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Fire suppression and burnt sediments: effects on the water chemistry of fire-affected wetlands

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1 **Fire suppression and burnt sediments: effects on the water chemistry of fire**
2 **impacted wetlands**

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8 preparation of this manuscript.

9 *Abstract.* Preventing fire from entering wetland areas during seasonal or prolonged drought, or
10 suppressing fire once it has entered a wetland, requires consideration of the consequences of the fire
11 management action on water quality. Two approaches can be taken to suppress such fires: chemical
12 fire retardants, or the flooding of sediments. We determine a lack of information relating to the effects
13 of these approaches for water quality within fire impacted wetlands. The aim of this study was to gain
14 a preliminary understanding of the effects of three treatments: two chemical treatments and saturation.
15 Microcosms were established to test sediments from a wetland on the Swan Coastal Plain, Western
16 Australia, which were exposed to temperatures ranging from 30-800 °C. The results indicate that one
17 of the fire retardant chemicals increased the soluble nutrient load present in the water column, as
18 predicted by the results of other research. However, the same chemical had a minor but important
19 effect as an acidity buffer when the organic, pyritic sediment was heated but not burnt. The second
20 chemical treatment did not increase the nutrient load but nor did it buffer the acidity generated by the
21 heating and burning of the organic sediment. It was virtually indistinguishable from the saturation
22 treatment in this regard.

23 *Additional Keywords:* Phos-Chek, Kilfire, Acid Sulphate Soils.

24 *Suggested running head:* Microcosm test of fire suppression and burnt sediment

25

26 **Introduction**

27 The subject of wildland fires and water quality has received some attention over the last two decades,
28 where research has focussed on the effects of prescribed burning (Stephens et al. 2004), changed fire
29 regimes (Townsend and Douglas 2004) or extreme fire events (Earl and Blinn 2003). Another
30 important area of focus has been the way water quality in a wetland ecosystem has responded to
31 attempts to either extinguish or suppress fire in the wetland or its catchment. Two approaches are
32 commonly used in these situations: chemical fire suppression and saturation with water.

33 Fire suppression commonly uses a variety of water-soluble chemicals including long-term fire
34 retardants (to inhibit combustion), short-term retardants (their effectiveness vanishes with the
35 evaporation of water), firefighting foams, and wetting agents (to increase the dispersal and penetration
36 of water) (Kalabokidis 2000). The principal mechanisms by which water quality might be affected by
37 these applications are through surface runoff, leaching into the soil profile and then subsurface
38 drainage, or direct deposition of the chemical into the waterbody (Kalabokidis 2000). Reviews of the
39 literature on the impacts of fire suppression activities on aquatic ecosystems (Backer et al. 2004;
40 Giménez et al. 2004; Little and Calfee 2002) refer to common features: because the chemicals are
41 essentially fertilisers they are likely to result in excess nutrient inputs and potential eutrophication.

42 The second technique considered for extinguishing wetland fires is saturation with water, either
43 extracted or diverted from a nearby source or from rainwater. Two consequences of this technique
44 arise for the water chemistry of a wetland. Firstly, the effects of saturation will depend on the chemical
45 characteristics of the source water used; salts or pollutants may be introduced which might react with
46 sediment chemistry. The second consequence arises when rehydrating sediments that may have been
47 chemically altered due to the severe oxidation of the fire, potentially resulting in the release of stored
48 acidity and the concomitant mobilisation of contaminants into connected ground- or surface waters.

49 Indeed one of Little and Calfee's (2002) conclusions, that the fire-related effects of aqueous leachates
50 of ash and high temperatures may exceed the effects of fire retardant chemicals, implies that saturation
51 of an overheated and burning sediment may not be the best solution for water quality and aquatic
52 ecosystems.

53 We believe this complication is one that has otherwise not been treated in the literature. Therefore, we
54 conducted a controlled microcosm experiment to answer the following questions: (i) does the
55 application of different chemical fire suppression agents to wetland sediments, which have been
56 mildly to severely oxidised, result in changes in water quality; and (ii) is the response influenced by
57 the organic content of the sediment and/or the temperature of the burn?

58 **Methods**

59 Sediments were taken from Lake Nowergup on the Swan Coastal Plain of Western Australia
60 approximately 38 km north of Perth. The lake is bordered by limestone and calciferous sands whilst
61 the interior of the lake is slowly infilling, comprised of sands and unconsolidated organic matter.
62 Unlike other wetlands in this bioregion which have suffered from groundwater drawdown and severe
63 oxidation either as a result of seasonal drying and/or a significant fire event, the sediments of Lake
64 Nowergup generally have been kept saturated and anaerobic (Loomes et al. 2003).

65 Stratified random sampling was designed to collect sediments with varying degrees of organic matter
66 content within the wetland based upon the hydrological zones of lakes (Semenuk and Semenuk
67 2005a): the permanently inundated zone (consisting of relatively deep accumulations of peat;
68 Sediment Type 1), the seasonally inundated zone (muddy sands; Sediment Type 2) and the seasonal
69 waterlogged zone (predominantly quartz sands with interstitial biogenic particles; Sediment Type 3),
70 where sediments are characteristic of internal biogenic processes superimposed on their internal basin
71 setting in a linear interdunal depression in the Spearwood Dune system (see Semenuk and Semenuk
72 2005a).

73 Bulk sediment samples were collected from a depth between 50 and 60 cm by digging a deep pit at
74 each of three sampling sites. This depth profile was chosen as the sediments at this depth had been
75 neither burnt, nor impacted by pyrolysis in another way (as evidenced by a lack of macroscopic
76 charcoal after visual inspection of the sediment profile), nor seriously dried in recent history.

77 Bulk sediment samples were maintained at field moisture, placed in sealable polyethylene bags, air
78 purged and stored at 2 °C in the dark. For each sample site, individual bulk sediment samples were
79 thoroughly homogenised to obtain a composite representative of the depth profile sampled. Sediment
80 subsamples (approximately 500 g wet weight) were then allocated to one of five temperature
81 treatments, field moist (FM), 30 °C ('air dried'), 300 °C, 550 °C and 800 °C, representing sediment
82 temperatures likely to be experienced during a fire (Usup et al. 2004; Rein et al. 2008). The 30 °C
83 samples were dried at temperature in a drying oven (Mettler UFP 800) until a stable weight was
84 attained. The remaining heat treated sediments were combusted for one hour at each of the three
85 temperatures using a muffle furnace (ModuTemp WW71A). Heat treatments were applied
86 concurrently.

87 Temperature treated sediments were further sub sampled for each of the thermal increments and three
88 fire suppression methods were applied. Method A is the water that was used to dilute the two
89 products: double de-ionised (Milli-Q) water. The method is therefore both a control for the other
90 treatments and a treatment in its own right since it is applied as if burnt sediments are saturated and
91 rehydrated. Method B is the product marketed as Phos-Chek D-75 (Astaris LLC 2003). The
92 ingredients are recorded as Diammonium Sulfate (>65 %), Monoammonium Phosphate (>15 %),
93 Diammonium Phosphate (>5 %), Guar Gum, Hydroxypropyl (<10 %), and Performance Additives +
94 Trade Secret (<5 %) before mixing with water. Method C is the product marketed as *Kilfire*TM; as a
95 liquid or powder it is diluted by water; the manufacturers regard the product as both suppressant and
96 retardant. It has been classified as a non-hazardous and non-dangerous material according to the

97 criteria specified by NOHSC; accordingly no disclosure is made concerning the chemical nature of
98 this product (Benign Technologies 2007) presumably to protect their commercial interests.

99 Fire retardants were prepared as per the manufacturers' specifications. The recommended mixing ratio
100 for Phos-Chek D-75 is 0.144 kg of retardant powder in one litre of water. *Kilfire*TM is prepared by
101 mixing 3.3 g of powder in 10 litres of water. Treated sediment was weighed (10 g) directly into a 500
102 gm black HDPE jar (Cospak 500STB) and 10 mL of either Method A, B or C solution was added to
103 create a slurry. The slurries were then made up to a 1:50 ratio with Milli-Q water to represent a likely
104 dilution in the field (microcosm). The microcosms were capped and mixed thoroughly and then let
105 stand to allow for hydro-chemical equilibration, in the dark with aeration. After 7 days, pH and
106 electrical conductivity (using an Orion 5-star multiparameter meter) were measured for each
107 microcosm and a 60 ml water sample was removed. Each sample was filtered, collected and stored,
108 frozen or acidified as required and kept dark. Measurement of sediment physico-chemical parameters
109 (pH and conductivity) were performed using 1: 5 sediment to water extract (note that this is a different
110 dilution to that used in the experimental procedure above). Additionally, sediment subsamples for each
111 thermal treatment were digested (using USEPA method 3050B) to establish sediment variability.

112 Analysis of Al, Cu, Fe, Mg and S was carried out using a Varian Vista-Pro inductively coupled plasma
113 (ICP) with optical emission spectroscopy (OES) detection. Ammonia, nitrate (includes any
114 contribution from nitrite) and ortho-phosphate analysis were completed using a Skalar flow injection
115 analyser. Due to low concentrations and a number of results at or below the limit of detection, Al, Cu
116 and Fe concentrations were not included in the statistical analysis.

117 Statistical analysis was performed in Primer (Version 6). Data were transformed where required and
118 standardised. A multivariate approach was taken to ascertain patterns of discrimination based on
119 changes in water quality parameters between fire suppression methods and between temperature
120 treatments. Significant differences among fire suppression methods temperature treatments were tested

121 by pair-wise and 2-way permutational analysis of variance (PERMANOVA) (McArdle and Anderson
122 2001). Where significant differences occurred pair-wise analysis of variance was used to establish the
123 source of variability.

124 Principal Component Analysis (PCA) was used to allow groups of variables to be mapped in multi-
125 dimensional space, which may otherwise not be evident in a two-dimensional relationship. Principal
126 component correlations (PCC) were then used to identify variables with the greatest absolute
127 coefficients associated with each principal component.

128 **Results**

129 PERMANOVA results (Table 1) show that significant differences in water quality were seen between
130 suppression methods however, they did not demonstrate a significant difference between heat
131 treatments. No interaction was seen between suppression method and heat treatment.

132 *Table 1 here*

133 The two-dimensional PCA ordination of the standardised data for all 45 microcosms shows that the
134 two axes account for 86.6% of the total variability in the dataset (Figures 1a-c). Most of the variation
135 is accounted for by PC1 that shows a clear separation between the 15 Method B microcosms
136 (application of the aqueous fire retardant Phos-Chek D-75), with elevated electrical conductivity
137 associated with increased concentrations of ammonium, nitrate, phosphate and total S in the water
138 (Figure 1a). Very little difference was evident between Method A (saturation water) and Method C
139 (aqueous Kilfire solution) with the exception of elevated electrical conductivity at 30 °C for Method
140 C. A pair-wise comparison between suppression methods shows that Method B is significantly
141 different from Method A and Method C (PERMANOVA, $P < 0.001$). The differences in water quality
142 between Methods A and C were not significant (PERMANOVA, $P = 0.94$).

143 *Figure 1a-c here*

144 Another separation occurs along axis PC2 between Sediment type 1 (predominantly organic with loss
145 on ignition (LOI) values of around 67%) and Sediment types 2 and 3 (predominantly mineral
146 sediments LOI values of 0.2% - 0.4%). This separation is attributable to a lower pH and a higher level
147 of Mg for the water in the microcosms containing the organic rich sediment (Figure 1b).

148 Whilst not considered significant, heat treatments were still capable of instigating a response. The
149 variability within Sediment type 1 (Figure 1b) is associated with different temperature regimes. This
150 organic sediment revealed higher levels of acidity at the three lower temperature treatments, and tends
151 to become neutral at temperatures above 550 °C, when the combustion leads to the volatilisation of
152 Total S from the sediment and when buffering is made available in the ash leachate and through the
153 combustion of carbonate minerals (see Figure 1c).

154 The application of Method B tends to neutralise the acidity at lower temperatures, and dampens the
155 extremes otherwise shown for the organic rich sediment (Figure 2a). However, Method B results in
156 the addition of Total S (likely SO_4^{2-}) to the water (Figure 2b).

157 It is interesting to note that in untreated sediments an increase in Mg levels with combustion
158 temperatures above 550 °C is observed, however there is a general decline in Mg levels of the water in
159 microcosms with increases in combustion temperature (Figure 2c). Also noteworthy is that Total S
160 amounts recorded in the sediments are consistently higher than those for the experimental treatments,
161 and reflects the loss of S on drying and heating due to volatilisation (Figure 2b).

162 *Figure 2a-c here*

163 **Discussion**

164 We assume that our method is a reasonable representation of a *post hoc* application of fire-
165 suppression, and that under these circumstances variable responses will be observed for (in this order

166 of magnitude) the method of suppression, the type of sediment exposed, and the temperature to which
167 sediments have been exposed.

168 In drawing our conclusions from this study design, we make two further assumptions. The first is that
169 the water quality of the field moist and heat treated sediments rehydrated with Milli-Q water (Method
170 A) would provide a response similar to that experienced in the field whereby soluble and loosely
171 bound ions in the sediment will be leached into solution, representative of the rehydration of dried,
172 oxidised and combusted sediments following fire.

173 Our second assumption is that the addition of a particular chemical suppressant will produce a water
174 quality response that is indicative of the chemicals added, and it will override any inherent chemical
175 characteristic of the sediment leachate. We controlled for this assumption using Milli-Q water as
176 above, and by testing across a range of field conditions (temperatures). The fact that we derived
177 consistent responses from our treatments, and that the results support those of previous findings (see
178 below) suggests that our assumption has not been violated. Even so we consider that the results
179 warrant further investigation into the interactions between different sediment types and the chemical
180 nature of suppressants.

181 Our work supports the experimental work of others who found that the application of nitrogen based,
182 phosphate rich retardants can find their way into drainage systems and surface water bodies where
183 they can influence trophic status (see Angeler and Moreno 2006) and enhance pH buffering, both of
184 which are consequences of the fire. For example, Stephens et al. (2004) noted (in the absence of fire
185 retardants) a large increase in ammonium on post-burn soils, and they attributed this to the fire
186 converting the organic N to this reduced form, which can then become nitrate and enter streams. Pappa
187 et al. (2008) examined, in experimental pots, the potential for nitrogen to leach into the groundwater as
188 a result of a retardant application; when added to the soil as ammonium, some was volatilized during

189 the fire, but the conversion of large amounts of the applied ammonium into nitrate exceeded what
190 could be taken up by the vegetation and resulted in mobile nitrogen which leached from the pots.

191 The degree to which bivalent cations can be detected in solution after sediments have been heated
192 appears to depend on the thermal intensity (i.e. degree of heating); in low heat microcosms much more
193 Mg^{2+} was detected in the water than in microcosms subjected to elevated temperatures, which may be
194 associated with the formation of $MgSO_4$ and precipitation from the water column. Sulphur will be lost
195 from the sediments due to volatilization in a fire, so fire retardants containing sulphur counterbalance
196 these losses by supplementing the sulphur that remains in the sediment and water column; the
197 suggested precipitation of sulphate with Mg^{2+} (and presumably Ca^{2+}) will contribute to a buffering
198 effect on pH. Conversely, the supplementation of sulphur in conjunction with iron species (commonly
199 found in organic rich sediments) under reducing conditions may lead to the formation of stored
200 potential acidity in the sediments. Couto-Vázquez and González-Prieto (2006) noted soil pH increases
201 after the application of fire fighting chemicals and attributed this to the accumulation of ashes, the
202 reduction of organic acids and the cations supplied by the chemicals. These processes will be
203 important if fires occur in organic rich, pyritic sediments where the severe heating will dry and crack
204 the sediments, aerating them and allow fire to enter, resulting in the creation of acidity through
205 oxidation (Horwitz and Sommer 2005; Semeniuk and Semeniuk 2005a).

206 A further complication in the study of the effects of fire retardants on organic sediments is whether the
207 organic matter can bind and assimilate some of the excess inorganic chemicals introduced as a
208 retardant. Little and Calfee (2002) were able to show experimentally that the toxicity of retardants
209 was dramatically reduced by both the presence of organic soils, and pyrolysis of soils with the
210 retardant.

211 Finally the negligible effects of Method A (saturation) and the chemically enigmatic Method C
212 (Kilfire) deserve mention; they were virtually indistinguishable in that they did not introduce

213 significant nutrients into the water, and were both unable to buffer the acidity produced at low
214 temperatures. If pyritic material is present in a wetland sediment, and given that the organic matter in a
215 wetland will not be completely consumed by the fire, there is the possibility that hydration with either
216 method will result in an acidification event. Ironically this will depend on the amount of sediment
217 burnt, the temperature of the burn and the amount of ash available to buffer the sediments.

218 We note that we have not subjected the fire retardants themselves to very high temperatures, and that
219 we need to examine organic chemistry responses as well as the inorganic ones shown in this study;
220 both of which require further testing.

221

222 **Acknowledgements**

223 The work described here is one component of a larger project examining the occurrence of fire within
224 wetland sediments and its effects on water quality, funded by the Fire and Emergency Services
225 Authority of Western Australia and the Centre for Ecosystem Management, Edith Cowan University.

226

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Table 1: PERMANOVA analysis of the differences in microcosm water quality associated with the method of suppressant and the temperature that sediments were exposed to.

Factor	Pseudo- <i>F</i>	<i>P</i> -value
Suppressant (Method A, B or C)	27.59	<0.001
Heat treatment (Field moist, 30 °C, 100 °C, 550 °C or 800 °C)	1.39	0.193
Suppressant x heat treatment	0.35	0.99

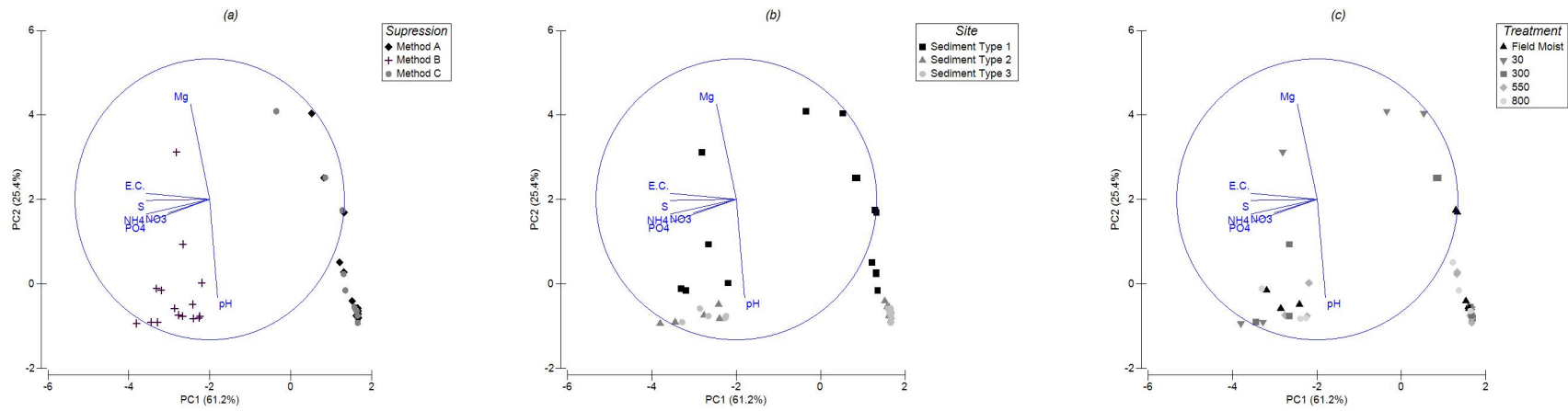


Figure 1: PCA ordination of the water data showing the same microcosm separations but labelled according to method (a), site (b) or thermal treatment (c). PC1 and PC2 combined account for 86.6% of total variability. The ‘environmental’ variables most influencing the ordination are overlain on the ordinations.

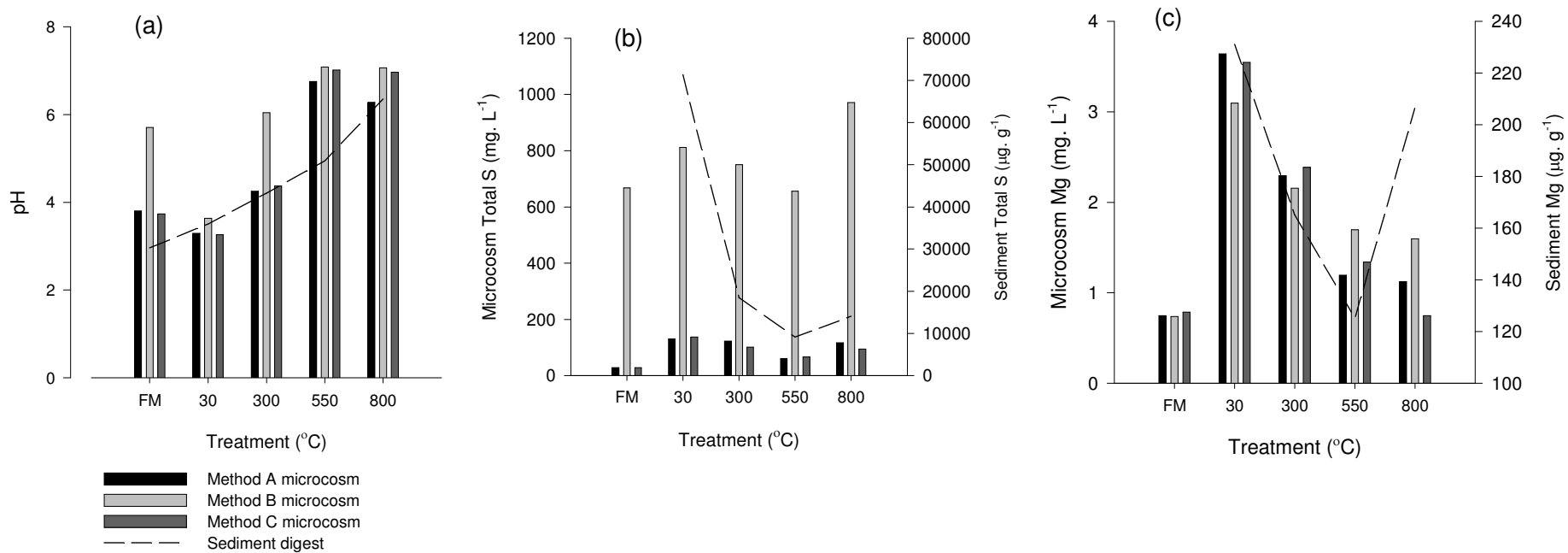
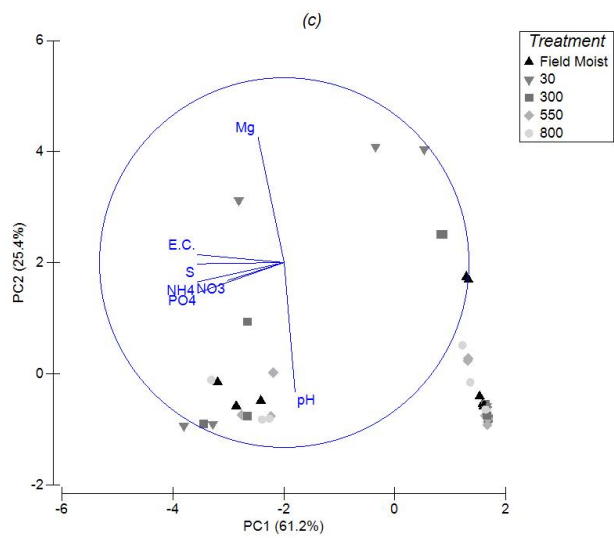
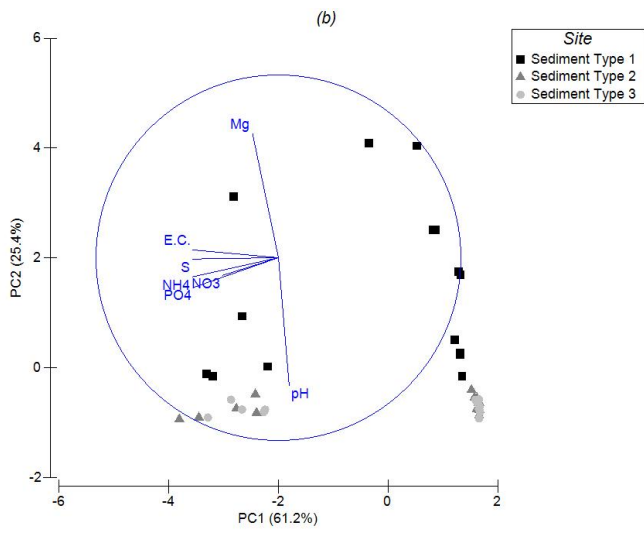
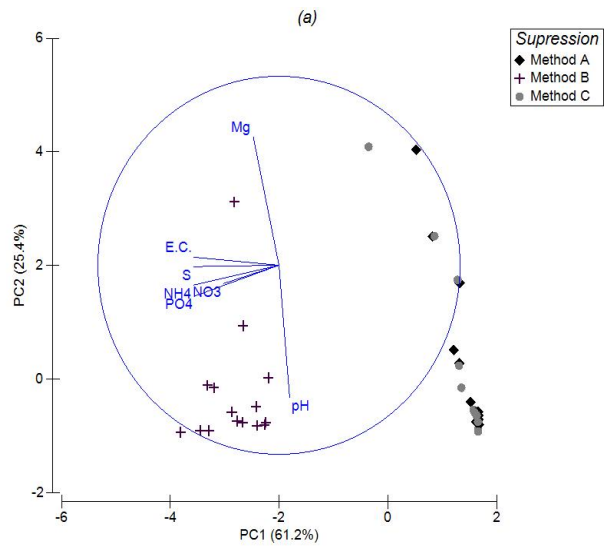
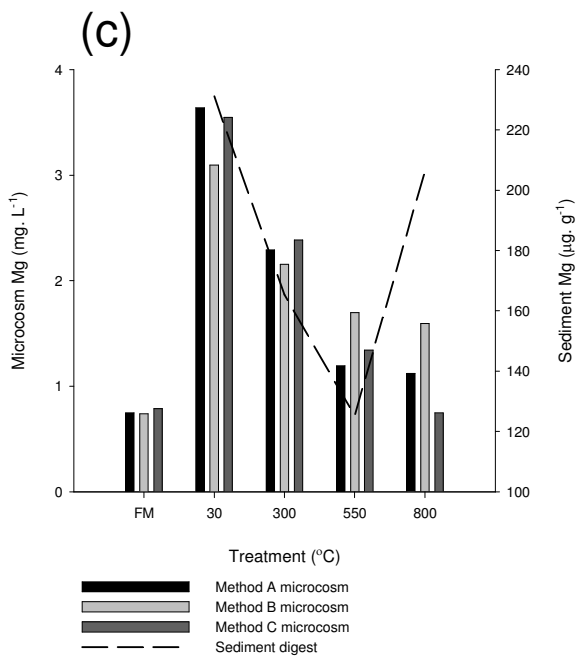
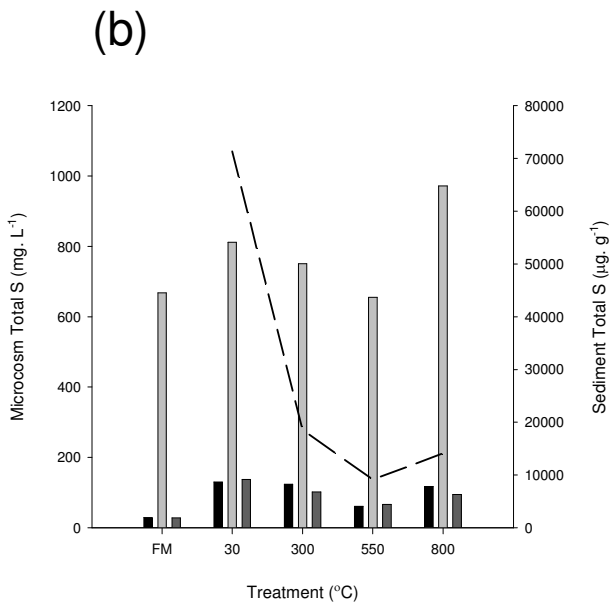
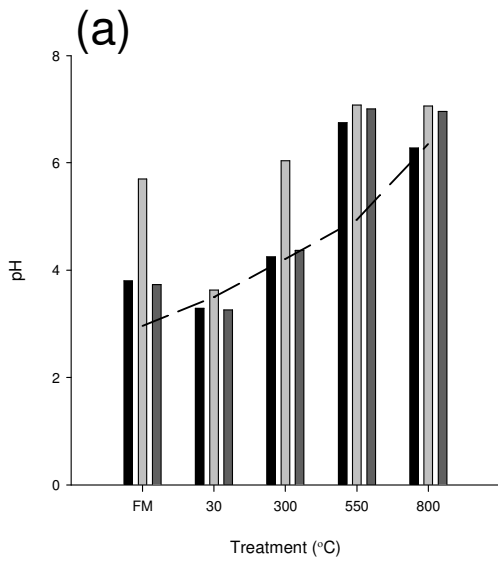


Figure 2: Microcosm water and sediment concentrations for pH (a), Total S (b) and Mg (c) for sediment type 1(organic) site only. ‘FM’ refers to field moist treatment.

The Figures on the next two pages are Figures 1 and 2 – they are in vertical format, not horizontal format (as suggested by Reviewer 1).





Treatment (°C)

- Method A microcosm
- Method B microcosm
- Method C microcosm
- Sediment digest