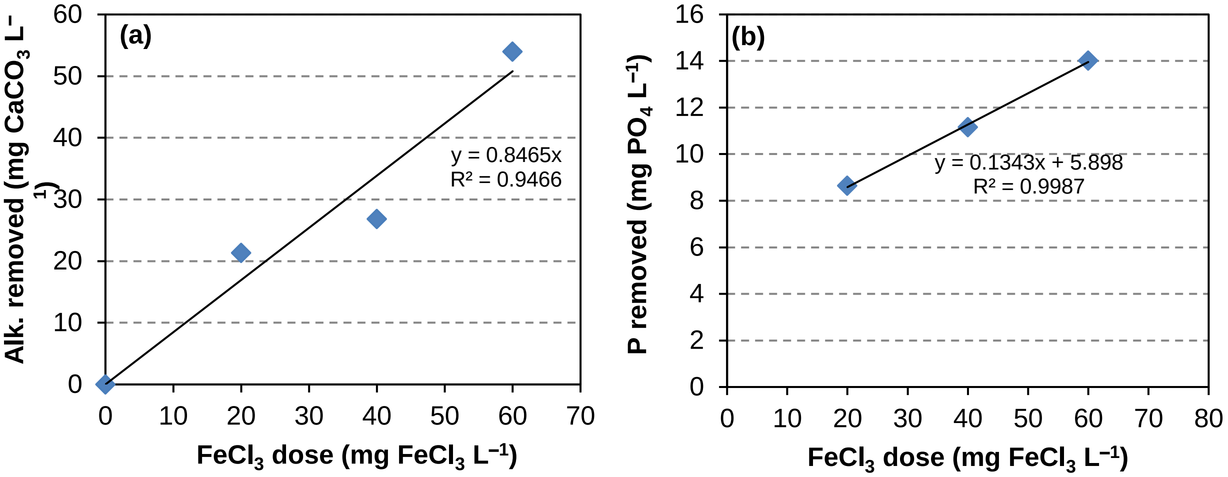


Fig. SI-3. Results of jar testing on wastewater influent to establish (a) alkalinity and (b) phosphorus removal as a function of ferric chloride dose. The best fit line for phosphorus removal was linear for the doses considered, which is in contrast to equations provided in the literature which is follow a log-normal curve.[13] However, for the purpose of estimating an appropriate dose, the linear relationship was sufficient. Alkalinity removal also demonstrated a linear relationship with 0.85 mg of alkalinity removed per mg of ferric chloride dosed, which compares well to stoichiometric calculation of 0.93 mg alkalinity removed per mg of ferric chloride dosed.

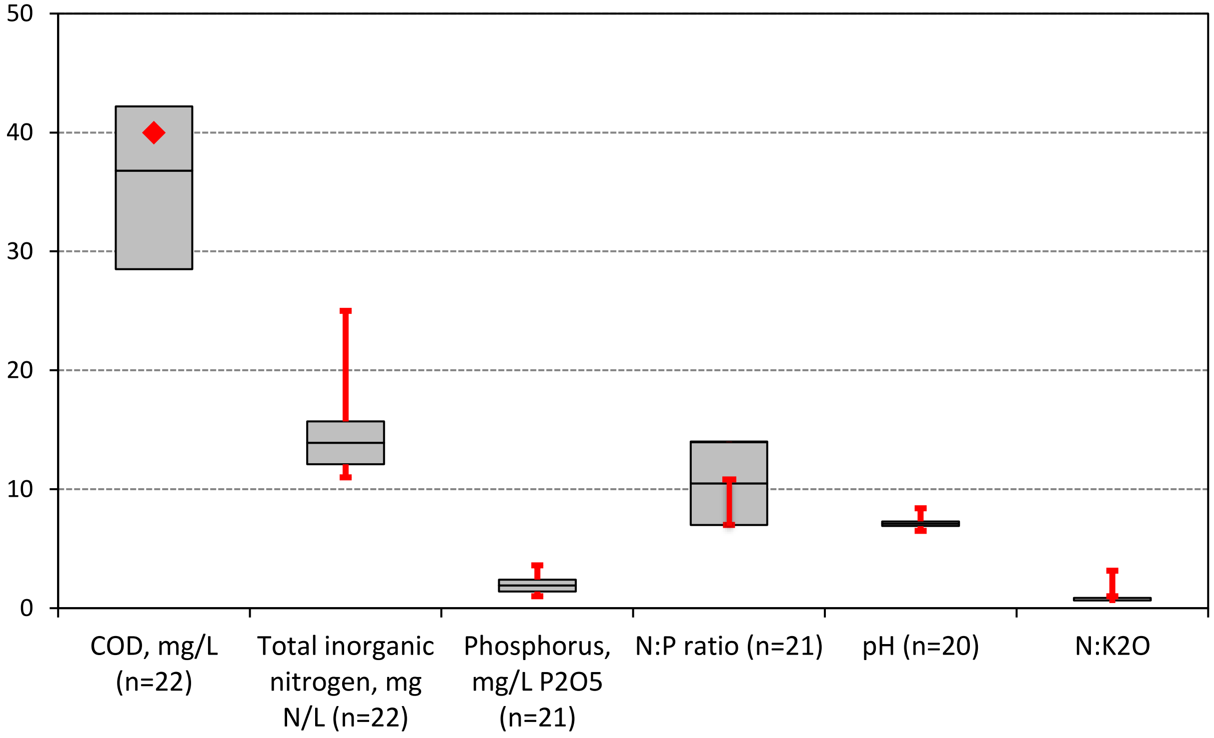


Fig. SI-4. Characteristics of fertigation water produced under current study conditions. Gray boxes depict the 90% confidence interval and mean value and the target values are shown in red.

Table SI-9. Inorganic constituents found in the influent, primary effluent, and final effluent (after biological treatment) of continuous EPC-SBR testing. Analyses were conducted at the beginning and after two months of continuous operation. The inorganic content was evaluated for trace mineral, and potential detrimental impacts.

Constituent	**Influent ($mg\ L^{-1}$)**		**EPC effluent ($mg\ L^{-1}$)**		**SBR effluent ($mg\ L^{-1}$)**		**Recom-mended Max**[1]
	Day 1	Day 35	Day 1	Day 35	Day 1	Day 35	
Aluminum	<0.0045	<0.0045	<0.0045	<0.0045		<0.0045	5.0
Arsenic	<0.0042	0.0139	0.0099	0.0180	5.0	0.0206	0.10
Beryllium	<0.0001	<0.0001	<0.0001	<0.0001	0.10	<0.0001	0.10
Boron	0.1556	0.0737	0.1135	0.1440	0.10	0.1905	0.75
Cadmium	0.0005	0.0008	0.0006	0.0006	0.75	0.0004	0.01
Chloride	82.6	111	143	159	0.01	166	
Chromium	0.0016	0.0011	BDL	0.0009		0.0007	0.1
Cobalt	<0.0003	0.0004	0.0007	0.0008	0.1	0.0010	0.05
Copper	0.0077	0.0041	0.0015	0.0024	0.05	0.0007	0.2
Fluoride	0.64	0.60	0.61	0.60	0.2	0.6	1.0
Iron	0.0433	0.0200	0.1331	0.2439	1.0	0.0225	5.0
Lithium	0.0188	0.0257	0.0197	0.0251	5.0	0.0246	2.5
Manganese	0.0131	0.0122	0.0737	0.0459	2.5	0.0464	0.2
Nickel	0.0058	0.0031	0.0099	0.0054	0.2	0.0048	0.2
Lead	0.0042	<0.0018	<0.0018	<0.0018	0.2	<0.0018	5.0
Selenium	<0.0061	<0.0061	<0.0061	<0.0061	5.0	<0.0061	0.02
Vanadium	<0.0027	<0.0027	<0.0027	<0.0027	0.02	<0.0027	0.1
Zinc	0.1215	0.0504	0.0809	0.0499	0.1	0.0244	2.0
Molybdenum	0.0081	0.0023	0.0232	0.0031	2.0	0.0012	0.01
Sodium	59.1	64.6	57.1	62.3	0.01	61.9	*2.
Calcium	46.9	44.1	45.6	43.1		47.4	*2.
Potassium (K)	13.4	16.0	12.8	15.0		13.6	
Potassium (K2O)	16.2	19.2	15.4	18.1		16.4	*3.
Magnesium	12.9	13.1	13.0	12.9		12.8	*3.
Sulfur	34.3	35.9	32.5	33.8		36.0	

1. Source: [USEPA 2012 Table 3-5] unless otherwise stated
2. Water with SAR greater than 3.0 may contribute to structural deterioration of soil.
3. The optimum N:K is 1:1 to 3:1 when potassium is expressed as K_2O].[4] The ratio of potassium in the primary effluents (31.5-40 mg N L^{-1}, 9.2-15.9 mg K_2O L^{-1}) is close to the optimal range, providing a balanced N:K profile.

Table SI-10. Evaluation of trace nutrients in primary and final effluent from continuous EPC-SBR testing. Samples were collected at the onset of biological testing and after 35 days of continuous operation. When compared to the examples of trace nutrient concentrates used for fertigation,[4] zinc and manganese are present in excess, and iron is lower than ideal ratios, with copper present near ideal proportions to molybdenum.

Nutrient	SBR effluent				Literature
	Day 1		Day 35		
	mg/L	ratio	mg/L	Ratio	Ratio[4]
Iron	0.0274	12.0	0.0225	19.1	37-51
Manganese	0.0729	32.1	0.0464	39.3	18-22
Zinc	0.1501	66.1	0.0244	20.7	7-9
Copper	0.0040	1.8	0.0007	0.6	1.3-2.3
Molybdenum	0.0023	1.0	0.0012	1.0	

Table SI-11. Comparison of measured conductivity and calculated salinity over the course of treatment (43 days for conventional primary clarification, 114 days for EPC). Analysis of conductivity and salinity in the EPC and CPC treatment systems. The conductivity and temperature of a sample were measured after the composite sampling was complete, and because the samples were stored in ice during the composite collection time, the salinity calculation included a correction for temperature.

	Conductivity (µS cm^{-1})			Salinity (mg L^{-1})		
	Influent	CPC Effluent	EPC Effluent	Influent	CPC Effluent	EPC Effluent
Start	952	764	808	906	677	744
End	899	798	787	788	860	764
Average	946	714	802	877	680	709
Stdv	106	119	66	97	124	112
cv	11	17	8	11	18	16
Max	1069	896	903	1055	860	1039
Min	583	471	690	664	447	566

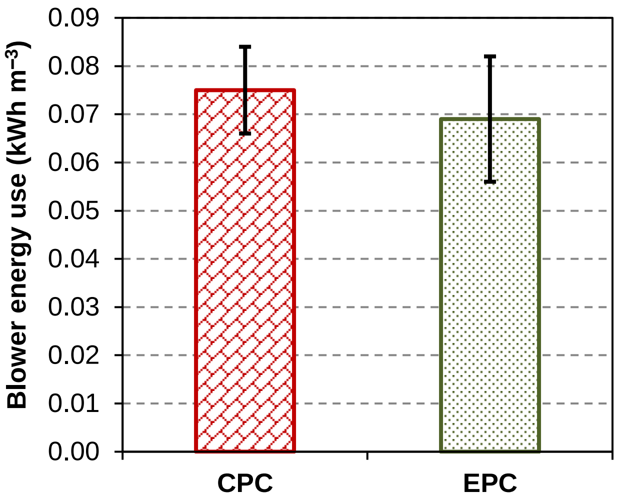


Fig. SI-5. Comparison of calculated blower energy use for the continuous CPC and EPC testing. The results show no significant difference in the average energy use per volume of wastewater processed.

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