

AGRICULTURAL MINERAL SOIL ADDITIVES FOR PASSIVE NITRATE REMOVAL

Christopher Jowett¹, Chris James, Sean Andrews, Craig Jowett & Andy McKinlay

ABSTRACT

Processes for removing sewage nitrogen at the individual residential scale must be low-maintenance with only annual service visits. A passive autotrophic process using a 50-50 mixture by volume of: (a) agricultural sulphur for nitrate reduction, and (b) limestone for pH adjustment, in an upflow configuration, was field-tested at 8 – 34 hours hydraulic retention times (HRT) at one site and at 14 hours HRT at another. An HRT of 8 – 12 hours was found to be the minimum without substantial nitrate breakthrough; pH was fully neutralized and little BOD and TSS addition resulted. The mass of sulphate formed versus nitrate + oxygen removed reflects a simple stoichiometry, possibly requiring ammonium to be included, and with intercepts near the origin suggesting that gypsum is not precipitated.

Keywords

Nitrogen Removal, *Waterloo NOx-LS*, Residential Scale, Sewage, Passive Upflow Reactor

INTRODUCTION

Removal of nitrogen (N) from individual sewage systems is desirable where residences are near saline estuarine water bodies, or on groundwater aquifers. Soil is the receiving body for on-site system dispersal, and a basic need is successful treatment and acceptance into the soil itself to minimize surface breakout of septic tank effluent, which otherwise enhances the nutrient content of stormwater runoff. This is especially important in clay soil where raised beds are prone to surface breakout.

Nitrate forms in the leach field, but then is typically non-reactive in soils, and therefore must be removed before entering the natural soil environment. For pre-treatment of nitrogen, the process must require simple, infrequent maintenance, be robust, and be cost-effective.

NITROGEN REMOVAL BY REACTIVE AGRICULTURAL MINERALS

Following recent work of other researchers (e.g., Anderson and Hirst, 2015, 2017; Hirst and Anderson, 2015; Jowett, 2017), we have experimented with autotrophic denitrification using the agricultural minerals limestone and natural sulphur, in a submerged, up-flow configuration, termed the '*Waterloo NOx-LS*'. Historical reports of problems using sulphur were likely due to incorrect design or use, and our present testing has determined design configurations and maintenance frequencies, revealed geochemical reactions and demonstrated sustainable performance.

Case Study 1: Rural School & Community Centre

¹ Waterloo Biofilter Systems Inc., PO Box 400, Rockwood ON Canada N0B 2K0

Process Train: Nitrate-rich effluent from a *Waterloo Biofilter* absorbent trickling filter at a school + community centre in Ontario was passed through a 210 L submerged upflow *NOx-LS* (limestone + sulphur pastilles) unit followed by an submerged upflow limestone chip *Polisher* in a 22-month field test. Samples of influent and effluent were taken twice monthly and analyzed for pH, dissolved oxygen (DO), temperature, cBOD, TSS, TKN, NO_{2,3}-N, sulphate, and alkalinity. Different loading rates of 60 – 240 L/day were used, giving hydraulic loading rates (HRT) of 8 – 34 hours using estimated 40% pore volume.

Analytical Data: Raw sewage at schools is typically weak in cBOD but with moderately strong TKN (Table 1), so recirculation generally removes only ~50% TN. The *NOx-LS* can be added before or after installation to remove >95% TN if the system is nitrifying well. Sewage temperature = 4.8 – 19.9°C.

The *Biofilter* nitrifies septic tank effluent to TKN < 2 mg/L, and removes 48% of the initial raw sewage nitrogen with ~60% recirculation. *Biofilter* effluent temperature = 4.8 – 19.9°C.

NOx-LS media lowers *Biofilter* NO_{2,3}-N down to < 2 mg/L, and lowers dissolved oxygen to < 1 mg/L. Neutral pH is maintained and cBOD is elevated a little over the *Biofilter* effluent, most likely due to autotrophic bacteria growth. *NOx-LS* effluent temperature = 8.9 – 24.3°C. The *Polisher* removes residual cBOD, and final effluent has neutral pH with TN = 4 mg/L, with cBOD and TSS both < 5 mg/L. *Polisher* effluent T°C = 7.7 – 24.8.

Table 1. Sewage TKN is thoroughly nitrified in the *Biofilter* trickling filter and nitrate is then reduced to nitrogen gas in the submerged *NOx-LS* reactive filter. Any excess cBOD or TSS is then removed in the *Polisher*. N = 25 – 39.

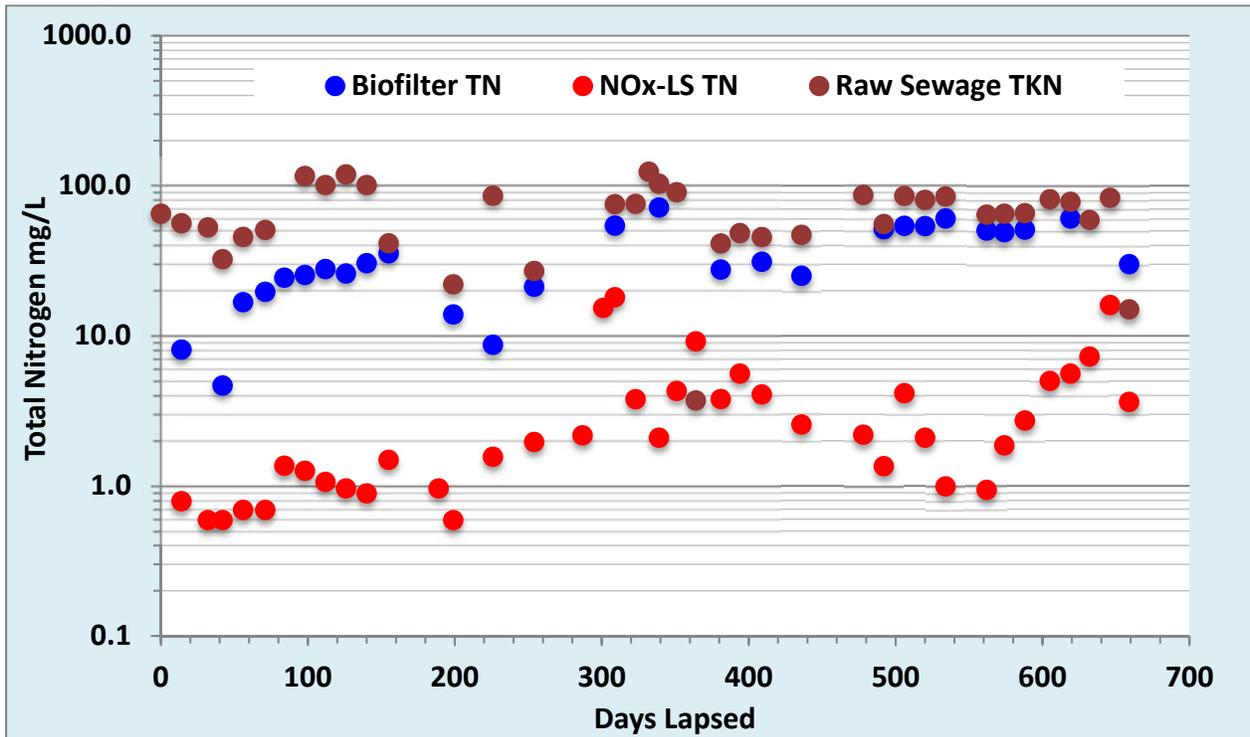
	<i>pH</i>	<i>DO</i>	<i>cBOD</i>	<i>TSS</i>	<i>TKN</i>	<i>TN</i>
<i>Raw Sewage</i>	7.13	1.10	124.0	41.9	66.9	66.9
<i>Waterloo Biofilter</i>	7.12	7.53	4.4	2.1	1.7	34.5
<i>NOx-LS</i>	6.95	0.93	9.3	2.7	1.7	3.6
<i>Polisher</i>	7.00	1.08	4.4	2.4	2.1	4.0

Removal of 88% and 94% TN was obtained from the *Biofilter* and raw sewage values, respectively, including the low HRT periods with high TN effluent. With the low TKN = 1.7 mg/L in the *Biofilter* effluent, an average of TN = 3.6 mg/L was attained, with 2.2 mg/L TN for

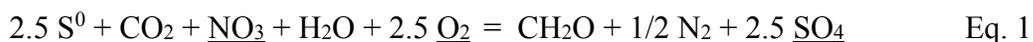
HRT > 10 hours and 1.0 mg/L TN for HRT > 15 hours, down from an average TKN = 66.9 mg/L in raw sewage (Figure 1). The average NO_{2,3}-N loading rate for the test period is 13.2 g/m²/day.

Essentially all NO_{2,3}-N is removed to non-detectable with HRT > 10 hours, but substantial NO_{2,3}-N breaks through at HRT = 8.4 hours. The cBOD increased from 4.5 to 9.3 mg/L in the NO_x-LS effluent, irrespective of HRT, with pH and TSS remaining similar at ~7 units and ~3 mg/L respectively. The NO_x-LS effluent is polished to cBOD = 4.4 mg/L in the subsequent filtration module.

Figure 1. Graphical presentation of the data points gathered along the NO_x-LS treatment train pathway.



Operative Reaction: Analyses of nitrite, nitrate, DO, and sulphate were taken before and after the NO_x-LS upflow filter to determine a stoichiometric relationship. Figure 2 shows the best fit is obtained by relating mass of sulphate produced versus the mass of NO_{2,3} + DO removed (laboratory values of NO_{2,3}-N must first be changed to NO₂ + NO₃ ions). The simple relationship;



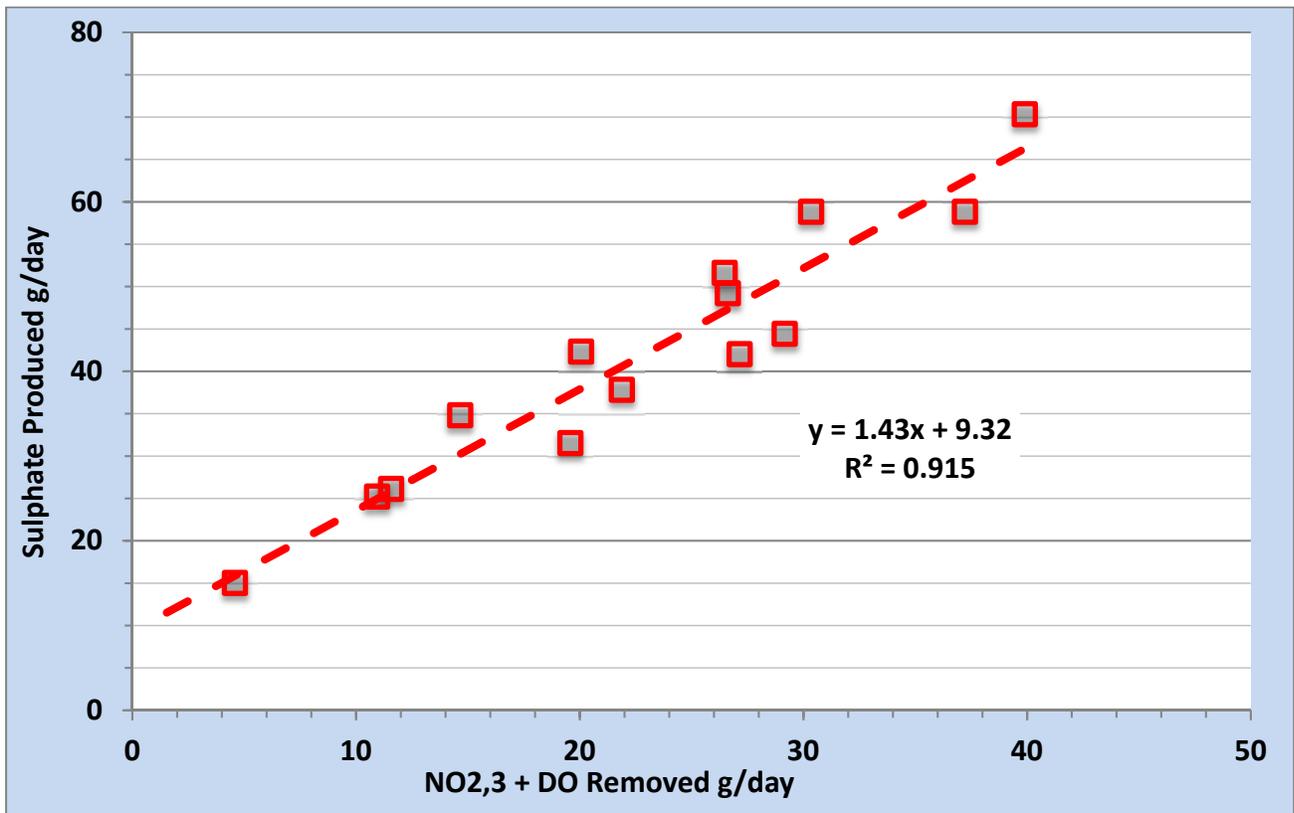
was used as a base as it includes the parameters measured in this work. The slope of a curve following Equation 1 would be;

$$\text{Slope} = \text{SO}_4 / (\text{NO}_3 + \text{DO}) = 96 / 56.8 = 1.69$$

Eq. 2

The slope of the curve from the data in Figure 2 is 1.43, not very dissimilar to the theoretical 1.69 and intersects the vertical at 9.3 g/day SO_4 . The positive intersection indicates that gypsum is not being produced, but may indicate that excess SO_4 is being leached from the limestone in the $\text{NO}_x\text{-LS}$ unit, or that other parameters, most likely NH_4 , have to be included in Equation 1.

Figure 2. Linear relationship between mass of sulphate produced and mass of nitrate + DO removed. Slope is 1.43 compared to theoretical 1.69 for very simple stoichiometry.



Case Study 2: Test Facility

Process Train: In an ongoing test at a commercial test facility, a single-pass *Waterloo Biofilter* is fed at a constant 1600 L/day with communal residential sewage. The nitrified *Biofilter* effluent is passed through a submerged $\text{NO}_x\text{-LS}$ reactor as above but designed for 14 hour HRT. The denitrified effluent passes through a subsequent submerged upflow *Polisher* filter of limestone chips designed to remove any excess cBOD and TSS from the $\text{NO}_x\text{-LS}$. Facility staff take composite samples after each of the components. Sewage temperatures range from 10 to 16.8°C.

Analytical Data: The Biofilter nitrifies the sewage to a residual TKN = 4.4 mg/L and removes 41% TN from the sewage (Table 2). Values of cBOD and TSS are <5 mg/L, and average DO is high at 6.20. During nitrification, alkalinity decreases from 245 mg/L to 74 mg/L and pH decreases by 1.1 units to 6.68.

After passing through the *NOx-LS*, at an average $\text{NO}_{2,3}\text{-N}$ loading rate of 17.3 g/m²/day, cBOD, TSS and TKN are slightly elevated to 6.3, 2.8 and 5.4 mg/L, respectively. DO and TN are decreased to 0.47 and 5.6 mg/L, respectively, and pH is neutralized from 6.68 to 7.23. Alkalinity is produced during removal of nitrate and DO from 74 mg/L to 172 mg/L.

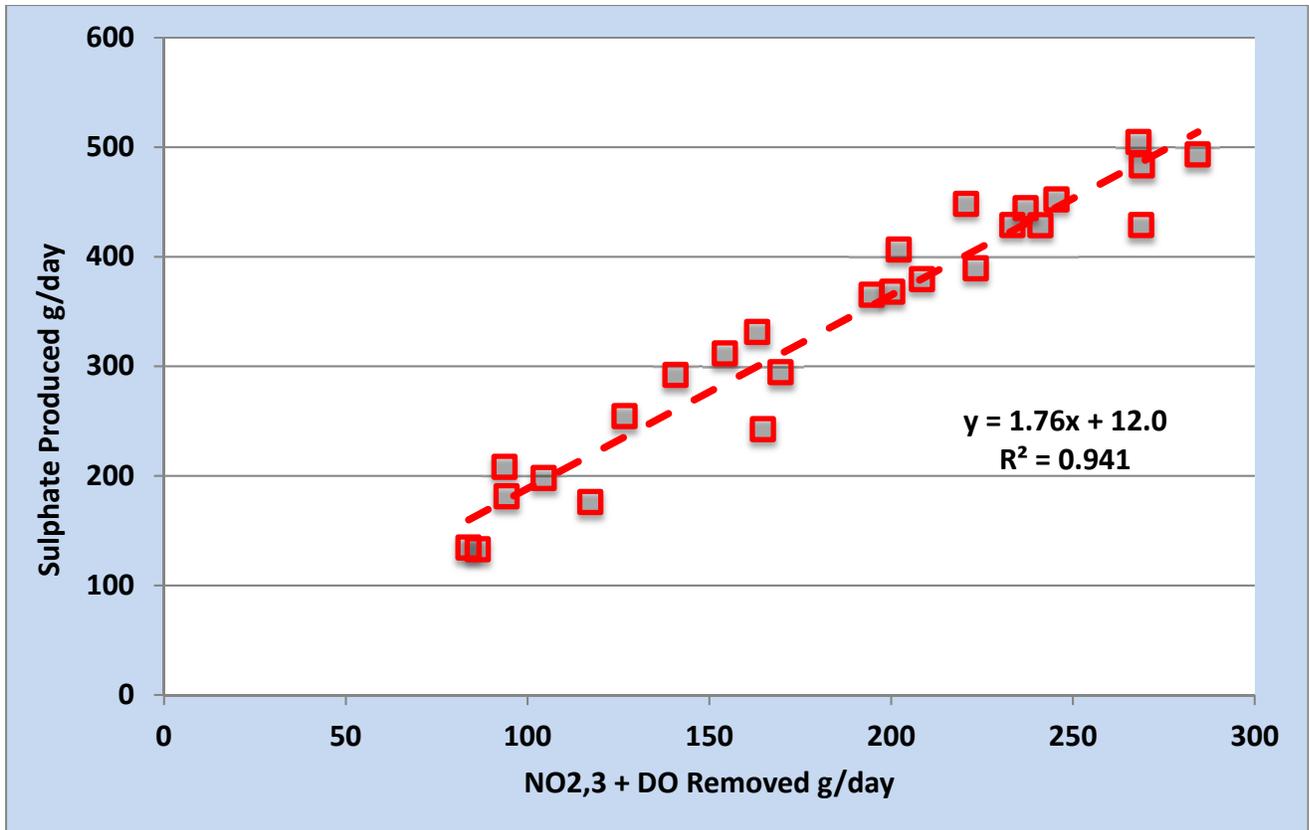
As designed, the limestone Polisher lowers cBOD and TSS to 4.1 and 1.9 mg/L, respectively, and increases pH slightly.

Table 2. This full-size residential system nitrifies well even in a single pass with no recirculation, and the *NOx-LS* thoroughly removes the nitrate + DO received. N = 25 – 40; for sewage, N = 187 – 214; T°C = 10.0 – 16.8.

	<i>pH</i>	<i>DO</i>	<i>Alkalinity</i>	<i>cBOD</i>	<i>TSS</i>	<i>TKN</i>	<i>TN</i>
<i>Raw Sewage</i>	7.80	--	245	204	289	52.3	52.6
<i>Waterloo Biofilter</i>	6.68	6.20	74	3.2	4.2	4.4	30.8
<i>NOx-LS</i>	7.23	0.47	172	6.3	2.8	5.4	5.6
<i>Polisher</i>	7.37	0.55	188	4.1	1.9	5.2	5.4

Operative Reaction: Analyses of mass of sulphate produced within the *NOx-LS* reactor and mass of $\text{NO}_{2,3}\text{-N}$ + DO removed are plotted in Figure 3. Similar to Figure 2, there appears to be a simple stoichiometry, and in this case, the slope of the curve is 1.76, not far off the theoretical value of 1.69 for Equation 1. The vertical intercept is 12.0 g/day SO_4 , similar to 9.3 g/day SO_4 in Figure 2.

Figure 3. Linear relationship between mass of sulphate produced and mass of nitrate + DO removed. Slope is 1.76 compared to theoretical 1.69 for very simple stoichiometry.



Hydraulic Retention Time Analysis: The performance parameters of the 22-month experiment for Case Study 1 were separated according to HRT values (Table 3). Percent removal was high during startup in the summer even with low influent TN values, and remained consistent during the winter until HRT was lowered to 8.4 hours. Performance, measured by percent TN removal, improved immediately when HRT was increased.

Note that at HRT = 8.4 starting April 11 2016, the percent removal decreases substantially, but the mass of TN removed increases substantially due to the higher volume of nitrate-rich sewage passing through it. Similarly the high HRT of 33.6 hours starting July 13 2015 results in high percent removal but a very low mass of nitrogen removed per day as very little volume is passing through the unit.

Table 3. The performance parameters are broken down according to HRT values. Percent removal varies with HRT, and likely influent TKN and temperature to some degree, primarily in the thoroughness of nitrification in the Biofilter.

HRT Analysis									
<i>Start Date</i>	<i>HRT hours</i>	<i>TKN¹ mg/L</i>	<i>TN in² mg/L</i>	<i>Temp in</i>	<i>TN out mg/L</i>	<i>TN out N³</i>	<i>TN %</i>	<i>Δ TN g/day</i>	<i>Δ TN N⁴</i>

				°C			<i>removal</i>		
Jul 13 2015	33.6	50.5	14.7	20.5	0.8	6	92.9	0.83	5
Oct 5 2015	22.4	112.0	26.4	15.2	1.1	3	95.8	2.3	3
Nov 16 2015	16.8	55.4	21.9	9.7	1.2	5	92.3	2.5	5
Apr 11 2016	8.4	75.3	54.1	9.7	11.9	3	66.6	8.7	1
May 17 2016	16.8	69.1	47.3	15.8	3.4	14	93.6	5.4	9
Jan 23 2017	22.4	63.9	47.6	8.3	6.0	4	92.4	4.0	4

¹ 'TKN' is raw sewage total nitrogen

² 'TN in' is nitrified Biofilter effluent, which averages 52% of raw sewage TN

³ 'TN out N' is number of samples to calculate TN mg/L value

⁴ 'Δ TN N' is number of samples to calculate Δ TN g/day value

Internal Biochemical Reactions: In Case Study 1, pore waters were sampled periodically with suction lysimeters to determine 'water-rock' biochemical reactions as the nitrate-rich water migrates up through the reactive media. Table 6 shows data from April 18 2017 sampling date and it is clear that reactivity is entirely within the lower part of the upflow filter.

Specifically the *NOx-LS 10"* sample data (actual = 8" below medium surface) show cBOD, TSS, alkalinity, TKN, NH₄, SO₄, and sulphide are all at their peak values, decreasing before and after. This peak location corresponds with a trough of pH (almost) and the disappearance of nitrate. This information is lost when only influent and effluent values are used, and the actual existence of sulphide and NH₄, for example, in the reactions would not be seen. The sharp peak in cBOD is possibly due to the biomass of S-reducing bacteria at this location coincides with the peak in SO₄ production, similar to a continuously advancing oxidation-reduction roll-front deposit in the mineral deposit world (e.g., Kesler & Simon 2015).

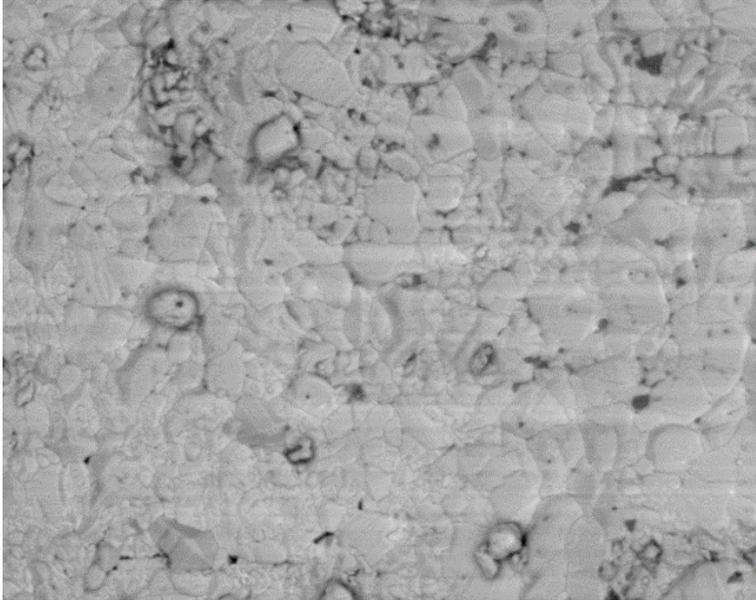
Table 4. The internal pore water chemistry shows reactions occurring that cannot be determined by influent and effluent samples alone (data from Glasauer et al., 2017).

April 18 2017 Samples: On-going treatment to right →							
	Biofilter Effluent	NO _x -LS 20" (act. 16")	NO _x -LS 10" (act. 8")	NO _x -LS Effluent	LST Polisher 20" (act. 20")	LST Polisher 10" (act. 12")	LST Polisher Effluent
Pore Water Analyses April 18 2017							
		HRT = 22.4 hours			HRT = 22.4 hours		
DO	7.03			1.12			1.72
pH	7.93	7.65	7.52	7.25	7.51	7.59	8.06
cBOD	< 4	7	38	6	< 4	< 4	< 4
TSS	< 2	2	5	4	2	2	< 2
Alkalinity	125	151	230	171	182	199	173
TKN	1.2	5.1	8.3	3.7	2.5	2.1	2.0
Ammonium-N	< 0.1	2.8	7.4	3.6	2.1	1.7	0.9
Chloride	340	370	390	400	420	460	720
Sulphate	110	270	370	350	340	350	350
Nitrite-N	0.03	0.03	0.03	0.03	0.03	0.03	0.20
Nitrate-N	28.2	12.3	0.06	0.06	0.06	0.06	1.38
<i>E. coli</i>	54	214	104	42	14	26	10
Aluminum	0.006	0.011	0.003	0.013	0.004	0.004	0.002
Iron	0.016	0.283	0.025	0.090	0.233	0.173	0.022
Sodium	212	246	255	256	272	271	291
Potassium	16.8	21.5	25.0	23.9	24.8	24.7	26.4
Sulphide	0.04	9.9	28.4	0.10	< 0.02	< 0.02	< 0.02
Hydrogen Sulphide	< 0.02	1.8	6.6	0.04	< 0.02	< 0.02	< 0.02
H₂S U-Guelph	-	0.63	26.5	0.5	0.25	0.25	-

Samples of the filter medium were also collected and compared to the original unused medium. Example SEM photographs in Figure 4 demonstrate the severe solution pitting (100 µm diameter pits) in the inlet area of the media, as expected, with less pitting (and less reaction) further along the flow path. The pastille in Figure 4b is taken from the level *NO_x-LS 20"* in Table 4 and is in the centre of the reactive zone. NO_{2,3} + DO would be depleted at this level as they react with the sulphur pastilles. Nitrate was effectively depleted within the first 20 cm at HRT > 12 hours.

Figure 4. SEM photographs of (a) pristine sulphur pastille before use (50 µm scale on photograph), and (b) corroded pastille with ‘caries’ texture at bottom of *NO_x-LS*, near source of NO_{2,3} (500 µm scale).

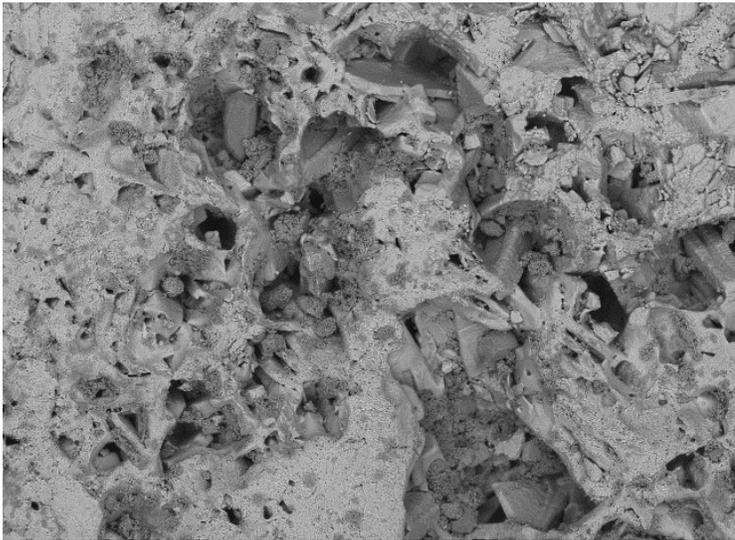
A.



S original

F L D7.5 x1.5k 50 um

B.



S-20

HL D7.8 x150 500 um

CONCLUSIONS

Full-scale on-site denitrification systems using the common agricultural mineral additives of sulphur and limestone have been successfully tested. An HRT of 8 – 12 hours was found to be the minimum without substantial nitrate breakthrough; pH was fully neutralized and little BOD and TSS addition resulted. Pore water chemistry and SEM work indicate that the ‘water-rock’ reactions in the upflow, submerged reactor are analogous in physical and chemical attributes to

an oxidation-reduction roll-front deposit in the natural environment. As nitrate-rich water advances through the 'rock', both nitrate and dissolved oxygen are reduced as sulphur is oxidized, with sulphide as an intermediary, temporary reaction product.

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