Response to Editor and Reviewers

Associate Editor Decision: Reconsider after major revisions

While all reviewers recognized the novelty of your manuscript, they were quite critical of your hypothesis on Fe toxicity. I agree with the reviewers and envisage that the manuscript would require a substantial revision to address reviewers' concerns and commensurately refocus data presentation and interpretation. Therefore, I have to recommend 'reconsider after major revisions' and might need to ask reviewers to reassess whether the revised manuscript has provided a reasonable, data-supported interpretation of the observed biogeochemical changes and potential linkage to the mangrove dieback.

Response: We thank the editor for the comments and have made extensive changes to the manuscript. The title has changed to prevent the perception of a strong conclusion. The manuscript now focuses more on differences in water availability using Fe as a proxy of sediment redox conditions. Discussion of the possibility of Fe toxicity has been greatly reduced and re-framed accordingly.

As the first reviewer suggested, please pay more attention to providing analytical details, particularly about Itrax core scanner (instrumental information, analytical accuracy, how you processed "semi-quantitative elemental profiles, etc.). In your response to the second reviewer's comment on Fe/Mn ratio, you said that "Because we have re-shifted the focus of the manuscript away from Fe toxicity, further exploration of this data may be beyond the scope of this study." In my view, Mn data would be still helpful for you to clear up any metal toxicity issues. I also wondered if you could compare Fe and other major metals (out of 34 elements) to single out changes in the concentration of Fe at the dieback site from drought-induced (little or small?) changes in the concentrations of other metals.

Response: We have made several changes following this comment. See revised methods from L184-190 "Wood samples and sediment cores were analysed for elemental composition with a micro X-ray fluorescence conducted at ANSTO using an Itrax core scanner (Cox Analytical Systems). The scanner produces a high resolution (0.2 mm) radiographic density pattern and semi-quantitative elemental profiles for each sample. The Itrax measured 34 elements and while trends occurred in some elements (see Supplementary Figures 1 & 2), here we focus on Fe. Itrax Fe results have been compared with absolute Fe_2O_3 concentrations with high accuracy ($R^2 = 0.74$) (Hunt et al., 2015)".

And also from L202 - 209: "To align radiocarbon calendar ages with Itrax data, we interpolated ages using the wood circumference. Itrax elemental and density data were normalized as the mean subtracted from each value divided by the standard deviation following Hevia et al. (2018) and are referred to hereforth as relative concentrations. We also normalized the Fe data to total counts and other measured elements following Turner et al. (2015) and Gregory et al. (2019) to confirm the trends did not change with different normalization approaches which they did not. This normalization reduces external effects (Gregory et al. 2019) and allows a more direct comparison between samples from living and dead forest areas".

We have particularly examined Mn and Fe/Mn ratio based on your comments and we have added Supplementary Figures 1 & 2 to the manuscript, as well as the following text L420 – 436: "The apparent mobilisation of Fe (loss from sediment and uptake in wood) was not observed in other elements (Supplementary Figures 1 & 2). Sediment Fe:Mn ratios in Itrax data displayed no clear differences between living and dead mangrove areas. These similarities may be because the sediment cores were taken after the dieback period when sediment geochemistry conditions returned to normal. Trends in Mn in the wood samples (Supplementary Figure 1) also show no clear differences between living and dead forest areas and the Fe:Mn ratios in the wood Itrax data overwhelmingly reflect the Fe concentrations".

Reviewer 1

Comment:

From the beginning, authors have made up their mind that since the Fe content in the dead mangrove is higher than the living, it must be the reason for toxicity and hence the eventual death. From the data, it is quite clear that Fe content is higher in dead mangrove compared to living but at the same time, authors have admitted that there is no report of Fe toxicity at the reported concentration level in this particular species C1 of mangrove. They have not discussed the physiological aspect of the Fe assimilation by the mangrove.

Response

We agree that we do not have enough data to directly assess Fe toxicity. We have now made changes throughout the manuscript to clarify that the evidence is strongly suggesting differences in water availability between sites but not necessarily a direct effect of Fe toxicity. For example we have changed the title of the paper to: "Reconstructing extreme climatic and geochemical conditions during the largest natural mangrove dieback on record". We have modified the manuscript to use Fe in wood and sediments as a proxy indicator of water availability and the possibility of Fe toxicity is now presented as one (of multiple) possible synergistic stressors (See marked up manuscript with changes throughout). We have also provided additional background to the manuscript about the physiological assimilation of Fe in mangroves:

L91 – 98: "Marchand et al. (2016) suggest that the presence of Fe2 + may result in an increased Fe uptake by the root system. Such uptake may be toxic for the plant by reducing photosynthesis, increasing oxidative stress, and damaging membranes, DNA and proteins (Marchand et al., 2016). Fe toxicity in some mangrove species is reported to occur at concentrations ~2 fold higher than the optimal Fe supply for maximal growth (Alongi, 2010). However, to our knowledge, Fe toxicity in A. marina at extremely high Fe concentrations has not been investigated."

Comment

Section 2 - Also, the linkages to the mangrove mortality with climate parameters such as rainfall, sea-level, ENSO etc. comes as a forced attempt. The very fact that these two regions are adjacent to each other with no geomorphic differences (i.e, similar elevation etc.), climatic factors are likely to affect them in almost equal measures. I am not sure if it makes sense to link death of mangroves in one part of the same region to a climatic phenomenon, particularly when it is not affecting the adjacently located mangroves with similar species. Having said that, it remains a fact that mangroves have died in one part and not in the other. I would expect the authors to explore more localised reasons for this dieback. In the end, after discussing regional climate at length, authors themselves have invoked the possible role of groundwater. How the creation of aerobic and anaerobic environments in these two adjacently located patches have varied with time leading to availability of bio-available Fe and higher assimilation of Fe by mangrove remains to be looked into. Moreover, Authors have not provided the information of about the history of tidal regime in the region. Was it different between the living and dead mangroves? From the manuscript it appears that sea level receded from the region leading to oxidation of pyrite and formation of bioavailable Fe leading to assimilation. If this was the case, why only in dieback patch?

Response

Our assessment of the climatic variables and time series analysis was not intended to determine between site differences, but to assess regional scale climate drivers in the area, and whether they provide insight into the mangrove dieback. We have clarified this in the methods L216-217 “Cross correlations with a time lag of one-month intervals were used to evaluate the relationships between regional climatic variables (the Southern Oscillation Index (SOI), sea level, rainfall and vapour pressure) with wood density, elemental relative concentrations and growth rates.”

We have now added a section to the discussion to discuss differences in water availability between living and dead forest areas from L519 – 538:

“We have no data to determine if regional groundwater availability was greater in living forest areas than dead forest areas during the mangrove dieback. No significant difference was observed in groundwater salinities 8 months post dieback. However, under normal sea level conditions (i.e. when groundwater samples were collected), tidal inundation is likely to be the predominant driver of groundwater salinities rather than groundwater flows. Duke et al. (2017) and Harris et al. (2017) provide strong evidence that water availability in the Gulf of Carpentaria was extremely low prior to and during the dieback event. In this study we have been able to build on this work by exploring links between changes in sediment geochemistry and low water availability.

We eliminate elevation as a potential driver of water availability in living and dead forest areas. Tree mortality occurred even in the lower intertidal zone of the dead mangrove area which are at the same elevation as the lower intertidal zone of the living forest area (see elevation DEM in Figure 1c). Since other potential water sources were comparable between the sites, differences in water availability were likely driven by groundwater availability. Groundwater flows have high spatial variability and have been demonstrated to be an important water source in mangroves from arid Australia. For example Stieglitz (2005) highlights that the interrelationships between confined and unconfined aquifers in the coastal zone can result in localised differences in groundwater flows. High resolution spatial analysis of groundwater salinities in living and dead forest areas during low sea level conditions would help to clarify how water sources may drive mangrove mortality".

We have also added evidence from a recent publication providing isotopic data of mangrove leaves in dead and living areas at the same study sites from L364: "Trends in wood density, mangrove growth rate and water use efficiency also reveal distinct differences in water availability between dead and living forest areas. Lower water availability in the dead mangrove forest area was also evident in lower plant growth rates and higher plant water use efficiency. Mangrove plant isotope data at the same sites from a study by Harada et al. (2020) also shows a similar trend with more enriched δ13C values in the dead mangrove zone".

Comment

Section 3 - Also, please keep yourself open for explanation other than Fe toxicity. I think, in general, Fe toxicity is linked to water logging and its likelihood is higher under the anaerobic conditions. Since mangroves are experiencing frequent tidal flooding, they are often anoxic and thus chance of Fe toxicity is normally high. Aeration through specialised roots and other biological activities makes rhizosphere of mangrove species often oxygenated. So, most iron is in oxidized form (Fe3+), which is insoluble, forming iron plaque in roots of many mangrove species. Thus, roots of mangroves potentially have high concentration of iron than the stem and leaves. If the tidal flooding is disturbed, oxic zones in mangrove region may increase, which leads the more oxidization condition. Though it favours the oxidation of pyrite and liberate Fe2+, most of the Fe2+ may quickly oxide to Iron oxyhydroxide due to high aeration. So, during dieback time also, despite the oxidation C2 of stored pyrite and subsequent increase in sediment iron concentration, availability of bioavailable Fe2+ should be less. Though Iron plaque formation prevent mobilization of toxic metals, due it is high cation affinities it can also block the mobilization of other nutrients. Considering this, during low inundation periods, formation of iron plaque could increase many folds, which in turn affect complete mobilization of other nutrients and ultimately to gradual mortality. In light of above, I would suggest that authors revisit their arguments through physiological aspects of Fe interactions with mangrove and more localized reasons for generation of different situations in adjacently located mangroves.

Response

We agree with the reviewer's general thoughts. However, our observations have not been designed to assess these mechanisms and we feel we should omit excessive speculation following advice from the Associate Editor and other reviewers. We have now reduced speculation about Fe toxicity in mangroves and instead focused the manuscript on using Fe as a proxy of water availability, and the role of climate drivers in sediment Fe geochemistry in mangrove ecosystems. The drivers of Fe availability in mangrove sediments are complex and now discussed within the manuscript from L414 – 422: "While our observations suggest complex sedimentary redox conditions occurred in dead zone mangrove sediments during the dieback event, linking drought and low sea level to porewater Fe concentrations requires further investigation. For example, crab burrows and root systems can induce conditions that increase O_2 diffusion into sediments and thus influence Fe^{2+} mobility over tidal cycles (Nielsen at al., 2003; Kirstensen et al., 2008). Localised Fe(III) oxide dissolution can also occur in redox / pH micro-niches and under suboxic conditions (Fabricius et al. 2014; Zhu et al. 2012). Further research on the mechanisms of bioavailable Fe release and the thresholds for Fe toxicities in *Avicennia marina* is required to clearly understand the impacts of porewater Fe on mangrove forests".

Comment

Section 4 - Apart from above, I have following comments: âA˘ c Abstract needs to be ´ re-written with focus on above comments. The last part pertaining to inputs to ocean and increased productivity appears to overstatement, given that you do not have data to prove so.

Response

We have rewritten the abstract in line with the above comments. The statement regarding oceanic productivity changes associate with Fe release has been removed from the abstract.

Specific comments from Reviewer 1

Material and method:
There are sentences which are repetition.
Response: Repetitive sentences were removed from the data analysis section.

No information about standards used.
Response: Information on standards used for AMS ^{14}C analysis was added to the text from L176: "Oxalic acid I (HOxI) was used as the primary standard for calculating sample ^{14}C content, while oxalic acid II (HOxII) and IAEA-C7 reference material were used as check standards" .

The d13C was directly done on Wood cellulose or it was performed on graphite as in 14C?
Response: This is specified in the manuscript L171: "A portion of graphite was used for the determination of $\delta^{13}C$ for isotopic fractionation correction using a Micromass IsoPrime elemental analyser/isotope ratio mass spectrometer (EA/IRMS) at the Australian Nuclear Science and Technology Organisation (ANSTO)".

CRS was used for what? How is it relevant?
Response: We have modified the methods L194-197 to read: "Chromium reducible sulfur (CRS) was measured from sediment samples collected with a Russian peat auger to 1 m depth to provide an estimate of reducible inorganic S (RIS) species such as pyrite (FeS_2 - a key oxygen-sensitive sedimentary Fe species) with a linear relationship of R^2 = 0.996 (Burton

et al., 2008)“. We have also added the following text to the discussion to clarify the relevance of CRS from L428: Similar trends were also observed in CRS (a proxy for pyrite) sediment core profiles, which have ~40 % lower FeS_2 concentrations in the dead mangroves in comparison to the living mangrove sediments (Figure 6).

Data analysis contains some sentences already covered in material and methods.
Response: Repetitive sentences were removed from the data analysis section.

You have used relative concentrations for Fe but later in discuss you invoke absolute concentration level to suggest that present concentration is not enough for dieback? Do not you think that the mention of absolute concentrations would provide a good idea to reader to compare their results if they work on this problem in their region?
Response: We have clarified the use of relative and absolute concentration in the data analysis section from L203: “Itrax elemental and density data were normalized as the mean subtracted from each value divided by the standard deviation following the calculation of Z-scores by Hevia et al. (2018) and are referred to hereforth as relative concentrations. Methods that provided absolute concentrations such as CRS are simply referred to as concentrations”.

The concept of time lag and why was it used needs to be justified.
Response: We have explained the use of time lag analysis in the Data analysis section from L222 – 233: “This time lag analysis was specifically chosen to examine relationships between climate variables and Fe over a two year period because records of all climate variables are in resolution of months, but the chronology of Fe (based on ^{14}C dates) is in years”.

Results
As mentioned before, it would be a good idea to provide absolute concentration of Fe in wood and sediment.
Response: This comment is addressed above where we have modified the manuscript to clarify the use of both relative and absolute concentrations.

In Figure 3: why there are less number of data points in living forest of upper and mid intertidal?
Response: We have explained this occurrence in the manuscript from L247: “Itrax trends are plotted against ^{14}C ages and since tree growth rates change over time, Itrax data is not evenly distributed over time”.

Figure 4. No explanation of figure as to how it helps in understanding the discussion.
Response: We feel this is an important Figure which visually shows the relationships between environmental variables and sedimentary Fe relative concentrations over time. We have respectfully left the Figure in the revised version, but we have added text to more fully explain the figure – see line 392-394: “Records of all climate variables are in resolution of months, but the chronology of Fe (based on ^{14}C dates) is in years. We therefore used time lag analysis to examine relationships between climate variables and Fe over a two year period (Figure 4)”.

Fig 6: Here you jump to absolute concentration instead of relative. Also, it would help if you explain the how is it relevant to discussion, probably related to pyrite oxidation. This fact is not coming out clear.

Response: The description of Figure 6 in results now reads L298: “Chromium Reduced Sulfur (CRS) absolute concentrations, which provide a proxy for pyrite concentrations in sediment cores, were also lower overall in the dead mangrove compared to the living mangrove area - by 36% in the upper and 38% in the lower intertidal zones respectively (Figure 6)”.

Reviewer 2

Although the scientific aspect of the paper by Sippo et al is quite novel, the reasoning of mangrove dieback due to Fe toxicity, drought period and strong ENSO is quite speculative that requires more careful handling before being conclusive.

Response

We have made changes throughout the manuscript to avoid excessive speculation. We have clarified that the evidence is strongly suggesting differences in water availability between sites. We have modified the manuscript throughout to use Fe in wood and sediments as an indicator of water availability and the possibility of Fe toxicity has now been presented as one possible stressor. For example we have changed the title of the paper to: “Reconstructing extreme climatic and geochemical conditions during the largest natural mangrove dieback on record”. We have also removed any overly conclusive text from the abstract and manuscript about the relationships between ENSO and Fe concentrations in wood.

Since 1985, drought condition during the occurrence of 7 El Nino events affected dead mangroves (34 ± 1 years old), in contrast to the living mangroves which are younger (21 ± 4 years old) are survived to 4 El Nino events in Gulf of Carpentaria. It was seen that Fe peak in the dead mangrove area at the time of tree mortality were 30 to 90 fold higher than baseline in contrast to the living mangrove which showed an Fe peak 25 fold higher than baseline. Authors argued that low sea level and low rainfall/ groundwater reduced soil water content, leading to oxidation of Fe sulphide minerals and release of Fe^{2+}. Fe was observed in the upper intertidal zone. Even in absence of El Nino event, these Fe bearing-phases dissolution can occur in suboxic conditions in mangrove ecosystems.

Response

We have modified the tone of the manuscript to be less conclusive about the role of Fe toxicity in the forest mortality and instead discussed Fe trends as a reflection of changes in sediment geochemistry over time. We have now included discussion of how Fe dissolution can occur in suboxic conditions and discussed the complexity of Fe speciation in greater depth from L415 - 423: “While our observations suggest complex sedimentary redox conditions occurred in dead zone mangrove sediments during the dieback event, linking drought and low sea level to porewater Fe concentrations requires further investigation. For example, crab burrows and root systems can induce conditions that increase O_2 diffusion into sediments and thus influence Fe^{2+} mobility over tidal cycles (Nielsen at al., 2003; Kirstensen et al., 2008). Localised Fe(III) oxide dissolution can also occur in redox / pH micro-niches and under suboxic conditions (Fabricius et al. 2014; Zhu et al. 2012). Further research on the mechanisms of bioavailable Fe release and the thresholds for Fe toxicities in *Avicennia marina* is required to clearly understand the impacts of porewater Fe on mangrove forests."

On the one hand, crab burrow and root system may induce these conditions allowing the renewal of electron acceptors with tides; and on the other hand, physiological activities of mangrove root system can lead to increased O2 concentrations in the sediment (Aquat. Bot. 89 (2), 210–219, 2008). Generally, roots absorb Fe+2 and is highly affected by several plant and environmental factors and their toxicity is often associated with salinity and a low phosphorus or base status of soils. Furthermore, injured leaves or necrotic spots on leaves indicate an accumulation of Fe above 1000 ppm (3 to 6 times as high as the Fe content of healthy leaves). However, the most pronounced symptom is the ratio of Fe to other elements and to heavy metals in particular. The proper Fe:Mn ratio seems to be the most obligatory factor in the tolerance of plants to Fe toxicity. The world average Fe (g g-1) conc in Avicennia marina is estimated to be 54000 (Lewis et al. 2011, Bayen 2012), and 120000 in New Caledonia, the South-West Pacific Ocean (Marchand et al. 2016). The increased uptake of Fe+2 in toxic level by the mangrove root system may reduce growth, DNA damage as evident by morphological or structural damage. Authors could highlight above aspects in their paper by comparing a possible impact of iron and substrate factors on mangrove that would be very relevant in this specific context.

Response

We have removed the perceived overstatement that Fe was the cause of mangrove mortality throughout the manuscript. We have also clarified that the Fe chronologies in wood and sediment are evidence of geochemical changes in the sediments, which also suggest that changes in water availability occurred during the dieback period. We have now provided Mn data from wood samples in Supplementary Figure 1 and from Ca in Supplementary Figure 2 and we have added the following text to the manuscript L438 – 444: "The apparent mobilisation of Fe (loss from sediment and uptake in wood) was not observed in other elements (Supplementary Figures 1 & 2). Sediment Fe:Mn ratios in Itrax data displayed no clear differences between living and dead mangrove areas. These similarities may be because the sediment cores were taken after the dieback period when sediment geochemistry conditions returned to normal. Trends in Mn in the wood samples (Supplementary Figure 1) also show no clear differences between living and dead forest areas and the Fe:Mn ratios in the wood Itrax data overwhelmingly reflect the Fe concentrations.".

Reviewer 3 - Fernanda Adame

We thank Dr. Fernanda Adame for the constructive feedback on the manuscript and have addressed the comments she raised.

This manuscript provides an interesting theory: increased Fe toxicity and water stress led to large-scale dieback of mangroves in northern Australia. The authors provide lines of evidence from wood and sediment cores to show that low mean sea level, low water vapour, and low precipitation contributed to changes in the biogeochemistry of the soil, which led to changes in the physiology of the trees. Their data shows a very high increase in wood Fe over the period when the dieback occurred, along with a possible decrease in water use efficiency, and decrease in wood density. However, there were no clear differences between the "dead" site compared to the "live" site, with differences mostly driven by the position in the intertidal (low vs high). Both sites had similar growth rates, similar CRS, WUE, wood density and salinity. The only significant difference was that the live site had higher Fe+ in the soil that the dead one, a result which appears to be contradictory to their hypothesis. At the moment, the manuscript is written in a way that implies that all the data support their theory, but I am still not convinced. I agree that the climatic conditions led to drastic biogeochemical changes in the soil and mangrove trees, however, this does not explain why some of them died and some of them not. A cause-effect link cannot be established yet.

Response

As noted in earlier responses, we have re-focused the manuscript to better highlight the differences between dead and living areas with a new section in the discussion titled 'Differences in water availability between living and dead forest areas' from L490 - 519. We have also made it clear throughout the manuscript that our results are not conclusive in establishing a cause and effect relationship, but do provide important clues and insights regarding key processes occurring during the mangrove dieback.

Overall, I think the data is of high quality and there is potential for it to form the basis of an interesting and novel hypothesis on the effects of drought and sea-level rise on mangrove forests. However, it has to acknowledge that this theory does not prove why mangroves died. The authors mention in the conclusion that differences in groundwater could be the cause of death in some forests, however, they also mention that salinity was similar in both sites. There are still many unanswered questions and the paper needs to be rewritten in a way that provides some answers but also acknowledges that new questions have emerged that are yet to be resolved.

Response

As discussed above, we have now re-focused the manuscript to have more circumspect conclusions and turn some of the speculation into a new hypothesis. Salinity concentrations in groundwater were taken eight months after the dieback event and may not represent the salinities that occurred during the dieback period. We have clarified this in the manuscript L520-524: "We have no data to determine if regional groundwater availability was greater in living forest areas than dead forest areas during the mangrove dieback. No significant difference was observed in groundwater salinities 8 months post dieback. However, under normal sea level conditions (i.e. when groundwater samples were collected), tidal inundation is likely to be the predominant driver of groundwater salinities rather than groundwater flows”.

END OF RESPONSES

~~Linking~~Reconstructing extreme climatic~~-driven iron toxicity~~ and ~~water stress to a massive~~geochemical conditions during the largest natural mangrove dieback on record

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Abstract

A massive mangrove dieback event occurred in 2015/2016 along ~1000km of pristine coastline in the Gulf of Carpentaria, Australia. ~~To gain insights into dieback drivers~~Here, we ~~combine~~use sediment and wood chronologies to ~~analyze~~ gain insights into geochemical and climatic changes~~.~~ related to this dieback. The unique combination of low rainfall and low sea level observed during the dieback event was unprecedented in the previous three decades. ~~Multiple lines of evidence from~~A combination of iron (Fe) chronologies in wood and sediment, wood ~~densities~~density and estimates of mangrove water use efficiency ~~suggest low~~, all imply lower water availability within the dead mangrove forest. Wood and sediment chronologies suggest a rapid ~~and~~, large mobilization of sedimentary Fe, which ~~was likely associated with pyrite oxidation within mangrove sediments. High resolution elemental~~is consistent with redox transitions promoted by changes in soil moisture content. Elemental analysis of wood cross sections revealed 30-90 fold increase in Fe concentrations in dead ~~mangrove areas~~ mangroves just prior to their mortality. ~~Fe concentrations in~~Mangrove wood ~~samples correlated strongly with the El Niño Southern Oscillation (ENSO) index, suggesting ENSO was a major driver of Fe mobilization. Large Fe losses from sediments~~ uptake of Fe during the dieback ~~are consistent with Fe uptake in the trees, further implying sediment pyrite oxidation. If our data are representative of the entire dieback region, we estimate that the dieback drove the mobilization and loss of 50 ± 173 Gg Fe, equivalent to 8-50% of annual global atmospheric Fe deposition into the oceans~~is consistent with large apparent losses of Fe from sediments, which ~~is one~~potentially caused an outwelling of Fe to the ~~major drivers of surface~~ ocean ~~productivity.~~. Although Fe toxicity may also have played a role in

the dieback, this possibility requires further study. We suggest that differences in wood and sedimentary Fe between living and dead forest areas reflect sediment redox transitions that are in turn associated with regional variability in groundwater flows. Overall, our observations ~~support the hypothesis~~ provide multiple lines of evidence that the forest dieback was associated with low water availability ~~and Fe toxicity driven by~~, coinciding with a strong ENSO event.

Introduction

Mangroves provide a wide range of ecosystem services~~ such as~~, including nursery habitat, carbon sequestration, and coastal protection (Barbier et al. 2011, Donato et al. 2011). Climate change is a major threat to mangroves~~ adding~~, which adds to ~~the threats~~existing stressors imposed by deforestation and over~~-~~-exploitation (Hamilton and Casey 2016, Richards and Friess 2016). ~~Rising sea levels, changing~~Sea level rise, altered sediment budgets, reduced water availability and increasing climatic extremes are all negatively affecting mangroves (Gilman et al. 2008, Alongi 2015, Lovelock et al. 2015, Sippo et al. 2018).

In Australia, an extensive mangrove dieback event ~~occurred~~ in the Gulf of Carpentaria~~, in~~ during December 2015 - January 2016, ~~coincident~~coincided with extreme drought and low regional sea ~~level~~levels. This extreme climatic event drove the largest recorded mangrove mortality event (~1000 km coastline, ~7400 ha) ~~driven by~~attributed to natural causes (Duke et al., 2017; Harris et al., 2017; Sippo et al., 2018~~).~~) and led to extensive changes in the coastal carbon cycle (Sippo et al. 2019; Sippo et al. 2020) and coastal foodwebs (Harada et al. 2020). Two other large scale mangrove dieback events occurred at the same time~~ in Australia. One was reported~~, one in Exmouth~~, Western Australia~~ (Lovelock et al. 2017) and ~~another occurred~~the other in Kakadu National Park, ~~Northern Territory,~~ Australia (Asbridge et al. 2019).

~~The mangrove~~Mangrove mortality has been previously attributed to low water availability associated with extreme drought. ~~The limited~~Limited rainfall and groundwater availability~~, and~~ combined with anomalously low sea ~~level~~levels, effectively reduced tidal inundation and soil water content (Duke et al., 2017; Harris et al., 2017). A strong El Niño event resulted in the lowest recorded rainfall in the nine months preceding the mangrove dieback since 1971, and was accompanied by regional sea levels that were 20 cm lower than ~~normal~~average (Harris et al., 2017). Atmospheric moisture was also unusually low during 2015~~,~~ - a feature which may influence the physiological functioning of mangrove trees (Nguyen et al. 2017). ~~The~~Such severe climatic and hydrologic changes may affect both plant physiology and sediment geochemistry. ~~Here, we explore whether low sediment water content and associated changes in sediment geochemistry may have played a role in the dieback.~~

In contrast to terrestrial forest soils, mangrove sediments are largely anoxic due to their water-logged nature, and high organic matter contents. Mangrove sediments also receive a supply of materials from both terrestrial environments (e.g. Fe, sediments) and oceanic water (e.g. SO_4) which results in distinctly different biogeochemical cycling ~~within the sediments~~ than terrestrial forests (Burdige 2011). As a result, mangrove sediments often accumulate substantial (~1-5%) bioauthigenic pyrite (FeS_2~~) which~~). Pyrite remains stable under waterlogged and reducing conditions (van Breemen 1988, Johnston et al. 2011). ~~Lowering~~However, lowering of water levels can alter sediment redox conditions and result in ~~the~~rapid oxidation of FeS_2, releasing acid and dissolved Fe (mostly as more soluble Fe^{2+}~~)~~ species) to ~~porewater~~porewaters (Burton et al. 2006, Johnston et al. 2011, Keene et al. 2014). Subsequent oxidation of Fe^{2+} and precipitation of ~~Fe^{3+}~~Fe(III) (oxy)hydroxide minerals can then lead to the accumulation of highly reactive Fe in sediments. ~~Reactive Fe^{3+}~~Such reactive Fe(III) minerals are in turn readily subject to reductive dissolution and (re)-formation of soluble Fe^{2+} species during any ~~switches~~subsequent switch to more reducing conditions. Thus, changes in sediment redox conditions~~, i.~~ (e.g. increased oxidation and

~~consequent~~followed by subsequent reduction~~,~~), in mangrove sediments that are rich in FeS_2 can cause a release of relatively mobile and bioavailable Fe^{2}~~$^{+}$.~~$^{+}$ during the redox transition(s).

Mobilisation of Fe due to fluctuating oxidation/reduction cycles could also have important consequences for coastal Fe cycling. For example, Fe is often a limiting nutrient in ocean surface waters and thus Fe outwelling from mangroves could have important implications for primary productivity in coastal zone waters (Jickells and Spokes , Fung et al. 2000, Holloway et al. 2016).~~Mangrove~~ Fe mobilisation also means that uptake of Fe^{2+} into mangrove tissues may be a powerful proxy ~~of~~for historic sediment redox conditions~~, driven by short and long-term variability in sea-level. High levels~~. However, the process of ~~bioavailable Fe~~ Fe assimilation into mangrove tissues remains poorly understood. Marchand et al. (2016) suggest that the presence of $Fe^{2\,+}$ may ~~also~~ result in an increased Fe uptake by the root system. Such uptake may be ~~associated with tree mortalities, although there is limited evidence of Fe toxicity.~~toxic for the plant by reducing photosynthesis, increasing oxidative stress, and damaging membranes, DNA and proteins (Marchand et al., 2016). Fe toxicity in some mangrove species ~~can~~is reported to occur at concentrations ~2 fold higher than the optimal Fe supply for maximal growth (Alongi, 2010). ~~Since Fe is often a limiting nutrient in ocean surface water, Fe outwelling from mangroves could have important implications for productivity in coastal waters (Jickells and Spokes , Fung et al.~~ However, to our knowledge, Fe toxicity in *Avicenia marina* at extremely high Fe concentrations has not been investigated. ~~2000, Holloway et al. 2016).~~

An extensive saltmarsh dieback in southern United States in 2000 provides an analogue to the mangrove dieback studied here. The saltmarsh dieback coincided with severe drought conditions (McKee et al. 2004, Ogburn and Alber 2006, Alber et al. 2008). McKee et al. (2004) found that sediments in dead saltmarsh areas had significantly higher ~~acidification~~acidity upon oxidation than alive areas. The dieback may have been caused by a combination of reduced water availability, increased sediment salinities and/or metal toxicity associated with soil acidification following sediment pyrite oxidation. However, the precise cause of the dieback ~~was debated~~is a matter of debate and remains inconclusive (McKee et al. 2004, Silliman et al. 2005, Alber et al. 2008). In contrast to the herbaceous salt marsh species affected in the US dieback, mangroves are woody~~,~~ - thus providing ~~opportunities~~opportunity for dendrochronological climatic ~~reconstructions~~reconstruction (Verheyden et al. 2005, Brookhouse 2006). To date, the use of dendrochronological techniques have not been used to assess changes in sediment geochemistry in mangroves.

Here, we combine multiple wood and sediment chronology techniques to reconstruct water availability, sediment geochemistry and assess the links to climate and sea levels. To evaluate the potential for mobilisation of Fe during the dieback, we combine multiple lines of evidence including: 1) micro X-ray fluorescence (Itrax) to analyse the elemental composition in wood and sediment cores; 2) wood density measurements, tree growth rates and $\delta^{13}C$ isotopes to assess historic changes in water availability (Santini et al. 2012, Santini et al. 2013, Van Der Sleen et al. 2015, Maxwell et al. 2018); and 3) sediment profiles of FeS_2 concentrations to ~~give~~provide insight into sediment redox conditions and possible Fe mobilisation. We assess these parameters in areas where mangroves died and where they survived the dieback event.

Methods

Study Site

This study was conducted in the South Eastern corner of the Gulf of Carpentaria, in Northern Australia (Figure 1). The Gulf of Carpentaria is a large and shallow (< 70 m) waterbody with an annual rainfall of 900mm per year and a semi-arid climate (Bureau of Meteorology; Duke et al., 2017). The region has low lying topography with ~~abundant~~*A. marina* and *Rhizophora stylosa* the dominant mangroves fringing the coastline and estuaries, and extensive saltpans in the upper intertidal zone (Duke et al., 2017). ~~The species *Avicennia marina* and *Rhizophora stylosa* dominate the~~ Widespread dieback of the mangroves ~~within~~in the ~~Gulf of Carpentaria~~region was observed in 2015-2016.

~~Widespread dieback of the mangroves in the region was observed in 2015-2016.~~ The dieback predominantly affected *A. marina* which occupy the open coastlines and upper intertidal areas (Duke et al., 2017). Although 7500 ha of mangrove suffered mortality some areas remained relatively unaffected, providing an opportunity to compare conditions ~~in~~within live and dead stands. We assessed a live and dead mangrove area 20 months after the dieback event. The two mangrove areas were separated by the Norman River and were ~ ~~-~~4 km apart (Figure 1). The living mangrove has an area of 175 ha and had some dead trees in the upper intertidal zone and living trees that showed signs of stress (dead branches and partial defoliation). Towards the seaward edge, the forest had no signs of canopy loss 8 months post dieback event. The dead mangrove area was 169 ha and had close to 100% mortality (Figure 1b), with only some trees at the waterline showing regrowth.

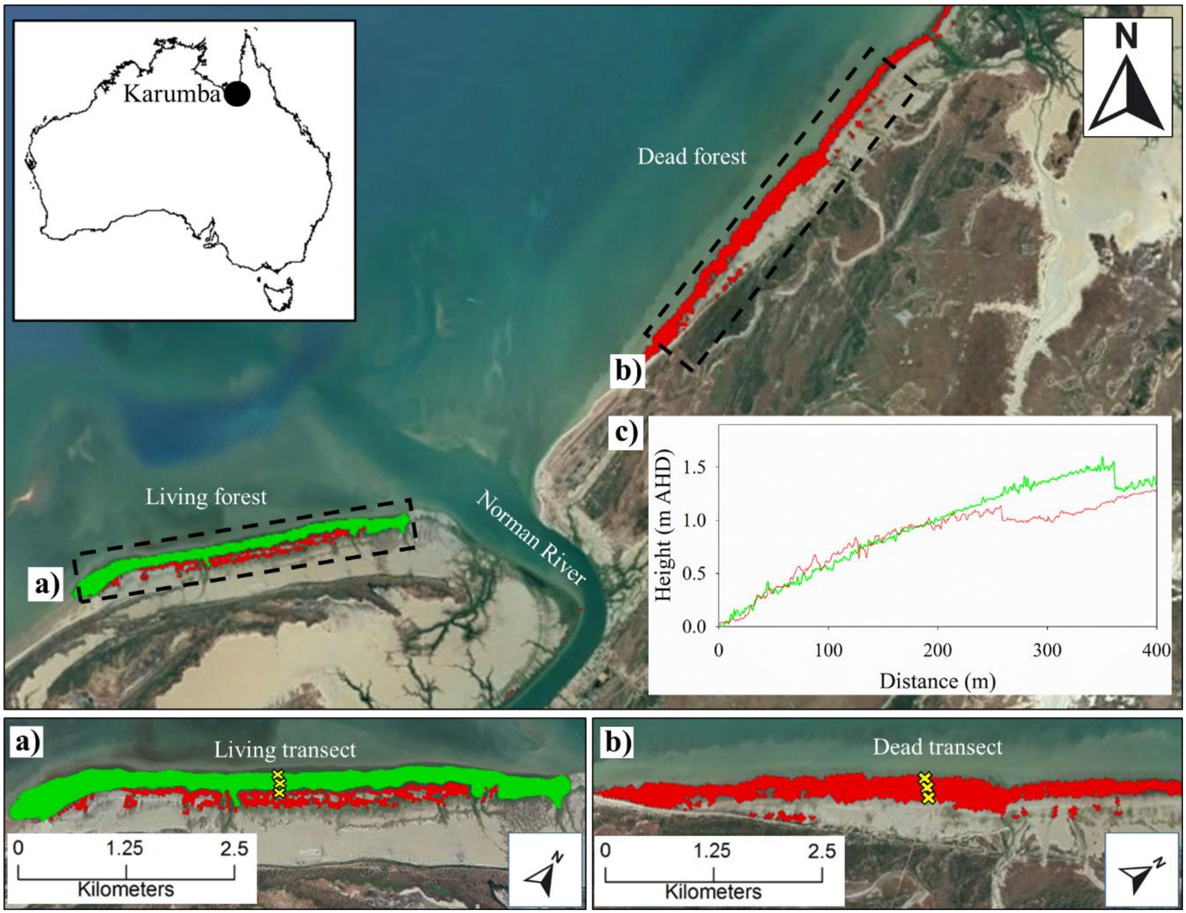
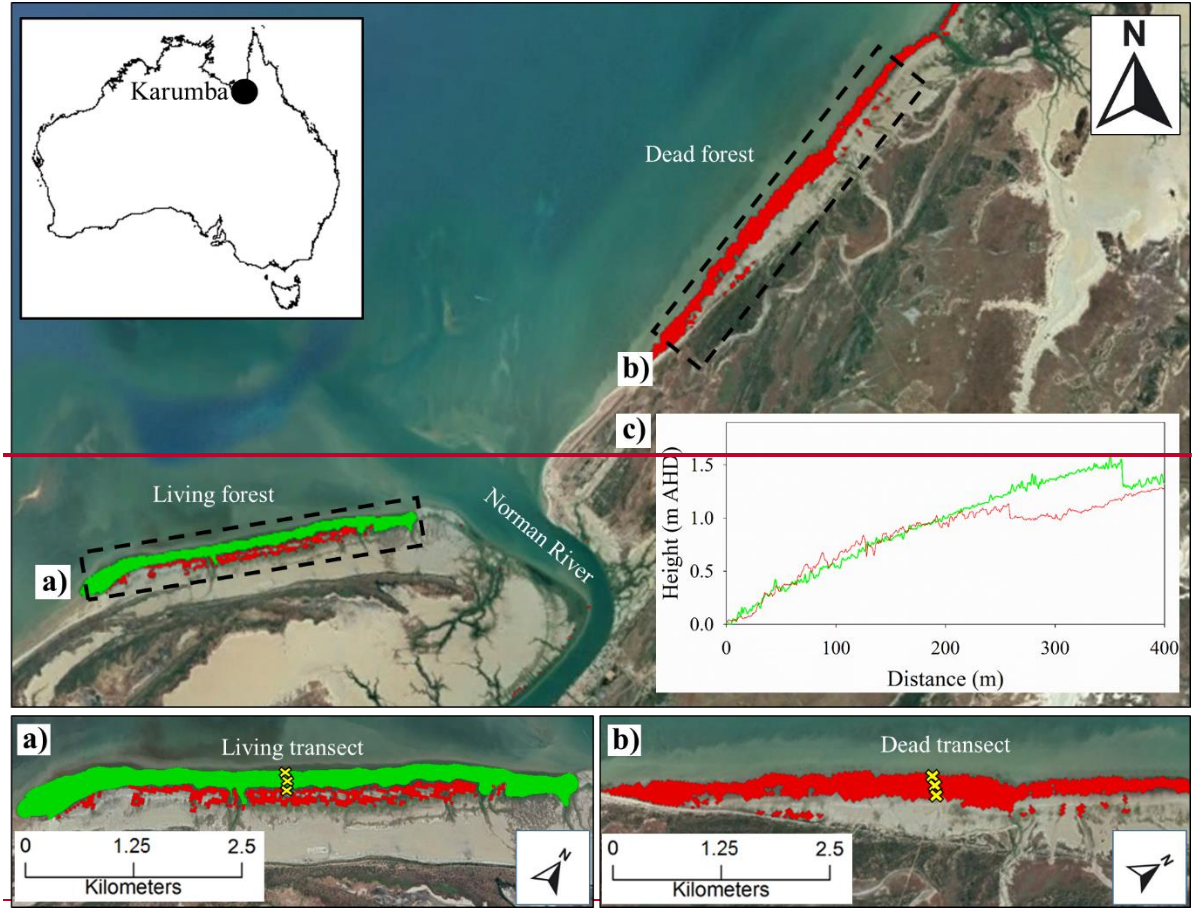


Figure 1. Study sites of a) living mangrove area (green) and b) dead mangrove area (red) near ~~to~~ the mouth of the Norman River, Karumba Qld. Note: The yellow ‘x’ symbols represent transects through the upper, middle and lower study sites. c) Elevation above the Australian Height Datum (AHD) from Lidar DEM were measured from the seaward mangrove edge in 2017 from the same transects as samples were

collected in 2016 through the living (Green line) and dead (red line) mangrove area (data available from http://wiki.auscover.net.au/wiki/Mangroves). Satellite images sourced from © Google Earth (2019) and Queensland Government (2019).



Field sampling and chemical and isotopic analyses

Tree and sediment samples were collected in August 2017 approximately 20 months after the dieback event. Wood and sediment samples were collected from transects from the lower intertidal zone to the upper intertidal zone (Figure 1). Fully mature trees were selected at ~20 m inward from the lower and upper intertidal forest edges and in the centre of the forest. One upper, mid and lower tide wood sample was taken in living and dead mangrove areas (Figure 1a and b). Wood samples from *A. marina* were taken from 50 cm above ground level by cutting a 1cm thick disk from the trunk. At the upper and lower intertidal sites, two sediment cores were taken. One core, taken to 2 m with a Russian peat auger with extensions, was sampled for elemental analysis with Itrax. A second core, taken to a depth of 1 m using a tapered auger corer in August 2018 at the same site, was sampled for analysis of chromium reducible sulfur (CRS).

Wood samples were dated using bomb ^{14}C (eg, Santini et al. 2013; Witt et al. 2017). Water-use efficiency (WUE), which is the ratio of net photosynthesis to transpiration, was assessed using wood cellulose stable isotopic composition δ^{13}C following ~~(~~Van Der Sleen et al~~.~~., (2015) as water use efficiency correlates with ~~larger values of~~ δ^{13}C (Farquhar and Richards 1984, Farquhar et al. 1989). ~~Wood elemental composition and density was assessed using micro X-ray fluorescence.~~ Sub-samples for ^{14}C and δ^{13}C were taken from tree samples (wood disks) along the longest radius of each ~~wood~~ disk at regular intervals from the centre ~~of the wood disc~~ to the outer edge (youngest wood). The sub-samples were collected using a scalpel parallel to tree rings to reduce errors. Alpha cellulose was extracted from the wooden sub-samples (Hua et al~~. (~~., 2004b), combusted to CO_2 and converted to graphite (Hua et al~~.~~., 2001). A portion of graphite was used for the determination of $\delta^{13}C$ for isotopic fractionation correction using a Micromass IsoPrime elemental analyser/isotope ratio mass spectrometer (EA/IRMS) at the Australian Nuclear Science and Technology Organisation (ANSTO). The remaining graphite was analysed for ^{14}C using the STAR accelerator mass spectrometry (AMS) facility at ANSTO (Fink et al. 2004) with a typical analytical precision of better than 0.3% (2σ). Oxalic acid I (HOxI) was used as the primary standard for calculating sample ^{14}C content, while oxalic acid II (HOxII) and IAEA-C7 reference material were used as check standards. Sample ^{14}C content was converted to calendar ages using the ‘‘Simple Sequence’’ deposition model of the OxCal calibration program based on chronological ordering (outer samples are younger than inner samples) (Bronk Ramsey, 2008), and atmospheric ^{14}C data from Baring Head (Wellington, New Zealand) extended to 2017.

Wood samples and sediment cores were analysed for elemental composition with a micro X-ray fluorescence conducted at ANSTO using an Itrax core scanner (Cox Analytical Systems). The scanner produces a high resolution (0.2 mm) radiographic density pattern and semi-quantitative elemental profiles for each sample. The Itrax measured 34 elements~~, but~~ and while trends occurred in some elements (see Appendix 1 & 2), here we ~~only report~~focus on Fe. Itrax Fe results have been compared with absolute Fe_2O_3 concentrations with high accuracy ($R^2 = 0.74$) (Hunt et al., 2015). Wood samples were scanned along the same transect as for ^{14}C samples, i.e. the longest radius from the wood core to the outer edge. Sediment cores were analysed using the Itrax in four 50 cm increments. Immediately upon collection, CRS sub-samples were placed in polyethylene bags with air removed and frozen prior to CRS analysis. Chromium reducible sulfur (CRS) was measured ~~from sediment samples collected with a Russian peat auger~~at 5 cm intervals to 1 m depth to provide an estimate of reducible inorganic S (RIS~~;~~) species such as pyrite (FeS_2 - a key oxygen-sensitive sedimentary Fe species) with a linear relationship of $R^2 = 0.996$ (Burton et al~~. (~~., 2008).~~ CRS subsamples were placed in bags with air removed and frozen prior to CRS analysis.~~ Groundwater salinity values were taken at the same sites as wood samples from bore holes dug to ~1m depth. Groundwater in the holes was purged and allowed to refill and salinities were measured using a Hach multi-sonde.

Data analysis

~~Radiocarbon values were used to calculate~~To align radiocarbon calendar ages~~. To align dates~~ with Itrax data, we interpolated ages using the wood circumference. Itrax elemental and density data were normalized as the mean subtracted from each value divided by the standard deviation following ~~the calculation of Z-scores by~~ Hevia et al. (2018) and are referred to hereforth as relative concentrations. We also normalized the Fe data to total counts and other measured elements following Turner et al. (2015) and Gregory et al. (2019) to confirm the trends did not change with different normalization approaches which they did not. This normalization reduces external effects (Gregory et al. 2019) and allows a more direct comparison between samples from living and dead forest areas. Methods that provided absolute concentrations such as CRS are simply referred to as concentrations. Growth rates in mm per year were calculated as the measured increment divided by the difference in years (~~calculated~~estimated from ^{14}C) between samples. De-trended growth rates were then calculated as the deviation from the exponential curve fitted to growth rates for each sample. Water use efficiency (WUE) was calculated from $\delta^{13}C$ isotope values (Van Der Sleen et al. 2015). Differences in WUE between living and dead mangrove areas were compared using T-test.

Cross correlations with a time lag of one-month intervals were used to evaluate the relationships between climatic variables (the Southern Oscillation Index (SOI), sea level, rainfall and vapour pressure) with wood density, elemental relative concentrations and growth rates. SOI data and other climate data were obtained from the Bureau of Meteorology (Station number 029028, 2019) and published reports (Jones et al. 2009, Harris et al. 2017). All climatic data were used with a one month resolution and were ~~standardised using a centred moving mean.~~ smoothed using a centred moving mean. This time lag analysis was specifically chosen to examine relationships between climate variables and Fe over a two year period because records of all climate variables are in resolution of months, but the chronology of Fe (based on ^{14}C dates) is in years.

Results

Climatic conditions

The climate records over the last three decades reveal an unprecedented combination of low sea level and low annual rainfall. SOI is significantly correlated to all climate variables (Pearson product moment correlation, $P < 0.05$). Lower sea levels and rainfall had previously occurred independently (Figure 2). Since 1985, trends in SOI index based on vapour pressure, precipitation and sea level observations show El Niño in 1983, 1987, 1992, 1994, 1998, 2015 and 2016.

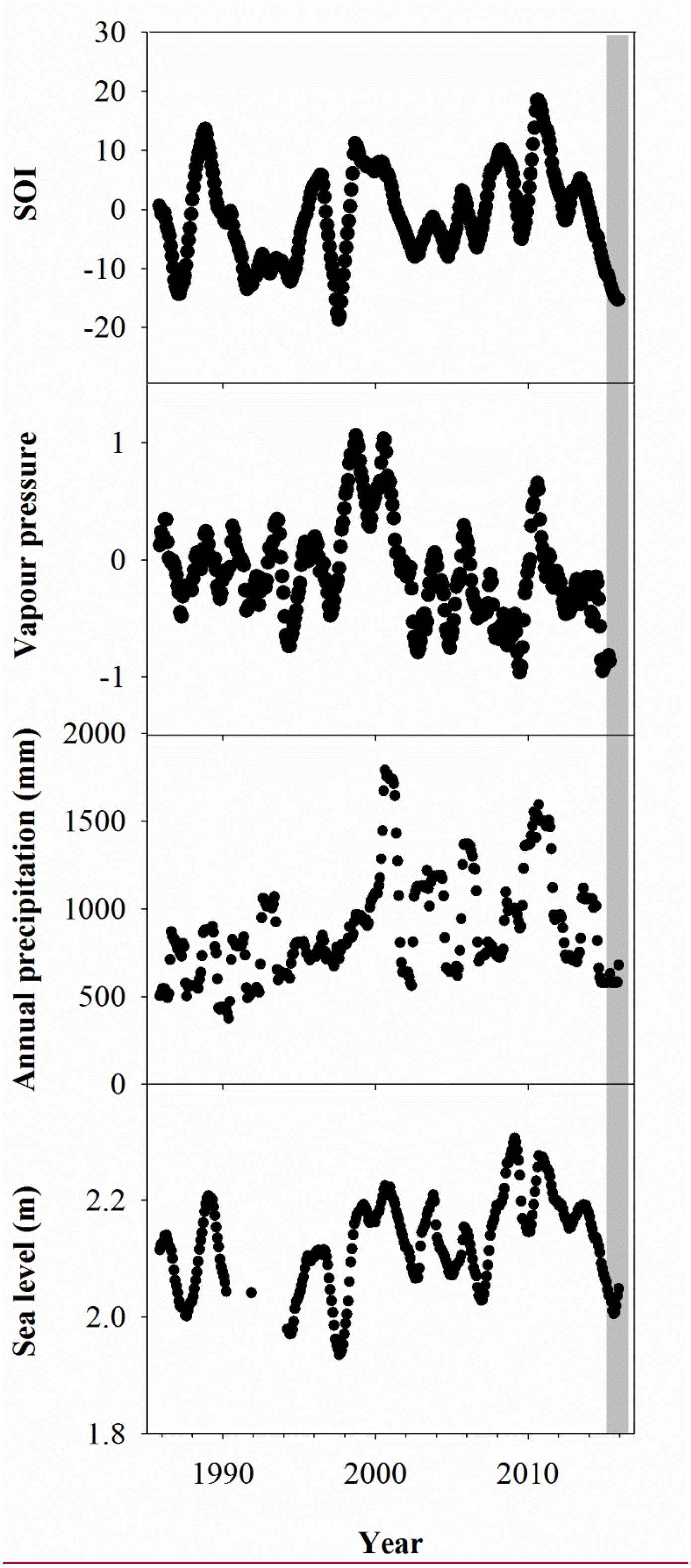


Figure 2. ~~Centred moving means of climate data~~Climate observations from the South Eastern Gulf of Carpentaria Australian (Jones et al. 2009, Harris et al. 2017, Bureau of Meteorology 2019). The grey bar represents the period during which the dieback event occurred.

Wood samples and ages –

The ages of *A. marina* ranged from 15 ± 2 to 34 ± 2 years (Table 1). On average, the trees in the living and dead mangrove forests were 21 ± 4 and 34 ± 1 years old respectively. Tree growth rates that were de-trended to negative exponential growth had no trends over time in either the living or dead mangrove areas (Table 1).

Table 1. Summary of radiocarbon ages and growth rates (deviation from negative exponential growth) for all wood samples taken from dead and living mangrove areas in the Gulf of Carpentaria, Australia.

Sample	Distance from pith (mm)	^{14}C Mean ±1σ (pMC) **	Modelled calendar age Mean ±1σ (year AD)	Deviation from negative exponential growth (mm per year)
		Dead mangrove		
Upper intertidal	2	121.98 ± 0.28	1984 ± 2	-
	17	119.82 ± 0.27	1986 ± 2	-2.6
	35	118.02 ± 0.27	1988 ± 2	-1.4
	52	116.07 ± 0.30	1990 ± 3	-1.2
	70	110.85 ± 0.26	1998 ± 2	-4.7
	87	105.35 ± 0.23	2010 ± 2	-1.3
	89		2015*	-0.9
Mid intertidal	2	123.56 ± 0.30	1983 ± 2	-
	12	122.81 ± 0.30	1984 ± 2	2.3
	24	119.07 ± 0.28	1987 ± 2	-4.8
	36	115.92 ± 0.38	1991 ± 3	-3.6
	49	110.06 ± 0.27	1999 ± 2	-3.7
	62	105.17 ± 0.29	2011 ± 3	-0.2
	64		2015*	-0.2
Lower intertidal	2	123.31 ± 0.38	1983 ± 2	-
	23	120.39 ± 0.36	1986 ± 2	-2.3
	45	117.35 ± 0.35	1989 ± 2	-1.8
	89	110.89 ± 0.33	1998 ± 2	-1.9
	110	105.75 ± 0.31	2009 ± 2	-2.1
	113		2015*	-2.5
		Living mangrove		
Upper intertidal	2	163.84 ± 0.48	1995 ± 2	-
	20	112.00 ± 0.42	1996 ± 3	2.3
	40	109.81 ± 0.44	2000 ± 3	-0.8
	58	103.71 ± 0.40	2013 ± 2	-2.3
	60		2017*	-2.9
Mid intertidal	2	113.32 ± 0.45	1994 ± 2	-
	16	111.13 ± 0.31	1997 ± 2	-1.0
	33	109.22 ± 0.37	2001 ± 2	0.8

	49	106.59	±	0.29	2014	±	2	-1.2
	50				2017*			-2.3
Mid intertidal	2	113.41	±	0.29	1993	±	3	-
	25	110.89	±	0.28	1998	±	2	-1.0
	50	101.91	±	0.30	2017	±	1	0.2
	51				2017*			-2.3
Lower intertidal	2	108.83	±	0.27	2002	±	2	-
	17	107.30	±	0.29	2005	±	2	-5.1
	33	104.92	±	0.37	2011	±	3	9.2
	46	104.30	±	0.34	2014	±	2	-2.3
	48				2017*			-2.2

* Date of collection of *A. marina* samples

**Measured ^{14}C content is shown in percent Modern Carbon (pMC; Stuiver and Polach 1977)

Fe in wood and sediment cores -

Fe relative concentrations in all dead mangrove samples peaked at the time of mangrove mortality in late 2015/early 2016 (Figure 3). In the living mangrove samples, Fe peaked in late 2015/early 2016 and then decreased in 2016 and 2017 ~~back~~ to long-term average levels. Peak wood Fe concentrations in the upper, mid and lower intertidal areas of the dead mangrove samples were 40, 90 and 30 fold higher than their mean baseline concentrations, respectively. In the living mangrove area, peak wood Fe concentrations in the upper, mid and lower intertidal areas were 25, 4 and 3 fold higher than their mean baseline concentrations, respectively. In the dead mangrove area, Fe levels were similar from the upper to the lower intertidal zone (Figure 3). In the living mangrove area, Fe was highest in the upper and mid intertidal zone and decreased in the lower intertidal zone. Itrax trends are plotted against ^{14}C ages and since tree growth rates change over time, Itrax data is not evenly distributed over time.

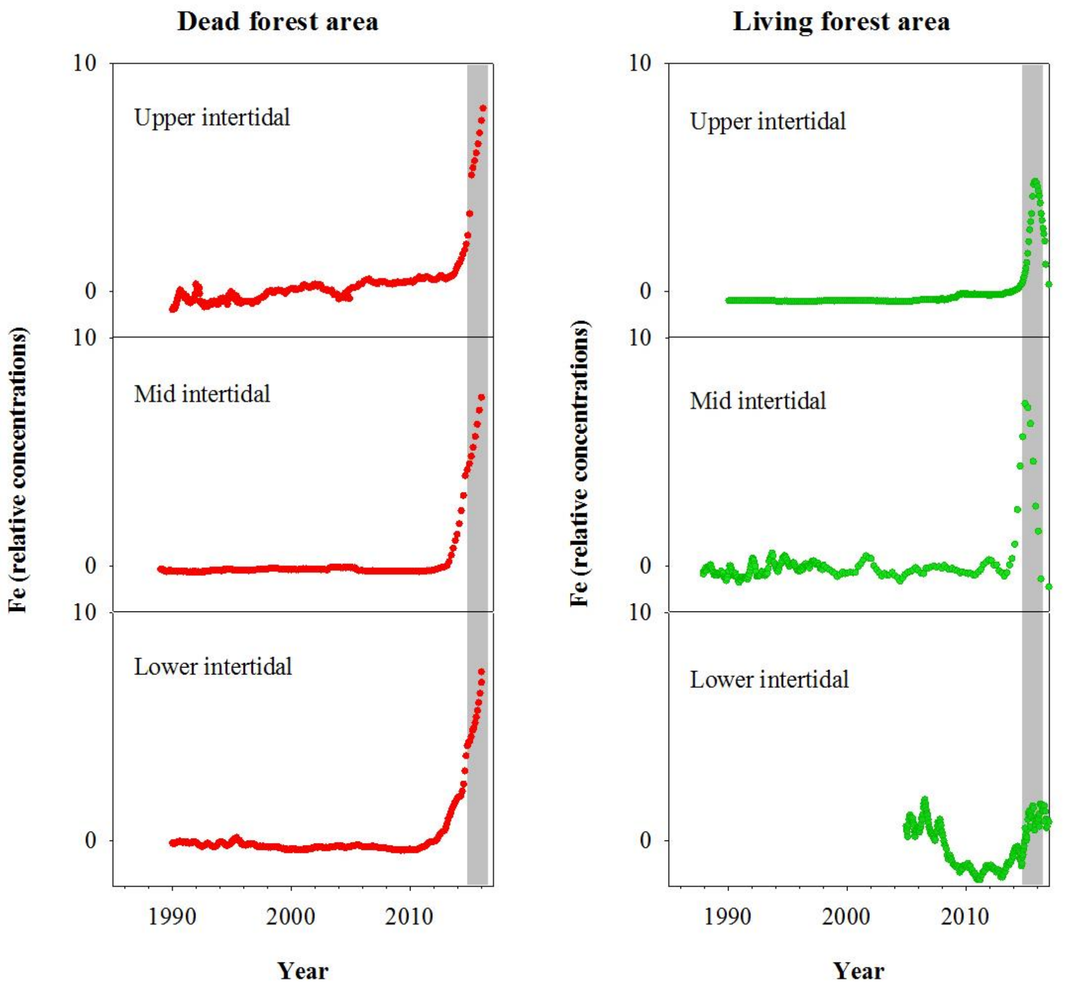


Figure 3. Fe relative concentrations in mangrove wood over time in living (green dots) and dead (red dots) from upper, mid and lower intertidal areas of mangroves of the Gulf of Carpentaria, Australia. Grey areas indicate the dieback event.

Significant correlations with no time lag were found between Fe in wood and vapour pressure, rainfall, sea level and SOI (Figure 4). All climate variables were strongly correlated with SOI. Therefore, we could not separate the influence of individual climate variables on wood Fe. In the dead and living mangrove areas, the strongest correlations with Fe occurred with no time lag (Figure 4).

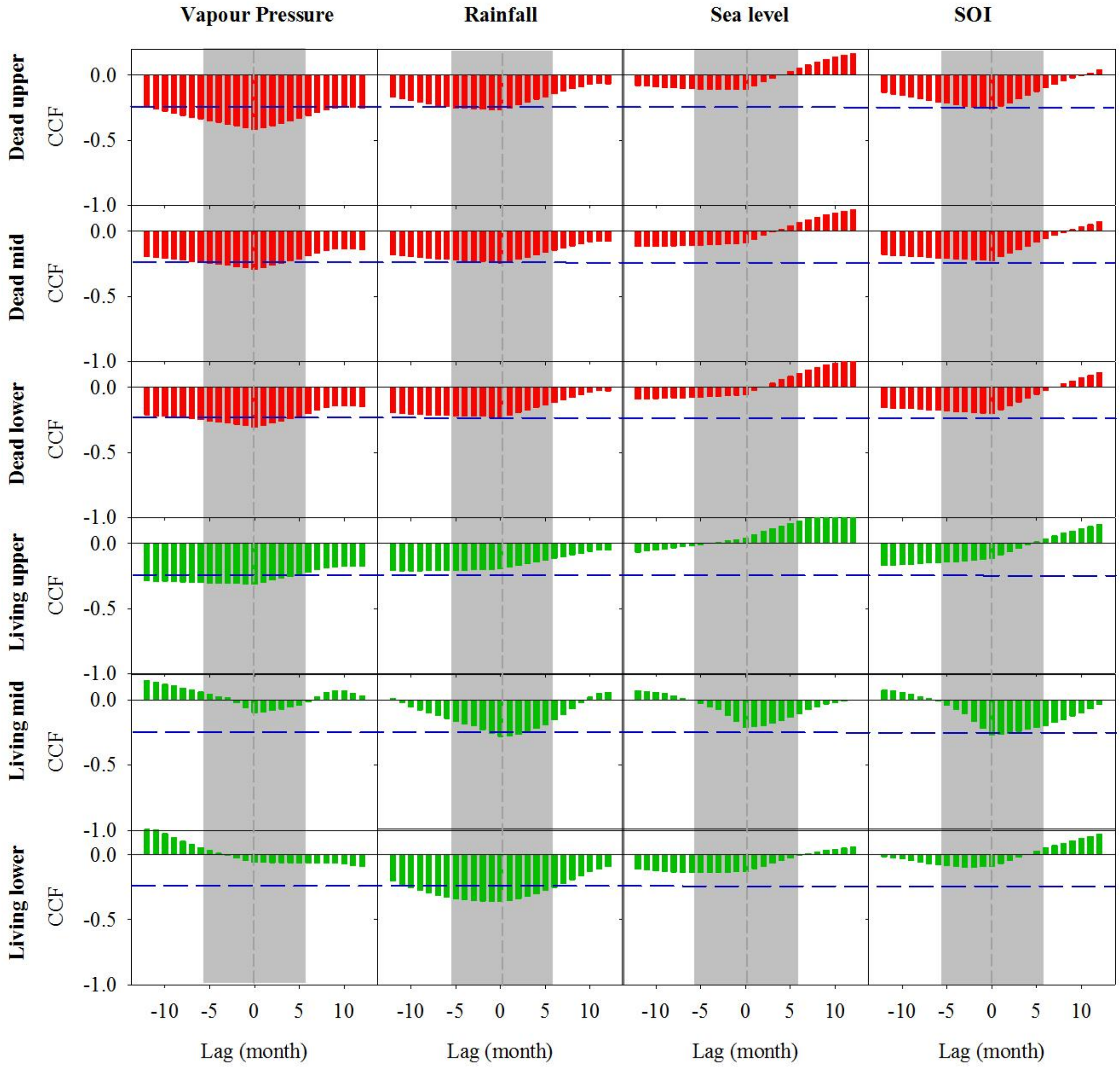


Figure 4. Cross correlation function (CCF) between Fe in wood samples and climate data at one month resolution over a 12 month period prior and post dieback. Wood samples are from the upper, mid and lower intertidal zones of the dead (red) and living (green) mangrove areas. Blue horizontal dashed lines indicate P< 0.01 with n=125. Grey dashed vertical lines at zero lag indicate dieback period and the grey bar represents the period during which the dieback event occurred.

Sediment cores had a similar pattern of decreasing Fe with depth in upper and lower intertidal areas, and in living and dead mangrove areas (Figure 5a). Dead mangrove areas were depleted ~~with~~in Fe by ~32% in the surface 50 cm and ~26% in the surface 1 m relative to the respective living mangrove areas in both the upper and lower intertidal area (Figure 5b, c and d). Fe relative concentrations were significantly higher in living mangrove areas compared to dead mangrove areas (Mann-Whitney Rank Sum Test, P < 0.001 for all depths).

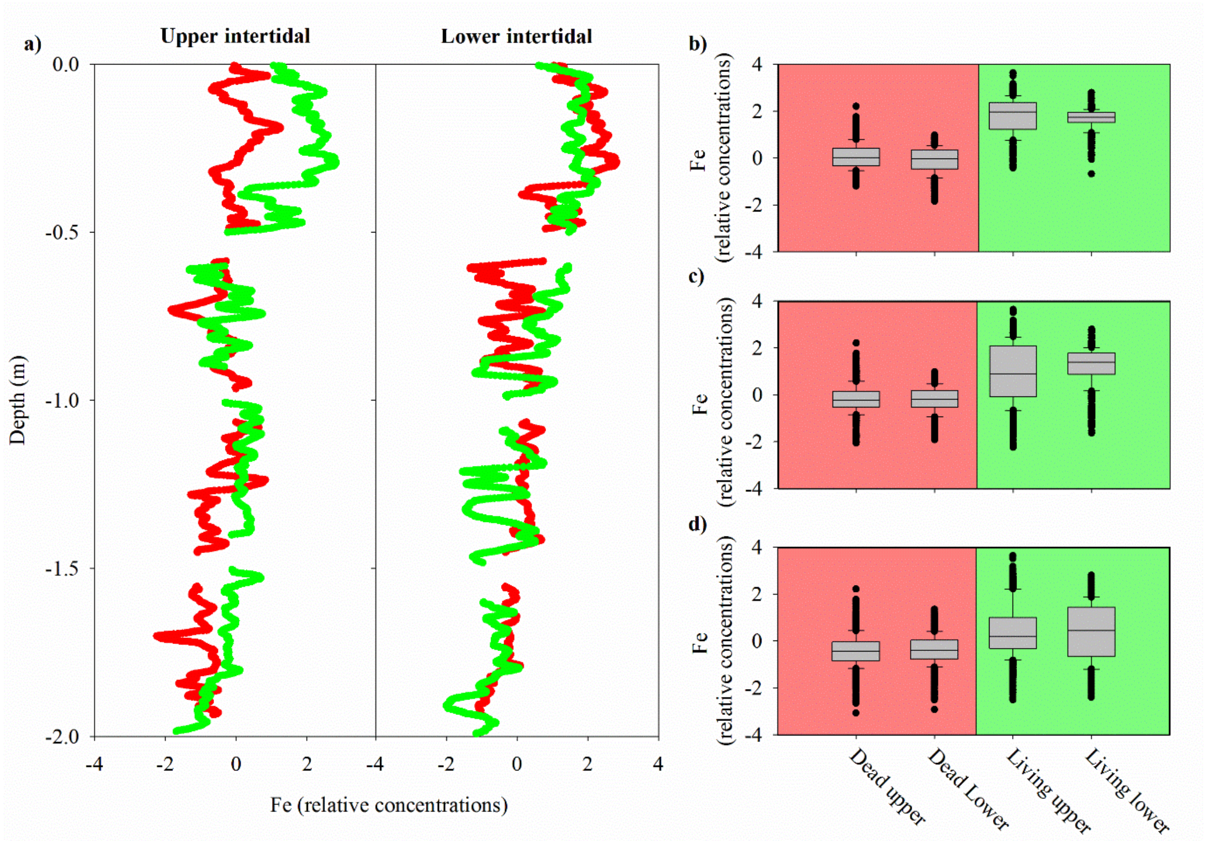


Figure 5. a) Fe relative concentrations in sediment cores to 2m depth from the upper and lower intertidal areas of living (green) and dead (red) mangroves in the Gulf of Carpentaria~~. b)~~, based on Itrax analysis. Box plots of normalised Fe relative concentrations from sediment cores to b) 0.5 m, c) 1 m and d) 2 m depth. The central horizontal line represents the median value, the box represents the upper and lower quartiles, and the whiskers represent the maximum and minimum values excluding outliers, i.e., black dots.

Chromium Reduced Sulfur (CRS) absolute concentrations, which provide a proxy for pyrite concentrations in sediment cores, were also lower overall in the dead ~~than~~ mangrove compared to the living mangrove area - by 36% in the upper and 38% in the lower intertidal zones~~. These~~ respectively (Figure 6). Although these differences were not significant (Mann-Whitney Rank Sum Test, P > 0.05~~) but~~), they were very similar to Itrax ~~differences (Figure 6). Dead mangrove sediment~~Fe trends. In the upper intertidal zone, CRS concentrations generally increased ~~from ~10 cm depth. Living mangrove CRS increased from ~30 cm depth compared to lower levels deeper~~with depth, while in the ~~soil profile, implying some recent CRS loss. In the~~ lower intertidal zone, CRS concentrations ~~were highest~~peaked from ~10 cm below the surface in both dead and living sediment samples and then decreased with depth.

Differences in CRS concentrations (in both the upper and lower intertidal zones) between the dead and living mangroves were most prominent in the upper ~60 cm of each core and tended to converge at greater depths (Figure 6).

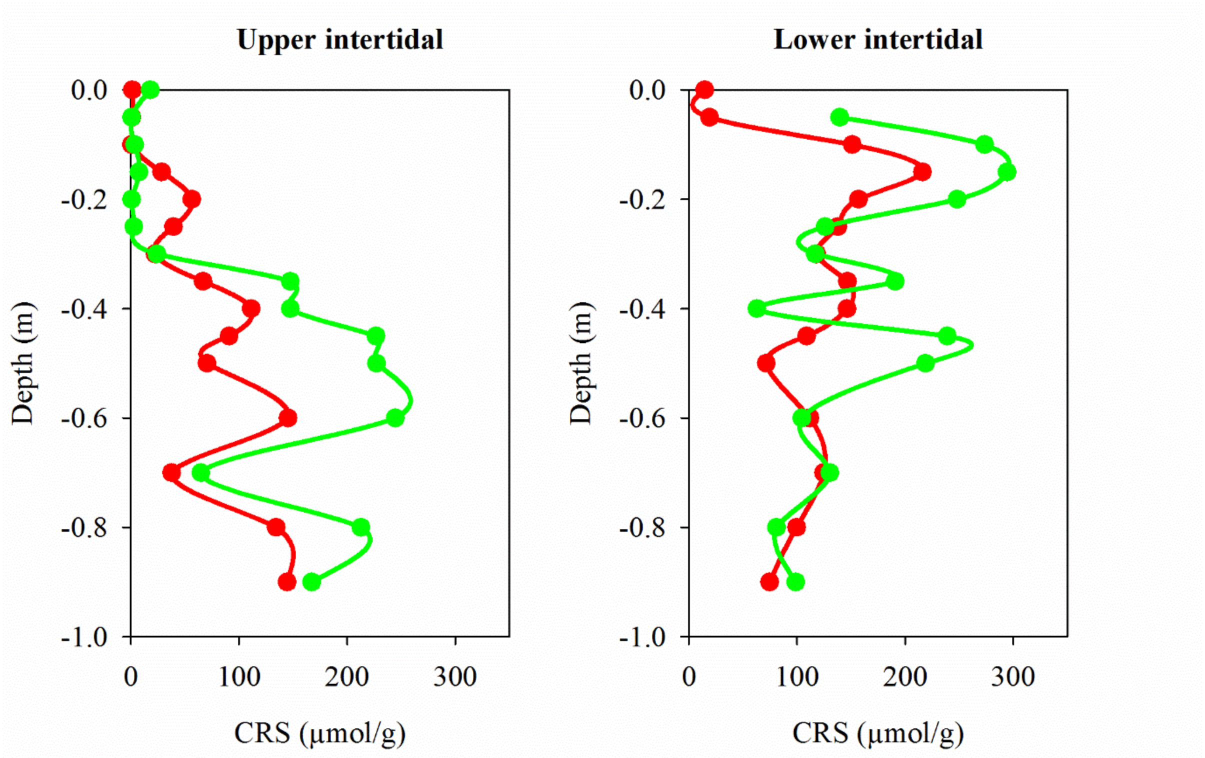


Figure 6. Chromium reducible sulfur (CRS) profiles (a proxy for pyrite) from sediment cores in dead (red) and living (green) mangrove areas in the Gulf of Carpentaria.

Water use efficiency (WUE) calculated from δ^{13}C decreased in all wood samples from 1983 to 2017 (Figure 7a), suggesting increasing water availability in the ~~Gulf of Carpentaria.~~study area. During the dieback event, median WUE values were higher in dead samples than in living samples, with the differences more pronounced in the upper intertidal zones (Figure 7b). Comparison of WUE in dead and living mangrove samples suggests lower water availability in the dead mangrove area (Figure 7b). However, the mean WUE values were compared from 1983 to 2017 and were not significantly different (T-test, $P = 0.2$) in dead and living mangrove areas. Groundwater salinity values were highest in the upper intertidal mangrove areas and lowest in the lower intertidal areas (Figure 7c). Salinities were not significantly different in the living and dead forest areas (T-test, $P = 0.913$).

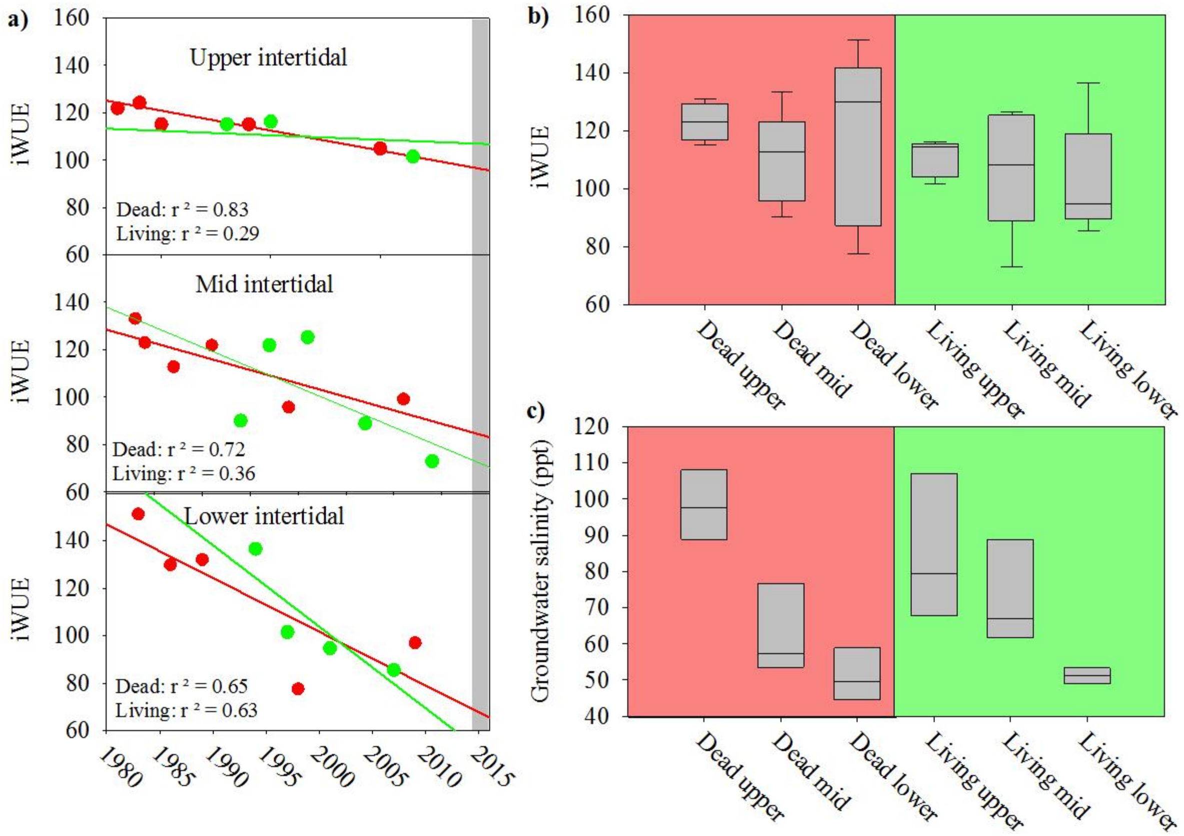


Figure 7. a) Changes to Water Use Efficiency (WUE) over time in wood samples collected from the upper, lower and mid intertidal zone in living (green) and dead (red) mangrove areas. The grey bar represents the mangrove dieback event. Error bars ~~represent standard error but~~ are not visible due to low error of individual samples. b) Box plot of water use efficiency in mangrove wood samples in dead and living mangrove areas in the upper, mid and lower intertidal zones. Sample size > 4 from each wood sample. The central horizontal line represents the median, the box represents the upper and lower quartiles, and the whiskers represent the maximum and minimum values. c) Box plot of groundwater salinity eight months post dieback event in dead and living mangrove areas in the upper, mid and lower intertidal zones. Sample size > 3 from each intertidal zone.

Normalised wood density values in the dead mangrove forest showed no change during the dieback event in the upper intertidal zone, but a decline in density values occurred in the mid and lower intertidal zones (Figure 8). In the living mangrove area, declines in wood density values occurred in the upper and mid intertidal zones during the mortality event, but no variation in density occurred in the lower intertidal zone (Figure 8).

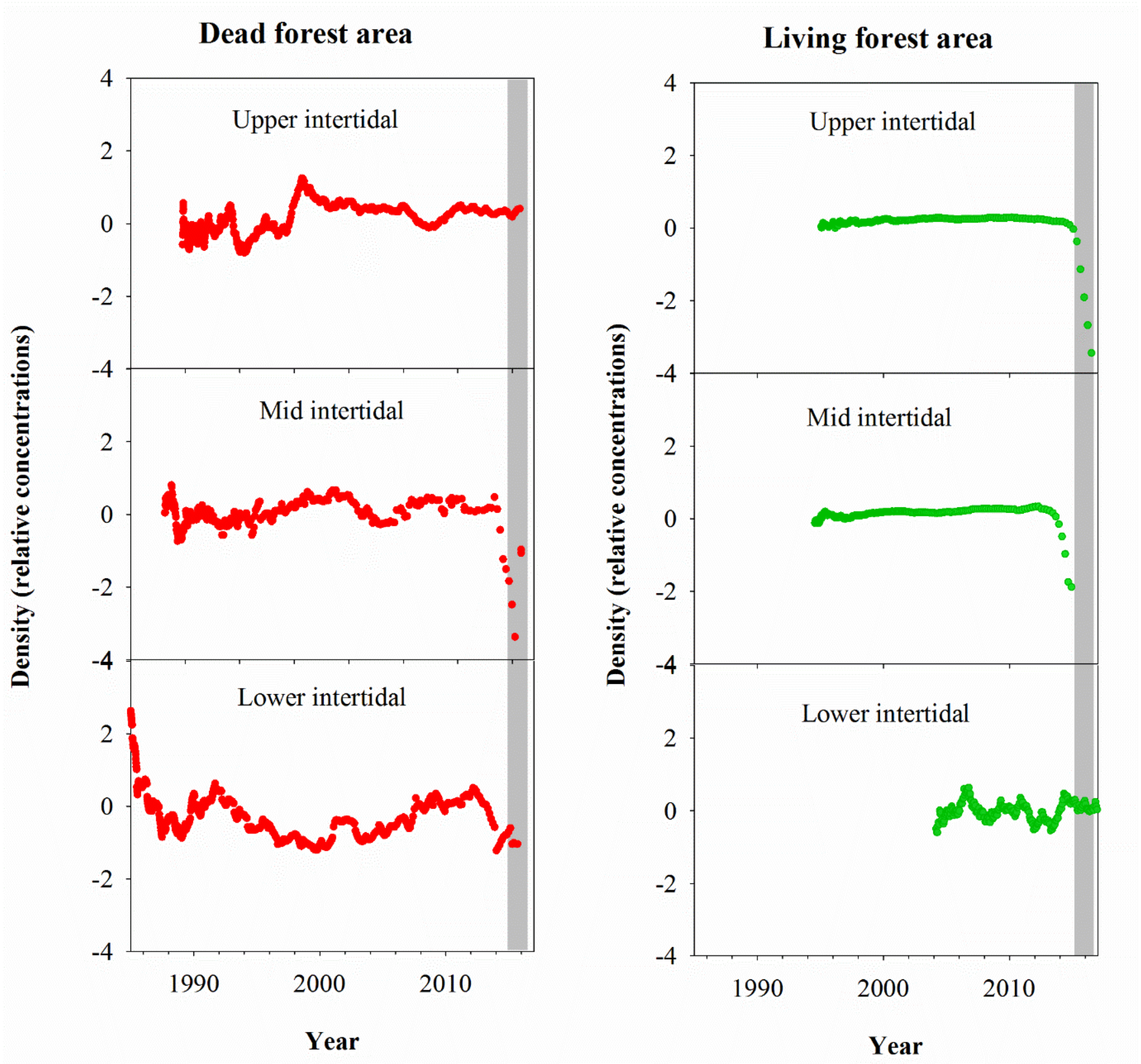


Figure 8. Normalised wood density (relative concentrations) in mangrove wood over time in living (green dots) and dead (red dots) mangrove areas of the Gulf of Carpentaria, Australia. The grey bar represents the time period of the dieback event.

Discussion

Evidence of ~~changes~~differences in water availability between living and dead forest areas from dendrogeochemistry

Multiple lines of evidence from wood samples and sediment cores ~~demonstrated~~point to substantial differences in water availability between the dead and living mangrove areas. ~~Most importantly~~For example, Fe trends in wood (comparative Fe gain) and sediment samples (comparative Fe loss) (Figures 3, 5 and 6) within the dead mangrove zone, both suggest the mobilisation of bioavailable Fe as Fe^{2}~~$^{+}$ when~~ $^{+}$.These observations are consistent with oscillations in sedimentary redox conditions, triggered by changes in water availability, promoting mobilisation of Fe - firstly as bioauthigenic pyrite is oxidised and ~~is also remobilised~~yet again during the reduction of ~~Fe^{3+} if~~Fe(III) oxide species when conditions return to being predominantly anaerobic (~~Johnson~~Figure 9). Increased oxygen diffusion into sediments during the period of low water availability likely resulted in the oxidation of bioauthigenic pyrite, which transformed into aqueous and bioavailable Fe^{2+} (e.g. Figure 9.2a; Johnston et al. 2011). With further oxidation, Fe^{2+} would likely have transformed into solid-phase Fe(III)oxides (Figure 9.2b). Such Fe(III) oxides are highly reactive and thus any subsequent short-term reduction (e.g. due to tidal inundation) would also result in re-mobilization of Fe as Fe^{2+} (Figure 9.2c). The fact that these trends in Fe that were observed in wood and soil samples were not observed for other elements analyzed by Itrax, supports the hypothesis that Fe trends were likely related to pyrite oxidation / redox oscillations (Appendix 1 & 2).

The most ~~likely~~probable cause for a shift from reducing to oxidising conditions in the sediment is a reduction in water content (Keene et al. 2014) associated with the intense El Niño of 2015/16 and associated low sea level and annual rainfall (Figure 2). Trends in wood density, mangrove growth rate and water use efficiency also reveal distinct differences in water availability between dead and living forest areas. Lower water availability in the dead mangrove forest area was also evident in lower plant growth rates and higher plant water use efficiency. Mangrove plant isotope data at the same sites from a study by Harada et al. (2020) also shows a similar trend with more enriched δ^{13}C values in the dead mangrove zone.

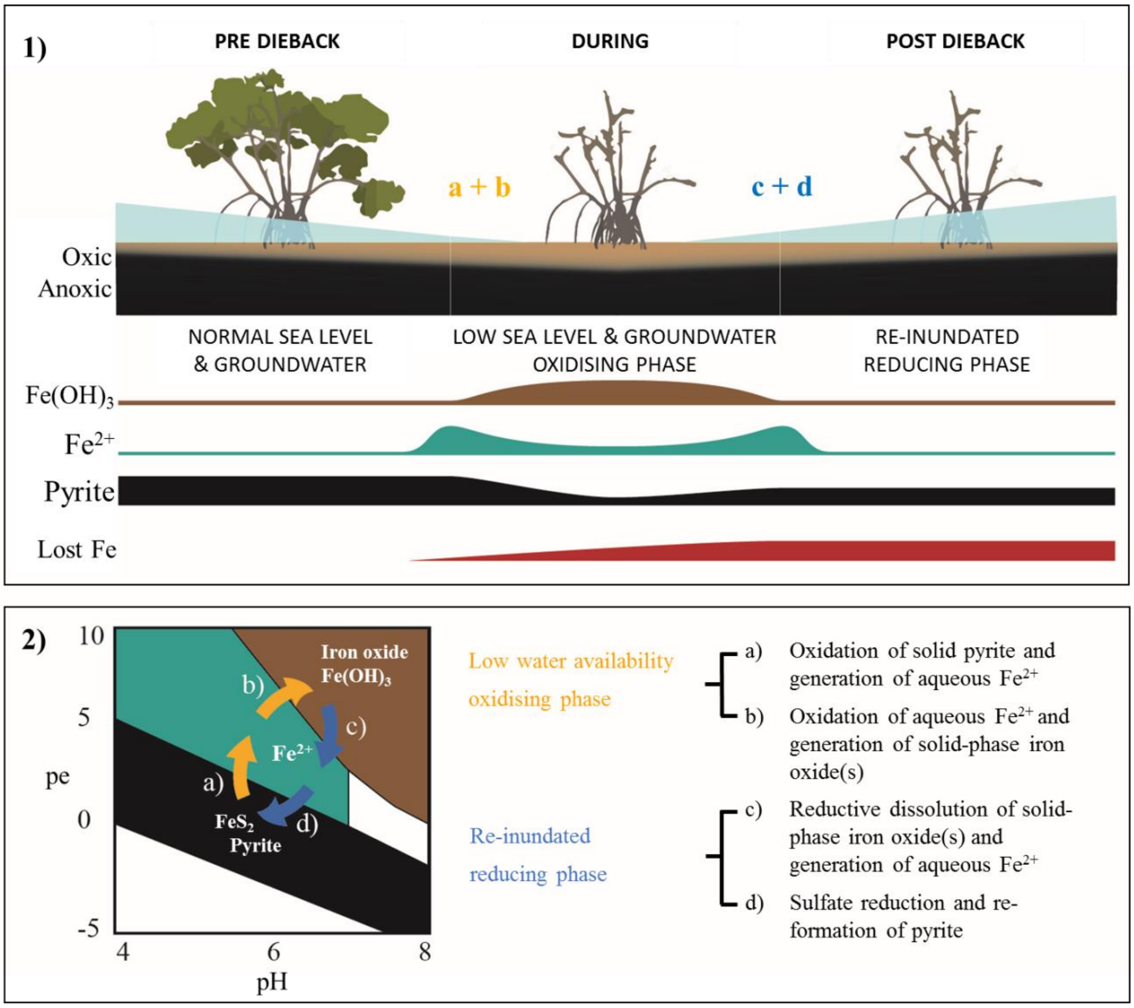


Figure 9. Conceptual diagram of Fe speciation under different sediment redox, pH conditions and 1) how speciation changes would be influenced by sea level and groundwater. Under initially elevated redox conditions due to low water availability 2) pyrite oxidation causes Fe transformation to (a) bioavailable Fe^{2+} and (b) particulate $Fe(OH)_3$, followed by eventual re-establishment of normal water availability / reducing conditions and (c) consequent reduction of $Fe(OH)_3$ and generation of Fe^{2+} followed by (d) sequestration of Fe(II) species via pyrite reformation.

Fe in wood –

Elemental composition from wood samples ~~provide strong evidence~~suggest that the mangrove forest experienced sharp changes in sediment geochemistry during the dieback phase (Figure 3). This is consistent with low sea level and low rainfall/groundwater reducing soil water content, leading to oxidation of Fe sulphide minerals and release of Fe^{2}~~$^{+}$.~~$^{+}$ (Figure 9.2a). The Fe ~~peak~~peaks in the dead mangrove area at the time of tree mortality were 30 to 90 fold higher than baseline Fe (the mean Fe concentration in the sample prior to the dieback event).

In the living mangrove area, an Fe peak 25 fold higher than baseline Fe was observed in the upper intertidal zone (Figure ~~1~~3). In the mid and lower intertidal areas of the living mangroves, Fe peaks were 4 and 3 fold higher than baseline respectively. In all living wood samples, Fe subsequently decreased after the dieback event, ~~which suggests~~thereby suggesting that Fe in new wood growth was ~~reduced~~diminished in ~~associated~~association with a return to sustained reducing sediment conditions and a concomitant ~~reduction~~attenuation in porewater Fe^{2+} availability~~.~~ (Figure 9.2 d).

Records of all climate variables are in resolution of months, but the chronology of Fe (based on ^{14}C dates) is in years. We therefore used time lag analysis to examine relationships between climate variables and Fe over a two year period (Figure 4). Fe wood concentrations ~~over time~~ were significantly correlated with both rainfall and vapour pressure in the dead and living forest areas (Figure 4). However, because all climate variables were strongly correlated to each other, we ~~were unable to~~cannot separate the relationships between individual climate drivers and Fe trends. We ~~anticipate~~speculate that the combination of low availability of fresh groundwater and low sea level ~~associated with~~during the strong El Niño event of 2015/16 are key drivers of the sediment redox conditions ~~which are~~, as reflected in wood Fe trends.

Considering the extreme increases in Fe concentrations observed in the wood samples ~~coinciding with~~during the dieback event, it is plausible that Fe toxicity could have ~~caused~~contributed to mangrove mortality. However, we cannot fully test this hypothesis in this study and are unaware of research testing the toxicity of Fe in *A. marina* at highly elevated concentrations of bioavailable Fe^{2+}. Alongi, (2010) found that Fe toxicity occurred in some mangrove species at high concentrations (~~100mmol~~100 mmol m^2 d^{-1} of water-soluble Fe-EDTA) that were approximately 2 fold higher than the Fe supply for maximal growth. However, *A. marina* (the dominant species affected by the dieback at the study site) ~~were unaffected by Fe at these concentrations. Fe concentrations can be~~appear relatively resilient to high ~~in acid sulphate soils, but~~porewater Fe^{2+}. For example, Johnston et al. (2016) observed no *A. marina* mortality ~~in Fe~~at porewater Fe^{2+} concentrations of 7-15 fold above normal~~. To our knowledge, no research has tested the toxicity of Fe in *A. marina* at highly elevated concentrations of bioavailable~~ ~~Fe^{2+}.~~ in a mangrove forest impacted by acid sulfate drainage. Considering that other mangrove species are affected by Fe toxicity at twofold the optimal Fe availability, it is ~~quite~~ possible that a 30-90 fold increase in Fe could ~~be~~have been an additional stressor to mangroves already stressed by low water availability.

~~**Fe in sediments** - Sediment cores also had~~While our observations suggest complex sedimentary redox conditions occurred in dead zone mangrove sediments during the dieback event, linking drought and low sea level to porewater Fe concentrations requires further investigation. For example, crab burrows and root systems can induce conditions that increase O_2 diffusion into sediments and thus influence Fe^{2+} mobility over tidal cycles (Nielsen at al., 2003; Kirstensen et al., 2008). Localised Fe(III) oxide dissolution can also occur in redox / pH micro-niches and under suboxic conditions (Fabricius et al. 2014; Zhu et al. 2012). Further research on the mechanisms of bioavailable Fe release and the thresholds for Fe toxicities in *A. marina* is required to clearly understand the impacts of porewater Fe on mangrove forests.

Fe in sediments

Sediment cores also displayed considerable differences in down core Fe profiles between living and dead mangrove areas (Figure 5a and b). Normalized Fe concentrations were lower in the upper 1 m of sediments in the dead mangrove area compared to the living, but were very similar in sediments deeper than 1 m (Figure 5a and b). Similar trends were also observed in CRS (a proxy for pyrite, FeS_2) sediment core profiles, which have ~40 % lower FeS_2 concentrations in the dead mangroves in the upper 60 cm of the profile, in comparison to the living mangrove sediments (Figure 6). ~~Although mangrove~~ The fact that differences in down core trends in Fe are most prominent in the upper parts of the sediment ~~conditions are highly heterogenous (Zhu et al. 2006, Zhu and Aller 2012),~~cores is consistent with decreases in water availability being more confined to the upper parts of the sediment ~~core results~~profile, whereas deeper sediments are ~~consistent with the wood data. Both sediment and wood suggest a general trend of iron sulphide mineral oxidation, leading to increased Fe mobility in the dead mangrove area compared~~more likely to ~~the living area~~have remained fully saturated.

Although mangrove sediment conditions are typically highly heterogeneous (Zhu et al. 2006, Zhu and Aller 2012), the sediment core results are broadly consistent with the wood data. The apparent mobilisation of Fe (loss from sediment and uptake in wood) was not observed in other elements (Appendix 1 & 2). Sediment Fe:Mn ratios in Itrax data displayed no clear differences between living and dead mangrove areas. These similarities may be because the sediment cores were taken after the dieback period when sediment geochemistry conditions returned to normal. Trends in Mn in the wood samples (Appendix 1) also show no clear differences between living and dead forest areas and the Fe:Mn ratios in the wood Itrax data overwhelmingly reflect the Fe concentrations.

Sediment Fe losses~~ due to variable periods of oxidation and reduction~~, as implied by comparative Fe profiles (Figures 3, 4 & 6), ~~would~~ also suggest ~~an~~a likely outwelling of Fe to the ocean. We estimate Fe outwelling by comparing FeS_2 concentrations in living and dead mangrove sediment cores based on the assumptions that (1) all Fe was originally in the form of FeS_2 and (2) tree Fe uptake is a minor loss pathway. The losses of Fe from the dead mangrove sediment would be equivalent to 87±163 mmol m^2 d^{-1}. The replication of CRS sediment cores (n = 4) greatly limits the accuracy of our estimates. However, these fluxes are remarkably similar to short-term porewater-derived dissolved Fe fluxes (79±75 mmol m^2 d^{-1}) estimated for a healthy temperate saltmarsh/mangrove system (Holloway et al. 2018), ~~building confidence in~~and provides some comparative restraint for our estimates.

If our sediment cores in dead and living mangroves ~~are~~were representative of changes within the entire dieback area (7400 ha), then total Fe losses from the dieback event could be equivalent to 87±163 Gg Fe. This loss is equivalent to 12 – 50% of global annual Fe inputs to the surface ocean from aerosols (Jickells et al. , Fung et al. 2000, Elrod et al. 2004). Since the surface ocean can be Fe limited, the consequences of Fe outwelling from this dieback event of such a magnitude ~~could~~may have had an ~~intense influence~~effect on ~~ocean~~ productivity in the Gulf of Carpentaria.

Wood density, growth trends and water use efficiency

~~– Trends in wood density also suggest differences in water availability between the living and dead mangrove areas.~~

Clear decreases in normalised wood density were observed during the mangrove mortality event (Figure 8). Similar to trends in wood Fe, the wood density values in the living and dead forest areas were correlated to climatic indicators (Appendix ~~1). Unlike most trees,~~ 3). In *A. marina* ~~has decreased wood density with decreased growth rates due to a reduction in large xylem vessels (Santini et al., 2012). Therefor~~ trees, the observed decreases in wood density likely ~~reflect lower~~indicates decreased growth~~ rates~~, however the annual scale resolution of ^{14}C ages prevented detection of this short term change in our growth rate data. These clear decreases in wood density prior to tree mortality are therefore an indication of stress since decreased growth rates of mangroves can be associated with decreased water availability (Verheyden et al. 2005, Schmitz et al. 2006, Santini et al. 2013) which is also directly related to increased salinity. Low rainfall conditions and increased temperatures increase both evaporation and evapotranspiration while reducing freshwater inputs (Medina and Francisco 1997, Hoppe-Speer et al. ~~2013), partially explaining tree stress prior to the dieback.~~2013).

Interestingly, no decrease in density was observed in the upper intertidal area of the dead mangroves (Figure 8), despite the clear increase in Fe during the dieback in this tree (Figure 3). This suggests that no change in growth occurred prior to tree mortality, implying rapid mortality in this case. The upper intertidal area of the dead mangroves may have been living at the limit of its tolerance range for water availability or salinity prior to the dieback, as suggested by extremely high groundwater salinities in the upper intertidal areas of dead and living mangrove forests eight months post dieback event (Figure 7c). No decrease in wood density was observed in the lower intertidal area of the living mangroves, which is consistent with both variation in concentration of Fe and tree growth rate data. Together, these data suggest that the lower intertidal area of the living mangroves was not exposed to the same conditions during the dieback event as areas in the dead mangroves higher in the intertidal zone (Figures 3, 8 & 9). These results suggest a gradient of water availability, from extremely low availability at the upper intertidal zone of the dead mangrove area to high/optimal availability at the lower intertidal zone of the living mangrove area. Since the elevation profiles are similar in the dead and living mangrove areas in the lower and mid intertidal areas (Figure 1), it is possible that the difference in Fe trends between the mangrove areas are associated with the influence of regional groundwater flows on sedimentary redox conditions.

Mean growth rates of trees in living (4.4 ± 3.6 mm yr^{-1}) and dead (5.3 ± 3.5 mm yr^{-1}) mangrove areas are similar to rates measured by Santini et al., (2013) in *A. marina* in arid Western Australia (4.1 to 5.3 mm yr^{-1}). However, there was ~10 fold greater variability because samples were collected from the upper, mid and lower intertidal zone, while Santini et al. (2012) sampled from the lower intertidal zone only. De-trended growth rate data showed no consistent differences in growth trends were identified between mangrove areas (Figure 8). The lower intertidal sample of the living mangroves grew more quickly during the dieback, which may suggest optimal conditions during this time. This may be due to increased nutrient availability due to litterfall inputs of organic matter from nearby stressed trees. All other ~~samples~~sampled trees show no indication of reduced growth prior to or during the mortality event (Table 1). We suggest that climatic conditions drove very low growth rates during the dieback event, as indicated by wood density data (Figure 8) and previous studies that found low growth during droughts (Cook et al., 1977; Santini et al., 2013).

A significant difference in mean δ^{13}C and WUE between living or dead mangrove areas was observed in the upper intertidal zone (T-test, P = 0.02), but not in the mid or lower intertidal zones (Figure 7b). This is consistent with the zonation of mangrove mortality which occurred predominantly in the upper intertidal areas (Duke et al., 2017). The consistent decrease in WUE suggests that water availability has been increasing over time in all intertidal areas since the 1990's (Figure 7a). This is supported by generally increasing precipitation since 1980's (Figure 2), which enhanced mangrove areas in the Gulf of Carpentaria prior to this dieback event (Asbridge et al. 2016). Therefore, climatic conditions were initially favourable over the plants lifetime and trees may have been insufficiently acclimated to withstand drought and low soil water availability during the dieback. Overall, this highlights the important role of extreme climatic events counterbalancing mangrove responses to gradual climate trends (Harris et al. 2018).

Differences in water availability between living and dead forest areas

We have no data to determine if regional groundwater availability was greater in living forest areas than dead forest areas during the mangrove dieback. No significant difference was observed in groundwater salinities 8 months post dieback. However, under normal sea level conditions (i.e. when groundwater samples were collected), tidal inundation is likely to be the predominant driver of groundwater salinities rather than groundwater flows. Duke et al. (2017) and Harris et al. (2017) provide strong evidence that water availability in the Gulf of Carpentaria was extremely low prior to and during the dieback event. In this study we have been able to build on this work by exploring links between changes in sediment geochemistry and low water availability.

We eliminate elevation as a potential driver of water availability in living and dead forest areas. Tree mortality occurred even in the lower intertidal zone of the dead mangrove area which are at the same elevation as the lower intertidal zone of the living forest area (see elevation DEM in Figure 1c). Since other potential water sources were comparable between the sites, differences in water availability were likely driven by groundwater availability. Groundwater flows have high spatial variability and have been demonstrated to be an important water source in mangroves from arid Australia. For example Stieglitz (2005) highlights that the interrelationships between confined and unconfined aquifers in the coastal zone can result in localised differences in groundwater flows. High resolution spatial analysis of groundwater salinities in living and dead forest areas during low sea level conditions would help to clarify how water sources may drive mangrove mortality.

Limitations -

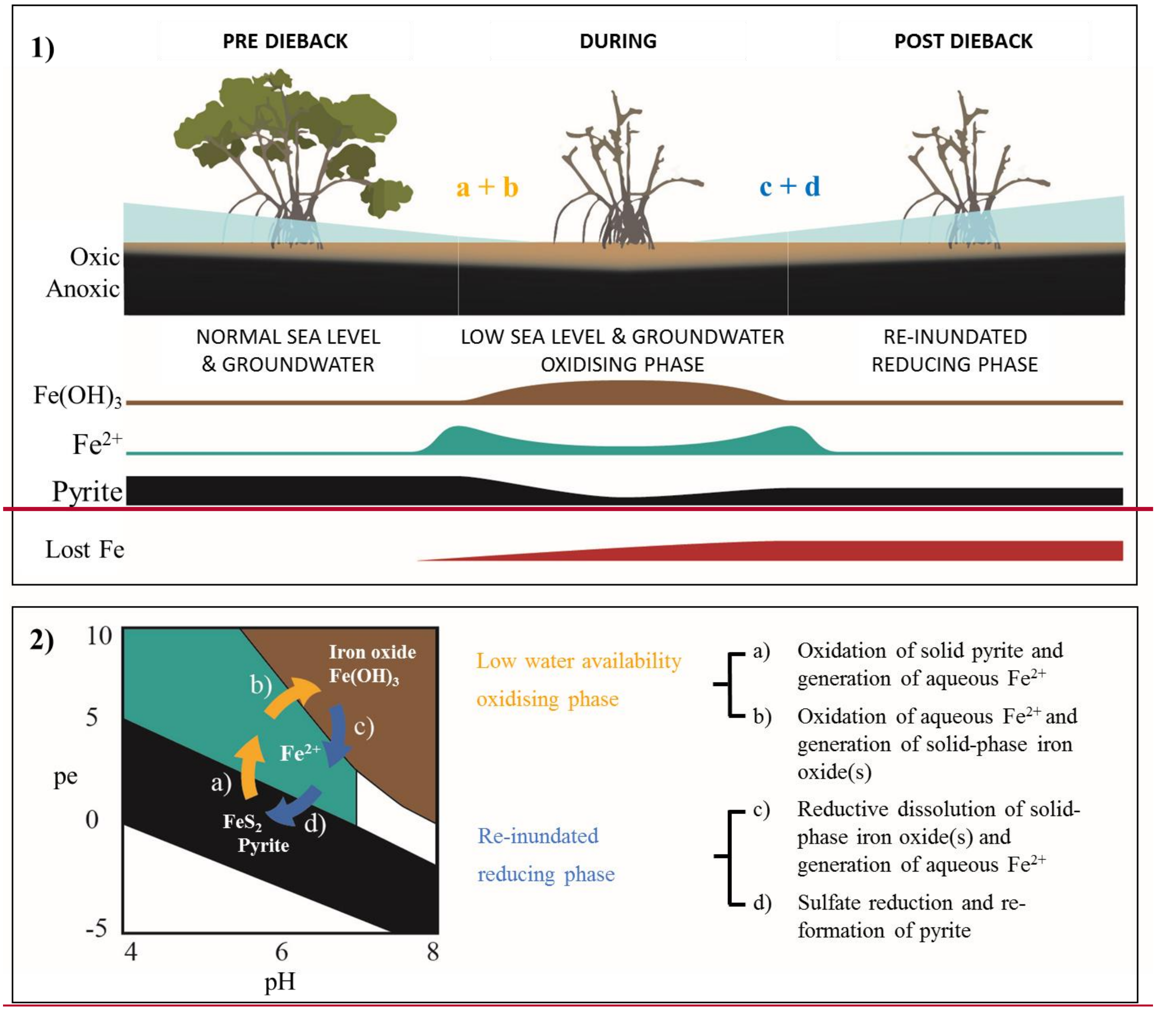
This study is inherently limited in its spatial extent. Thus, the differences in Fe between samples from living and dead mangrove areas may be due to causal factors ~~other than mangrove mortality.~~beyond the scope of this study. However, the consistency of results from multiple methods and divergent sample types ~~gives~~provides some confidence in the interpretation that recent changes in sediment geochemistry have occurred associated with extreme drought and low sea level events.

Our analysis benefited from the development of high precision ^{14}C dating of mangrove wood samples (with age uncertainties of 1-3 calendar years~~;~~ (1σ); see Table 1) that rely on atmospheric bomb ^{14}C content resulting from above-ground nuclear testing mostly in the late 1950's and early 1960's (Hua and Barbetti 2004a). The complexity in the wood development of *A. marina* creates uncertainties (Robert et al. 2011). *Avicennia marina* secondary growth is atypical, displaying consecutive bands of xylem and phloem which can result in multiple cambia (i.e. the tissue providing undifferentiated cells for the growth of plants) being simultaneously active (Schmitz et al., 2006; Robert et al., 2011). Furthermore, *A. marina* cambia display non-cylindrical or asymmetrical growth (Maxwell et al. 2018). These characteristics of *A. marina* atypical growth can influence our results as there is variation within each stem.

As younger wood grows on the exterior of the tree, errors associated with the estimated ages do not introduce uncertainty in the direction of trends but decrease the ability of finding correlated trends with climatic variables (Van Der Sleen et al. 2015). In spite of these uncertainties, the strong cross correlations displayed in Figure 4, with minimal time lag suggest that the dendrochronology results are robust, and that climate variability drives long-term Fe cycling in the coastal mangroves of the Gulf of Carpentaria.

Summary and Conclusions

~~Differences in sediment redox conditions during the dieback event were evident in all wood~~Wood and sediment geochemical data from living and dead mangrove areas~~. Patterns~~ suggest there were substantive differences in their comparative sediment redox conditions during the dieback event. Climatic data and patterns in Fe concentrations in wood and sediment samples~~ and climate~~, suggest that sediment oxidation occurred in combination with unprecedented low sea levels and low rainfall. As the elevation of dead and living mangrove areas was very similar, we suggest that the differences in tree survival between areas were probably due to higher groundwater availability in the living site. ~~The increased oxygen permeation into sediments likely resulted in the oxidation of bioauthigenic pyrite, which transformed into aqueous and bioavailable Fe^{2+}. If further oxidation occured, Fe^{2+} transforms into particulate Fe oxides. These Fe oxides are highly reactive and any subsequent short-term reduction (e.g. with tidal inundation) would also result in mobilization of Fe as Fe^{2+}.~~ Evidence of plant Fe uptake and losses of Fe from sediments are consistent with this hypothesized Fe mobilization~~.~~ associated with low water availability in sediments. The dieback event was likely a period of transitioning redox states in a ~~heterogenous~~heterogeneous sediment matrix, which resulted in areas of mangrove sediments with low water availability combined with porewaters enriched in bioavailable Fe (Figure 9).



~~**Figure 9. Conceptual diagram of Fe speciation under different sediment redox, pH conditions and a) how speciation changes would be influenced by sea level and groundwater. Under increased redox conditions b) pyrite oxidation causes Fe transformation to bioavailable Fe^{2+} and particulate Fe(OH)$_3$, consequent reduction of Fe(OH)$_3$**~~

Our data suggest that ~~the climate-driven changes in sediment geochemistry resulted in~~ extremely low water availability ~~and~~ drove the mangrove dieback. ~~Mangrove~~However, mangrove dieback may also be associated with increased concentrations of bioavailable Fe^{2+} in porewaters that occurred during this time of low water availability. Estimated losses of Fe from sediments were consistent with the observed plant uptake and suggest Fe mobilisation due to sediment oxidation (and subsequent reduction). This Fe mobilisation may also have led to significant Fe inputs to the ocean.

This study supports climate observations suggesting that the Gulf of Carpentaria dieback was strongly driven by an extreme ENSO event (Harris et al. 2017). Climate change is increasing the intensity of ENSO events and climate extremes (Lee and McPhaden 2010, Cai et al. 2014, Freund et al. 2019) and increasing sea level variability (Widlansky et al. 2015), which is impacting on mangrove forests in arid coastlines (Lovelock et al. 2017). This study therefore ~~revealed a geochemical mechanism that may also contribute to mangrove stress and dieback, building~~builds on the premise that the dieback event was associated with climate change (Harris et al. 2018). Further research is necessary to ~~confirm~~understand the role of Fe in ~~the mortality event~~tree mortalities, to constrain potential Fe losses to the ocean and from sediments and to understand thresholds for Fe toxicities in ~~*Avicennia*~~ A. *marina*.

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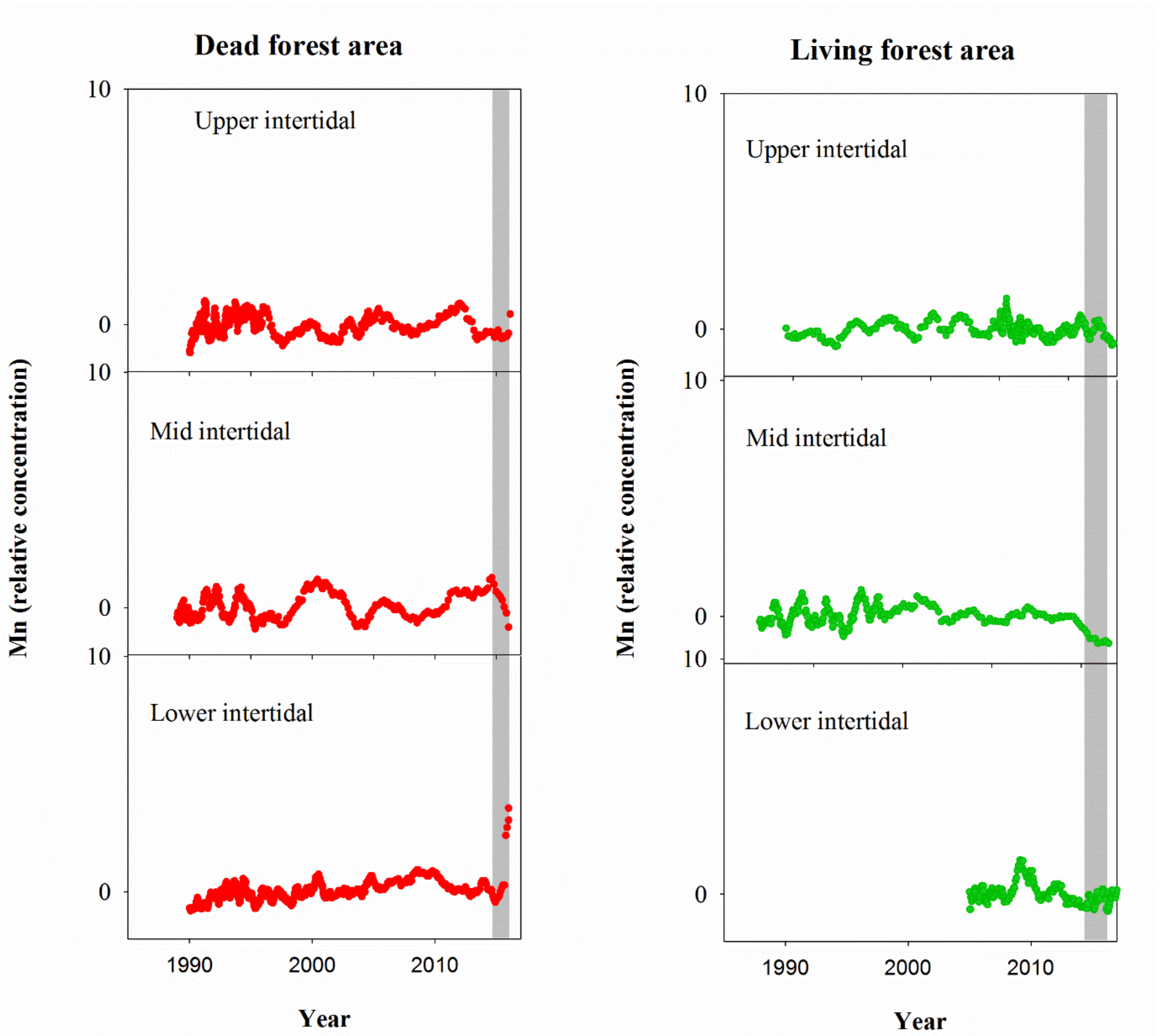
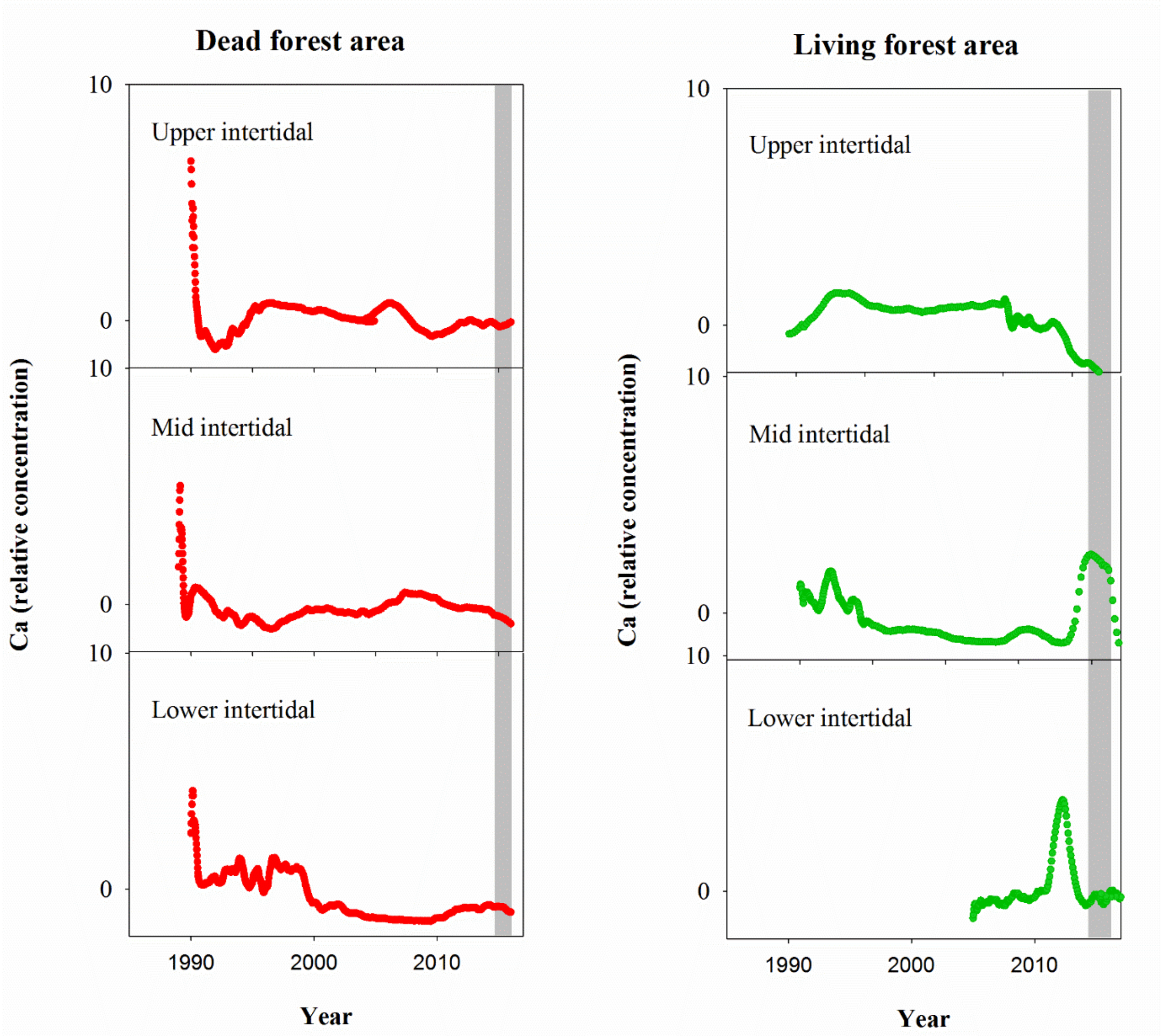
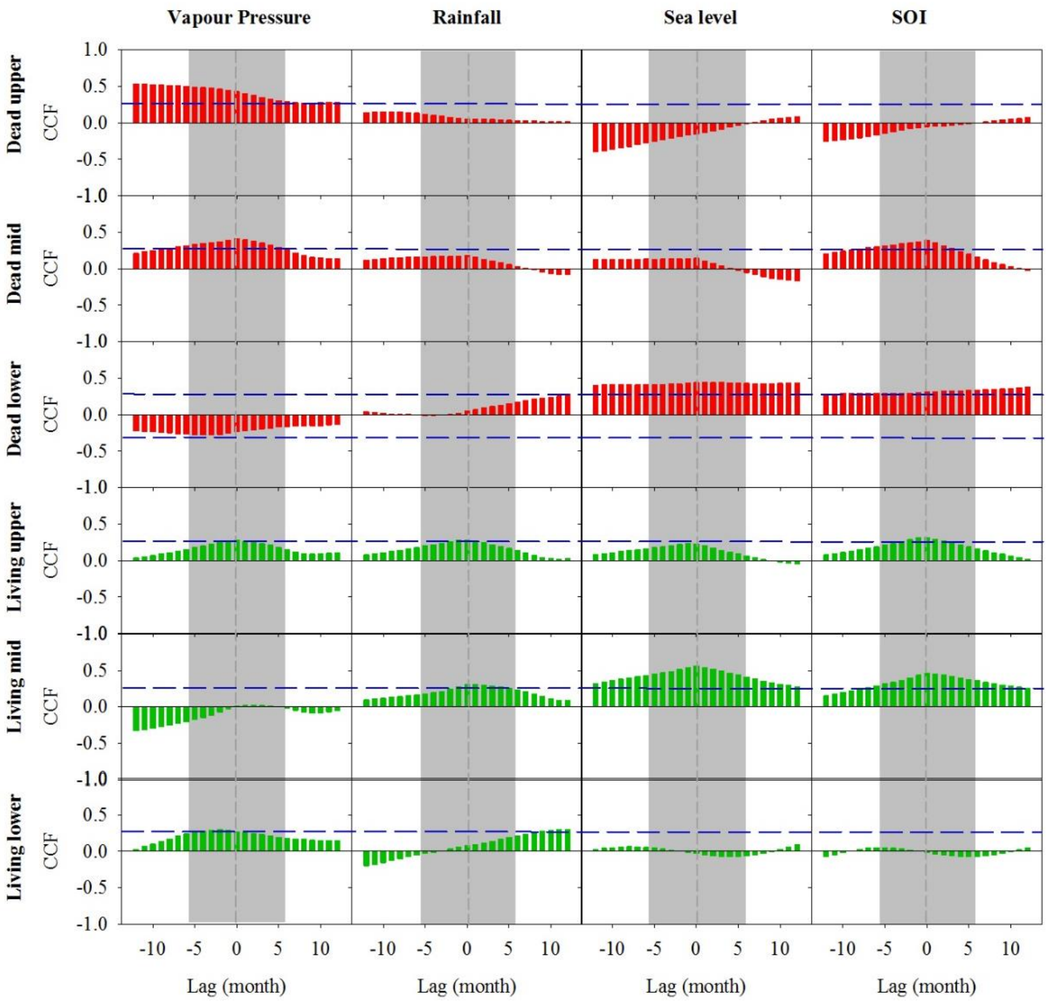
~~Appendix 1.~~



Appendix 1. Normalized Mn relative concentrations in mangrove wood over time in living (green dots) and dead (red dots) from upper, mid and lower intertidal areas of mangroves of the Gulf of Carpentaria, Australia. Grey areas indicate the dieback event.



Appendix 2. Normalized Ca relative concentrations in mangrove wood over time in living (green dots) and dead (red dots) from upper, mid and lower intertidal areas of mangroves of the Gulf of Carpentaria, Australia. Grey areas indicate the dieback event.



Appendix 3. Cross correlation function (CCF) analysis of the relationship between wood density and climate data over time at one month resolution over a 12 month period prior and post dieback. Wood samples are from the upper, mid and lower intertidal zones of the dead (red) and living (green) mangrove areas. Blue horizontal dashed lines indicate P< 0.01 with n=125. Grey dashed vertical lines at zero lag indicate dieback period.