Supplementary information

In Situ Electrochemical Monitoring with an Open Circuit Auxiliary Electrode in Microbial Electrochemical Cells treating sediments

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Electrolyte characterization

Differences in the electrolyte composition between reactors were obtained between the end of Phase III and the end of Phase IV for the high [Table 2] and low salinity [Table 3] reactors. Differences between these two timepoints were more acute for the high salinity treatment, showing significant differences ($p \leq 0.05$) for ammonia, iron, pH, barium and acetic acid with all values tending to increase except the pH that tended towards a more acidic environment [Table 3]. The low salinity reactors, however, showed only a significant change ($p \leq 0.05$) in the ammonium concentration that tended to increase [Table 2]. Overall, the variability between the reactors tended to increase over time for all the analysed components with some exceptions [Tables 2 and 3].

While the sampling of the electrolyte was limited to the time before and after the propionate spikes, more changes in the electrolyte composition of the low salinity treatment were observed (Tables 2 and 3). The low salinity makes conductivity changes more significant. Similarly, the lower salinity showed a significant drop in pH after reactions [Table 2], probably due to a lower buffering capacity than the high salinity medium. The increase in ammonium concentrations was even more apparent, which was most probably slowly released from the sediment matrix and was likely stimulated by the polarization and propionate additions. However, due to the absence of a non-MET experimental control, it is difficult to consider if this release of ammonium was stimulated in the MET or just due to the natural decomposition of the sediment. Acetate and propionate were not detected in the high salinity reactors, (Table 2), but this could be caused by analytical errors as salinity is known to cause issues with HPLC analysis[1]. Additionally, the high variability found between the reactors also propagates large differences in statistical analyses. This is difficult to solve in batch reactors due to feedback processes caused by microbial activity and the effect of redox on MET performance. Therefore, improved reactor setups with continuous flow need to be developed for future studies that focus on more detailed analyses of the effect of MET operational parameters on the electrolyte composition.

Reference

1. Dulaquais, G.; Breitenstein, J.; Waeles, M.; Marsac, R.; Riso, R. Measuring dissolved organic matter in estuarine and marine waters: Size-exclusion chromatography with various detection methods. Environ. Chem. **2018**, *15*(7), 436–449.

Table 1S: Electrolyte composition of the artificial seawater at two different concentrations and the composition of the sediment pore water for the same parameters.

Parameter	Unit	Sediment pore-water	Artificial Seawater (12 mS cm^{-1})	Artificial Seawater (50 mS cm^{-1})
Amonium	ppm	62.50	27.23	15.02
Conductivity	mS cm-^{1}	14.88	13.00	58.06
Iron (Fe^{2}+)	ppm	0.00	0.15	0.01
pH	u	8.64	8.85	8.86
Phosphate	ppm	1.56	13.13	0.43
Sulfate	ppm	456.33	102.01	749.95
Chloride	ppm	2800.00	4056.55	15555.96
Nitrate	ppm	8.02	9.92	77.15
Phosphate	ppm	58.37	36.02	348.73
	ppm	644.84	644.84	3539.00
Barium	ppm	0.01	0.01	0.06
Potassium	ppm	47.1	42.3	233.7
Manganese	ppm	0.05	0.02	0.1
Strontium	ppm	0.5	0.84	4.02
Acetic acid	ppm	58.06	0.00	0.00
Propionic acid	ppm	6.63	0.00	0.00

pH	-	7.75	8.5	8.2-8.5
Conductivity	mS.cm^{-1}	12.3	12-12.5	50-52

Table 2S: Electrolyte differences for the high salinity reactors between the time 0 (before the propionate spikes) and the time1 (after all the propionate spikes).

Analyses	Mean Reactors A, C, E (Time 0)	Standard deviation	Mean Reactors A, C, E (time 1)	Standard deviation	t-test
Ammonium	101.60 (ppm)	19.36	133.48	13.63	0.05
Conductivity	54.25 (mS cm^{-1})	0.19	52.49 (mS cm^{-1})	3.75	0.49
Iron (Fe^{2+})	0.02 (ppm)	0.02	0.07 (ppm)	0.07	0.47
pH	8.32 (U)	0.01	8.59 (U)	0.17	0.10
Phosphate	5.99 (ppm)	2.64	10.51(ppm)	1.27	0.14
Sulfate	740.07 (ppm)	58.09	663.52 (ppm)	57.10	0.08
Chloride	13301.53 (ppm)	264.08	12077.84 (ppm)	3002.79	0.63
Nitrate	67.49 (ppm)	5.48	70.28 (ppm)	19.55	0.78
Phosphate	152.86 (ppm)	97.62	55.62 (ppm)	39.85	0.23
Sulfate	2600.25 (ppm)	275.78	1911.70 (ppm)	885.77	0.21

Barium	0.07 (ppm)	0.00	0.06 (ppm)	0.01	0.18
Potassium	212.28 (ppm)	7.88	212.22 (ppm	19.27	1.00
Manganese	0.25 (ppm)	0.02	0.19 (ppm)	0.06	0.23
Strontium	3.32 (ppm)	0.05	2.06 (ppm)	1.80	0.35
Acetic acid	0.00 (ppm)	0.00	0.00 (ppm)	0	NA
Propionic acid	0.55 (ppm)	0.90	0.00 (ppm)	0.00	0.40
pH	7.07 (U)	0.20	7.24 (U)	0.99	0.78
Conductivity	43.29 (mS cm-1)	2.18	52.62 (mS	5.53	0.16

Table 3S: Electrolyte differences for the low salinity reactors between the initial time 0 (before the propionate spikes) and the time 1 (after all the propionate spikes).

Analyses	Mean Reactors B, D, F (Time 0)	Standard deviation	Mean Reactors B, D, F (Time 1)	Standard deviation	t-test
Ammonium	98.41 (ppm)	14.00	136.26 (ppm)	11.30	0.03
Conductivity	15.25 (mS cm^{-1})	0.09	13.32 (mS cm^{-1})	2.31	0.27
Iron (Fe^{2+})	0.02 (ppm)	0.01	1.00 (ppm)	0.42	0.05
pH	8.16 (U)	0.21	7.08 (U)	0.24	0.00
Phosphate	8.31 (ppm)	4.52	10.43 (ppm)	1.51	0.534
Sulfate	134.03 (ppm)	161.89	28.20 (ppm)	5.11	0.36

Chloride	3676.40 (ppm)	140.40	3181.21 (ppm)	1206.00	0.59
Nitrate	9.54 (ppm)	0.34	8.95 (ppm)	3.88	0.83
Phosphate	13.72 (ppm)	6.52	6.82 (ppm)	2.49	0.24
Sulfate	47.18 (ppm)	1.97	37.67 (ppm)	14.13	0.71
Barium	0.00 (ppm)	0.00	0.10 (ppm)	0.02	0.01
Potassium	41.43 (ppm)	0.96	34.70 (ppm)	5.18	0.13
Manganese	0.16 (ppm)	0.05	0.19 (ppm)	0.05	0.25
Strontium	0.93 (ppm)	0.01	0.70 (ppm)	0.14	0.11
Acetic acid	2.09 (ppm)	3.61	227.13 (ppm)	82.38	0.04
Propionic acid	31.74 (ppm)	27.51	121.96 (ppm)	101.84	0.18
pH	6.71	0.17	6.18 (U)	0.10	0.01
Conductivity	11.91 (mS cm^{-1})	0.43	16.62 (mS cm^{-1})	4.00	0.15