

An examination of the ability of coral geochemical records to reconstruct suspended sediment loads to the Great Barrier Reef lagoon

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CONTENTS

List of Tables.....	ii
List of Figures.....	ii
Acronyms	iii
Abbreviations	iii
Acknowledgements	iv
Executive Summary	1
1.0 Introduction	2
2.0 Methodology.....	3
3.0 Results and Discussion	7
4.0 Recommendations and Conclusion	18
References.....	19

LIST OF TABLES

Table 1:	Details of coral cores collected and analysed in this study.....	3
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LIST OF FIGURES

Figure 1:	Map showing the coral coring locations and the location of the Burdekin River.	4
Figure 2:	Map showing the detailed coral coring locations including (A) Magnetic Island, (B) Havannah Island, (C) Pandora Reef and (D) Pelorus Island.	5
Figure 3:	Timeseries plots of coral Ba/Ca ratios for the cores collected from Magnetic Island for Geoffrey Bay (top graph) and Nelly Bay (bottom graph). Note that only NEL29A displays clear relationships with Burdekin discharge events.....	9
Figure 4:	Timeseries plots of coral Ba/Ca ratios for the cores collected from Havannah Island (top graph) and Pandora Reef (bottom graph). Note that only the HAV32A and PAN31B cores display clear relationships with Burdekin discharge events (also note bottom scales are not comparable across graphs – for direct comparisons see Fig. 6).....	10
Figure 5:	Timeseries plots of coral Ba/Ca ratios for the cores collected from Pelorus Island. Note that only PEL30A displays clear relationships with Burdekin discharge events.	11
Figure 6:	Timeseries plots of coral Ba/Ca ratios for the cores that displayed clear trends with Burdekin River discharge.	11
Figure 7:	Correlation plots of the annual peak Ba/Ca ratio with sediment load (top graph) and with total Burdekin discharge (bottom graph) for the HAV32A core.	12
Figure 8:	Correlation plots of the annual weighted sum (minus background ratio) Ba/Ca ratio with sediment load (top graph) and with total Burdekin discharge (bottom graph) for the HAV32A core.....	13
Figure 9:	Correlation plots of the mean flood Ba/Ca ratio with sediment load (top graph) and with total Burdekin discharge (bottom graph) for the HAV32A core.....	14
Figure 10:	Correlation plots of the annual peak Ba/Ca ratio with sediment load (top graph) and with total Burdekin discharge (middle graph) and Burdekin peak daily discharge for the NEL29A core.....	15
Figure 11:	Correlation plots of the annual peak Ba/Ca ratio with sediment load (top graph) and with total Burdekin discharge (middle graph) and Burdekin peak daily discharge for the PAN31B core.	16
Figure 12:	Graphs showing the mixing of barium concentration over the salinity gradient in the 2008 and 2009 flood plumes.	17

ACRONYMS

DOE Department of the Environment
GBR Great Barrier Reef
NESP National Environmental Science Programme
RRRC Reef and Rainforest Research Centre Limited
TWQ Tropical Water Quality
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GBR Great Barrier Reef
NESP National Environmental Science Programme
RRRC Reef and Rainforest Research Centre Limited
TWQ Tropical Water Quality

ABBREVIATIONS

B/Ca boron to calcium ratio
Ba/Ca barium to calcium ratio
LA-ICPMS Laser Ablation Inductively Coupled Mass Spectrometry
Mn/Ca manganese to calcium ratio
Sr/Ca strontium to calcium ratio
SST Sea surface temperature
U/Ca uranium to calcium ratio
Y/Ca yttrium to calcium ratio

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EXECUTIVE SUMMARY

Certain trace elemental ratios in coral cores (Ba/Ca, Y/Ca and Mn/Ca) have long been linked to terrestrial runoff and used to reconstruct changes in river loads over time. However, limited catchment/river data exist to directly compare with these coral ratios and so they remain somewhat unvalidated. This study examined the variability of these coral ratios in duplicated coral cores collected from 5 locations along a gradient of river discharge for which long term records exist of river discharge and sediment load. The study found that no correlation could be established between the river discharge/sediment load and with coral Y/Ca and Mn/Ca ratios and so these were discarded from further analysis. The coral Ba/Ca ratio displayed trends consistent with regional (Burdekin) river discharge in 4 of the 10 corals analysed and the records showed poor replication across individual locations. Hence coral core records should be carefully analysed to examine if they are recording regional-scale trends or are more reflective of localised scale changes before they can be properly interpreted. The Ba/Ca ratio in the corals that showed trends consistent with river floods were somewhat correlated with sediment load but stronger correlations were observed with total river freshwater discharge. A closer inspection suggests that the coral Ba/Ca ratios on the Great Barrier Reef may in fact be recording changes in salinity/terrestrial freshwater input rather than sediment load. A reanalysis of the full (i.e. 1650 to ~2000) Havannah Island coral core (previously analysed by McCulloch et al., 2003) would be required to confirm our contention.

1.0 INTRODUCTION

Massive *Porites* spp. corals can live for hundreds of years constructing annual skeletal growth bands which faithfully record high resolution changes in the chemistry of the surrounding seawater. As a result the geochemistry of coral skeletons have been analysed to reconstruct past variability in sea surface temperature, seawater salinity and terrestrial runoff. Previous studies have shown that the ratios of Ba/Ca, Y/Ca and Mn/Ca in coral skeletons provide evidence for increased sediment fluxes to the Great Barrier Reef (GBR) (McCulloch et al., 2003; Lewis et al., 2007, 2012; Jupiter et al., 2008) and the Ba/Ca ratio has been applied to examine sediment flux variability in other parts of the World including Kenya (Fleitmann et al., 2007), Hawaii (Prouty et al., 2010) and Guam (Prouty et al., 2014). However, the coral cores analysed in the GBR studies were collected prior to (or at the beginning of) long-term river monitoring programs and so no direct comparisons could be drawn between the trace element composition of the coral and the sediment loads delivered from the adjacent river catchments. Furthermore, some studies have revealed that coral Ba/Ca ratios display 'anomalous peaks' that do not correspond to river runoff (Sinclair, 2005; Lewis et al., 2012) and hence the reliability of this proxy is questionable. A validation of these coral proxies is required particularly given that long-term records produced using them have been frequently cited as evidence for increased sediment discharge to the GBR and elsewhere.

A transect of coral cores have been collected from Magnetic Island, Havannah Island, Pandora Reef and Pelorus Island on the central GBR in August 2012. These sites receive varying influence from the Burdekin River flood plume (i.e. the sites closer to the Burdekin mouth receive more terrestrial materials than the sites further away: see Bainbridge et al., 2012) and provide an opportunity to compare the incorporation of trace elements in the corals from the different locations across single flood events. Moreover, a recent publication has calculated annual suspended sediment loads (with improved statistical techniques which include uncertainty bounds) exported from the Burdekin River using monitoring data from 1987 to 2010 (Kuhnert et al., 2012). These loads along with other sediment load data from the 1973/74, 1974/75 (i.e. pre-Burdekin Falls Dam: the dam now traps a considerable proportion of the upstream sediment load: Lewis et al., 2013), 2010/11 and 2011/12 water years can be directly correlated to the coral trace element records.

2.0 METHODOLOGY

In August 2012, a series of coral cores (duplicate cores from separate *Porites* colonies) were collected from Magnetic Island (Geoffrey and Nelly Bays), Havannah Island, Pandora Reef and Pelorus Island by staff from the Australian Institute of Marine Science and James Cook University (Table 1; Figs. 1 and 2). The cores range between 40 and 80 cm in length which cover periods ranging from 1934 to 2012 (most cores cover 1985 to 2012). Two cores from each site were selected and sliced into 7 mm thick slabs and X-rayed and photographed. The core slabs were then cut into pieces to fit into the cell for the Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICPMS) analysis. Prior to analysis each piece was cleaned in analytical grade sodium hypochloride for ~24 hours before being repeatedly rinsed and sonicated in milli-Q water (repeated 3 times) according to the method developed by Nagtegaal et al. (2012). This cleaning step is designed to remove residual organic components from the skeleton.

Table 1: Details of coral cores collected and analysed in this study

Collection Date	Site	Core ID	Core Length (cm)	Latitude degrees	Latitude minutes	Longitude degrees	Longitude minutes	Estimated water depth
9/08/2012	Geoffrey Bay, Magnetic Island	GFB-33	52	19	9.292	146	51.965	3-4 m
9/08/2012	Geoffrey Bay, Magnetic Island	GFB-34	58	Not taken but likely close to GFB33B				3-4 m
9/08/2012	Nelly Bay, Magnetic Island	NEL-29	40	19	9.874	146	51.217	3-4 m
9/08/2012	Nelly Bay, Magnetic Island	NEL-39	43	19	10.138	146	51.011	3-4 m
11/08/2012	Havannah Island	HAV-32	70	18	50.106	146	32.642	3 m
11/08/2012	Havannah Island	HAV-34	59	18	50.222	146	32.898	3 m
10/08/2012	Pandora Reef	PAN-31	58	18	48.769	146	25.611	5.7 m
10/08/2012	Pandora Reef	PAN-36	47	18	48.766	146	25.617	4.5 m
12/08/2012	Pelorus Island	PEL-30	80	18	32.309	146	29.393	5 m
12/08/2012	Pelorus Island	PEL-33	64	18	32.268	146	29.468	5 m



Figure 1: Map showing the coral coring locations and the location of the Burdekin River.

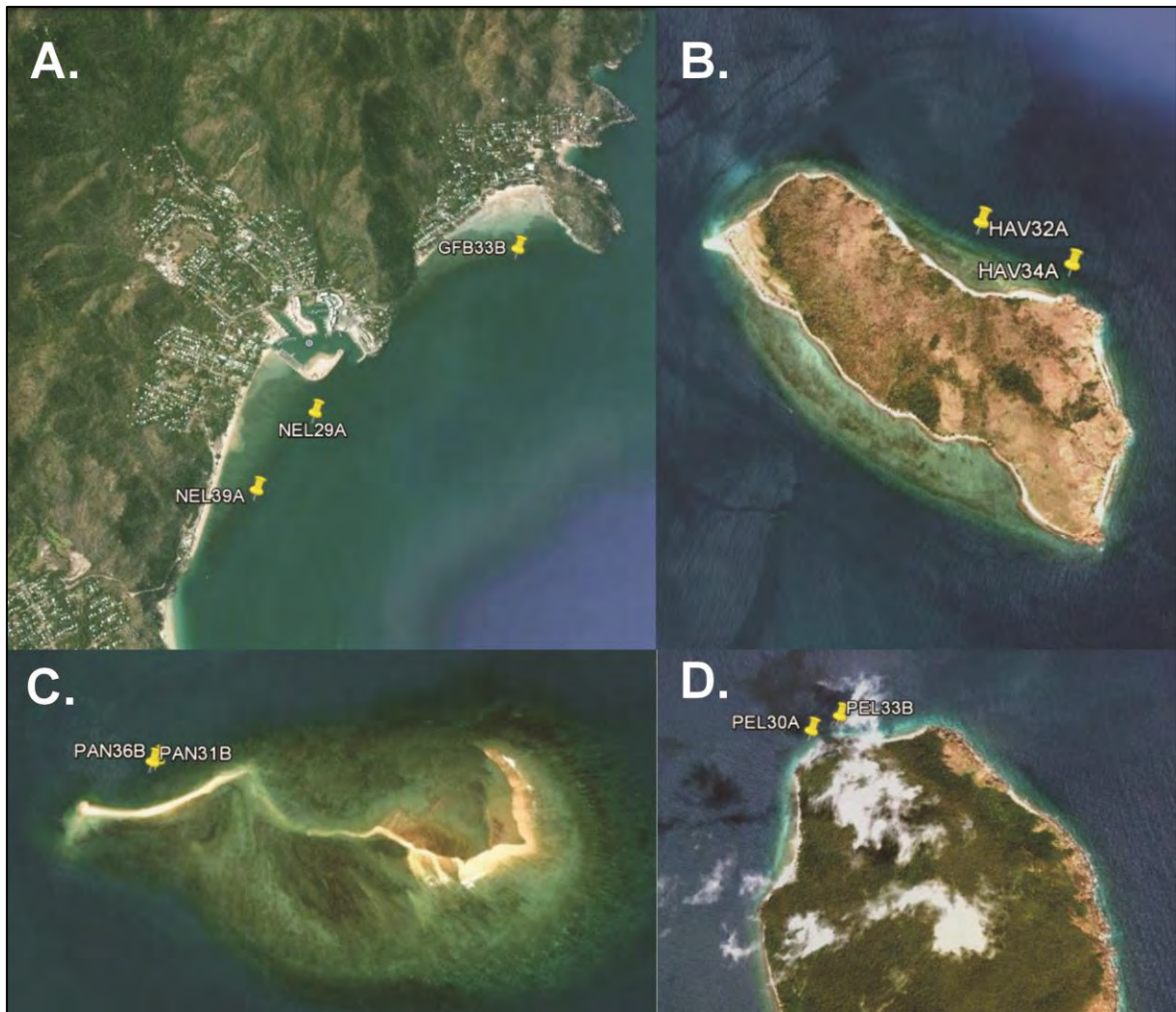


Figure 2: Map showing the detailed coral coring locations including (A) Magnetic Island, (B) Havannah Island, (C) Pandora Reef and (D) Pelorus Island.

The LA-ICPMS analytical methods were identical to those reported in Jupiter et al. (2008). Briefly, the coral blocks were mounted on a stage containing standards and analysed using a Varian 820 inductively coupled mass spectrometer. The resultant data were then normalised to ^{43}Ca using a Varian Laser Scanning analysis software program developed internally at the Australian National University (ANU)'s Research School of Earth Sciences (by L. Kinsley). Data were then smoothed using a 10 point running mean to reduce the influence of outliers, followed further by a 10 point mean to reduce data volume (Jupiter et al., 2008). Replicate tracks were performed on selected coral slices to confirm that features of the trace element record represented true incorporation into the coral skeleton and were not a result of surface contamination (although note a pre-cleaning ablation run was performed before each analysis).

The chronology of the coral geochemical records was assigned using prominent coral luminescent lines as markers for large flood events in the region (e.g. 1970, 1974, 1991, 1997, 1998, 2008, 2009, 2011) (Lough et al., 2015). Geochemical proxies of sea surface temperature (SST) (Sr/Ca, U/Ca and B/Ca ratios) were then used to match peak ratios with

winter (8th August) and trough values with summer (8th February). These dates represent the mean of peak and trough sea surface temperatures from the IGOSS SST dataset for the region (<http://www.irdl.ideo.columbia.edu/SOURCES/.IGOSS/.nmc/>). The combination of these proxy markers allows a robust chronology to be established and also allows a fixed date to be assigned to the minimum and maximum SST's to capture seasonal coral growth rates (see Jupiter et al., 2007; 2008). The timing of the intervening data points is approximated by assuming a uniform growth rate (i.e. by linear approximation). We note however that due to the complex nature of coral skeletal growth, the trace element signal assigned to each decimal day also represents the integration of aragonite deposition over several weeks of growth. After depositing new aragonite skeleton on the outer surface layer over a period of days, *Porites* corals continue to thicken their skeletons through a more diffuse process by adding layers (Barnes and Lough 1993). This thickening process produces a smoothing effect on trace material incorporation on at least a weekly timescale that tends to reduce the overall amplitude and broaden the shape of a sharp environmental signature (e.g. river flood) (Barnes et al. 1995). In addition during the summer months when the extension rates are greatest there is likely to be an enhanced broadening of the summer period.

Once a robust coral chronology had been developed time series plots were constructed to examine the replicability of the coral geochemical proxies at each site. The corals that recorded a clear signal related to Burdekin River floods were then used for further analysis (the corals that did not display such trends were discarded from further analysis). The peak Ba/Ca ratio for each year for the three coral cores that displayed relationships with Burdekin River flow was recorded (i.e. identical approach to that used in McCulloch et al., 2003) and compared with the corresponding measured sediment load from the Burdekin River as well as annual and peak daily discharge. Further detailed examination of other statistical approaches was performed on the HAV32A core which included annual mean Ba/Ca, mean Ba/Ca for each flood event, sum of the Ba/Ca for each flood event, a weighted/accumulation Ba/Ca ratio (i.e. mean Ba/Ca for each flood event multiplied by the event days), weighted/accumulation Ba/Ca minus Ba/Ca background.

3.0 RESULTS AND DISCUSSION

The coral Y/Ca and Mn/Ca ratios (data not shown) did not appear to respond to flood events and preliminary analysis (using peak values for each year or annual mean values) did not reveal any correlation with sediment load or discharge from the Burdekin River. Hence the remainder of this report will focus primarily on the Ba/Ca ratio. Interestingly, the replication of the Ba/Ca ratio between the two coral cores from each location was poor and many of the corals (i.e. GFB33B, GFB34A, NEL39A, HAV34A, PAN36B and PEL33B) did not show clear trends with regional discharge events (Figs. 3, 4 and 5). This poor replication highlights that the corals are responding to their local environmental conditions and that not all corals respond to regional factors. The four coral cores that displayed clear trends with river discharge (PAN31B, NEL29A, HAV32A and PEL30A) also displayed close correlation in Ba/Ca peaks (Fig. 6). In fact, those same three corals also showed no influence of the upper coral tissue layer on coral geochemistry which greatly affected the other corals (i.e. from 2007-2008 the Ba/Ca ratios become greatly elevated). The reason for this difference is unknown but highlights that the new cleaning approach applied (Nagtegaal et al., 2012) was effective for the coral cores of interest. Furthermore these data highlight that not all *Porites* corals are suitable for reconstructing regional signals. These reasons are also unclear but may relate to a number of factors including species, feeding (autotroph versus heterotroph) and hydrodynamic differences. Similar findings were made on coral cores from the Whitsunday Islands (Lewis et al., 2012). As the purpose of this research was to determine the ability of coral geochemical proxies to reconstruct regional sediment loads, we will now focus only on the corals that displayed the regional signals.

The comparison of the Ba/Ca ratios for the corals that responded to regional river discharge show the Nelly Bay coral consistently had the higher peaks (Fig. 6) which is to be expected given that this location is closer to the Burdekin River mouth (Fig. 1). Importantly, barium concentrations measured in the Burdekin River flood plumes during 2008 and 2009 at the same coral core locations were in the same range as those measured in the coral cores during those years (10-13 ppm: Fig. 12). Hence the corals are faithfully recording the variability of the barium content in the seawater.

A detailed statistical analysis of the correlation of the coral Ba/Ca ratios and the sediment loads on the HAV32A coral core consistently showed that the peak Ba/Ca ratio best correlated with sediment load and also with Burdekin discharge compared to the other approaches (Figs. 7, 8 and 9). This finding was unexpected as the weighted sum approach was originally thought to best capture the full barium accumulation over the flood event and account (or normalise) for the variability in stream flow duration. However, in all cases the correlation between annual peak coral Ba/Ca and total Burdekin discharge was higher than for the sediment load. This result was also reflected in the correlations from the NEL29A (Fig. 10) and PAN31B (Fig. 11) cores. Therefore the question becomes: Is the coral Ba/Ca ratio recording variations in sediment load or salinity/terrestrial water runoff?

The first approach to address this question is to examine flood years of similar water discharge but vastly different sediment loads. In that regard, the years such as 1997 (sediment load = 8.4 Mt, discharge 8.7 GL) and 1998 (sediment load = 5.0 Mt, discharge 9.0 GL) can be compared as well as the 2008 (sediment load = 14.8 Mt, discharge 27.5 GL),

2009 (sediment load = 10.9 Mt, discharge 29.4 GL) and 2011 (sediment load = 6.2 Mt, discharge 34.8 GL) water years. When these years are examined, the Ba/Ca in the NEL29A coral does not follow the pattern that would be expected if it was primarily related to the regional sediment load from the Burdekin River (i.e. it would be expected that Ba/Ca in 2011 to be lower than 2008 and 2009 and lower in 1998 compared to 1997) (Fig. 6). However, it is possible that the coral in Nelly Bay is also responding to more localised variations in either salinity or sediment load (i.e. from Townsville-based rivers or Gustav Creek in Nelly Bay). While the HAV32A and PAN31B do show some of the variations that would be expected if sediment load was the primary cause of Ba/Ca ratios (i.e. 2008 Ba/Ca peaks are higher than 2011), other comparisons such as 1997 and 1998 (i.e. 1997 peaks should be much higher than 1998) and 2011 and 2009 (i.e. 2009 peaks should be higher than 2011) do not display the expected trend (Fig. 6). Hence this provides a second line of evidence that Ba/Ca ratios may be responding to salinity/terrestrial freshwater discharge rather than sediment load.

A third line of evidence relates to direct measurements of barium concentrations in riverine flood plumes. The coral Ba/Ca-sediment load relationship is based on the hypothesis that barium is desorbed from clay particles in the esturine mixing zone (i.e. as freshwater in the flood mixes with seawater) (see McCulloch et al., 2003). In fact, monitoring of large Burdekin River flood plumes in 2008 and 2009 showed that barium concentrations acted conservatively (i.e. the barium concentration becomes further diluted as the salinity content increased) in the plume waters along the salinity gradient and no evidence for desorption of barium was measured (Fig. 12).

The finding of McCulloch et al. (2003) that coral Ba/Ca ratios increased post European settlement is more likely related to the increase in river flow events that have also occurred at this same period (see Lough et al., 2015 who analysed the luminescent lines in the same coral core). Indeed since there is a general relationship between river flow and sediment load (i.e. river flow is used to calculate sediment load along with suspended sediment concentrations), the increased flows likely translate to increase sediment loads and it is not surprising to observe a correlation between coral Ba/Ca, river discharge and sediment load. While McCulloch et al. (2003) considered the relationship between peak Ba/Ca ratio and river flow (see Fig. 3 in that paper) where the Ba/Ca ratios prior to European settlement were shown to be much lower than in similar river flows that occurred post settlement, on reflection the river discharge reconstructed for the pre-European settlement period appear overestimated based on Lough et al.'s (2015) latest Burdekin River reconstruction. The Burdekin River discharge record of Lough et al. (2015) also highlighted that a period of higher river flows occurred in the 1650-1750 period of the core which was not analysed in the McCulloch et al. (2003) record (Ba/Ca record starts ~ 1760). Hence a reanalysis of the Havannah Island coral core including the full record would allow a direct comparison to be made with the luminescent line record and provide an independent assessment whether coral Ba/Ca reflect river discharge or sediment load.

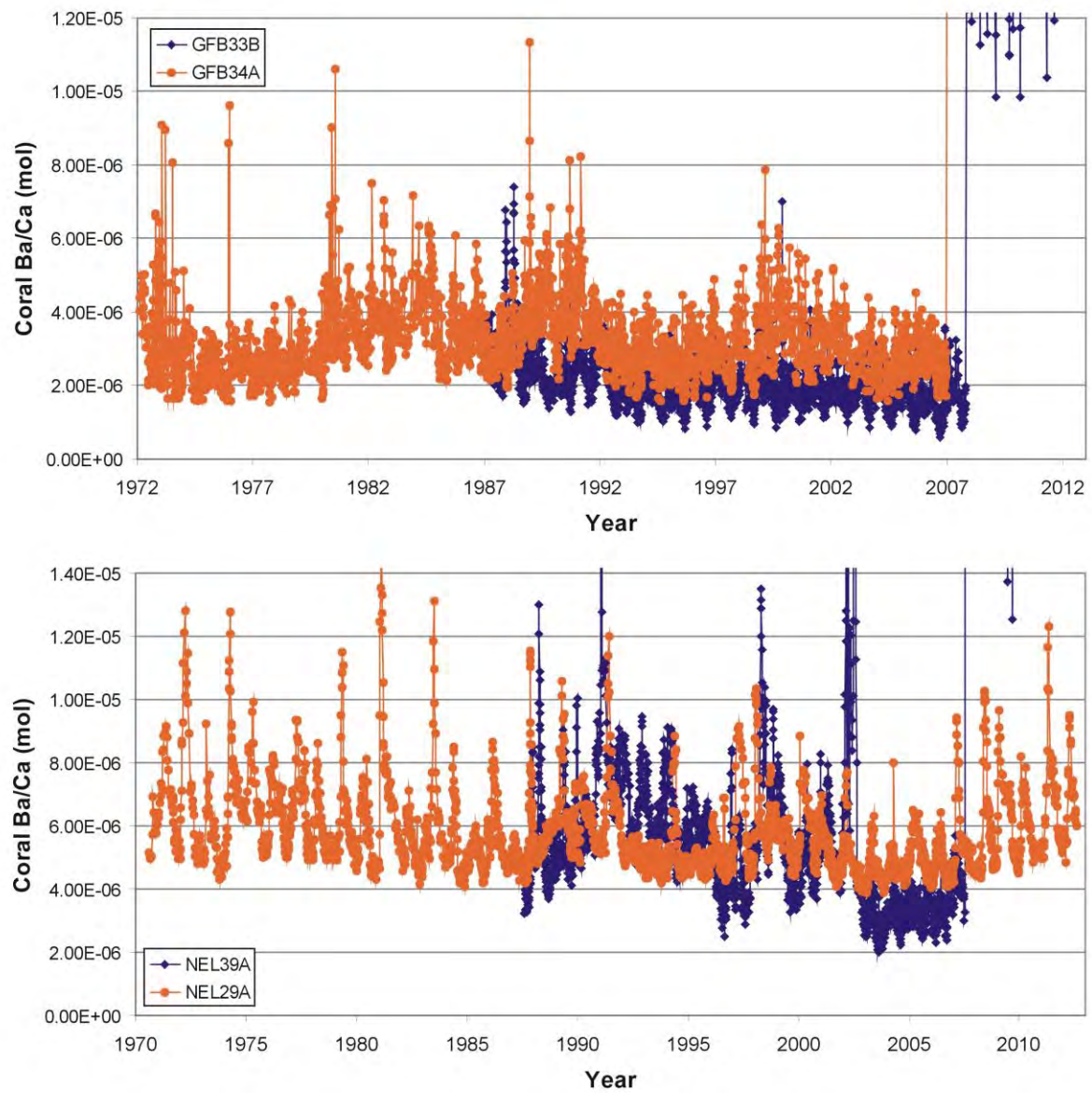


Figure 3: Timeseries plots of coral Ba/Ca ratios for the cores collected from Magnetic Island for Geoffrey Bay (top graph) and Nelly Bay (bottom graph). Note that only NEL29A displays clear relationships with Burdekin discharge events.

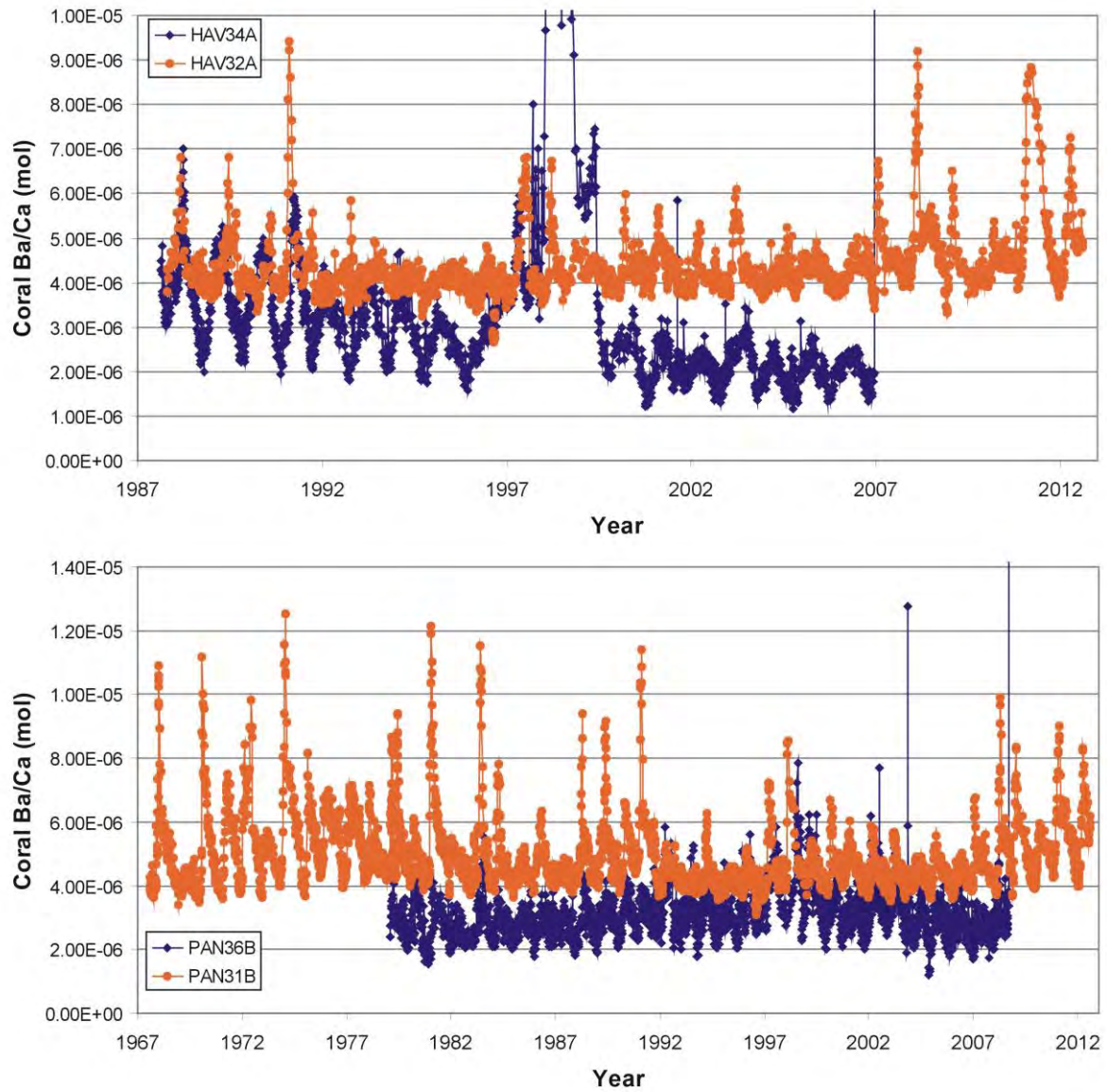


Figure 4: Timeseries plots of coral Ba/Ca ratios for the cores collected from Havannah Island (top graph) and Pandora Reef (bottom graph). Note that only the HAV32A and PAN31B cores display clear relationships with Burdekin discharge events (also note bottom scales are not comparable across graphs – for direct comparisons see Fig. 6).

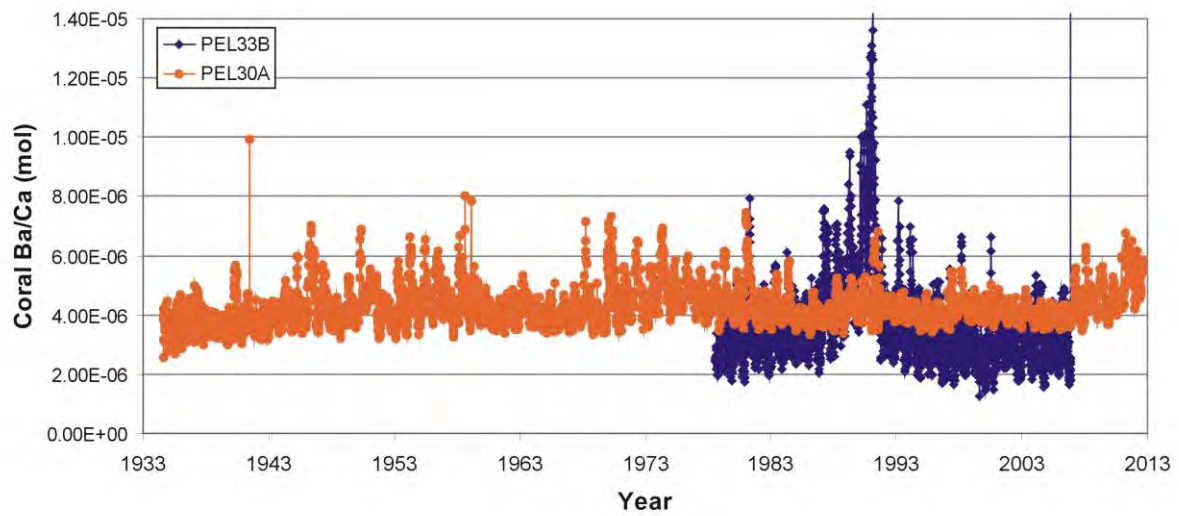


Figure 5: Timeseries plots of coral Ba/Ca ratios for the cores collected from Pelorus Island. Note that only PEL30A displays clear relationships with Burdekin discharge events.

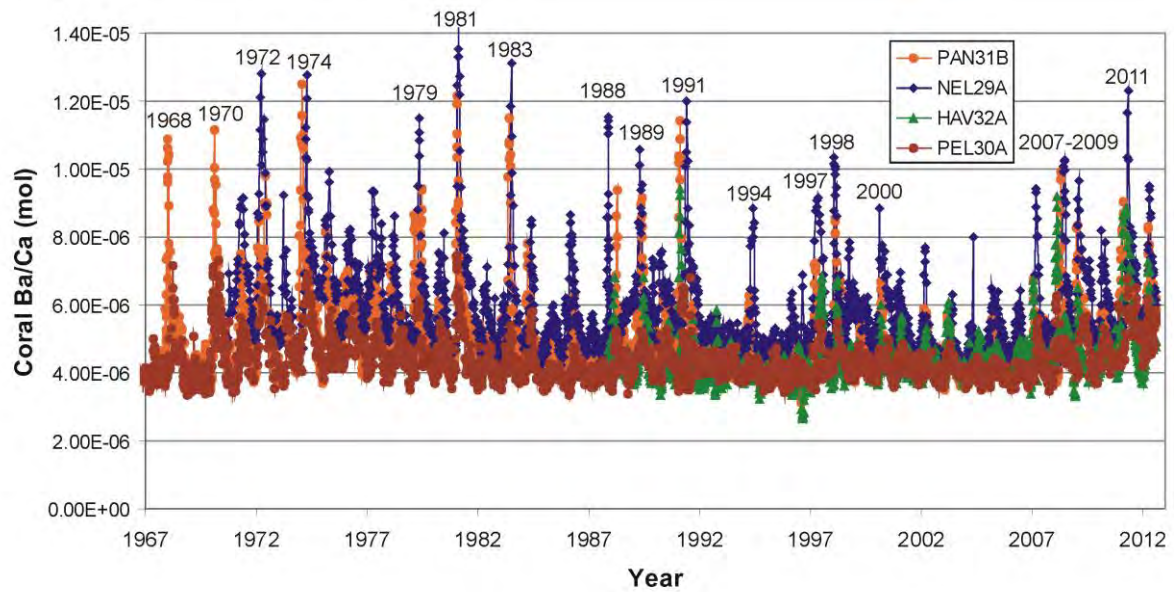


Figure 6: Timeseries plots of coral Ba/Ca ratios for the cores that displayed clear trends with Burdekin River discharge.

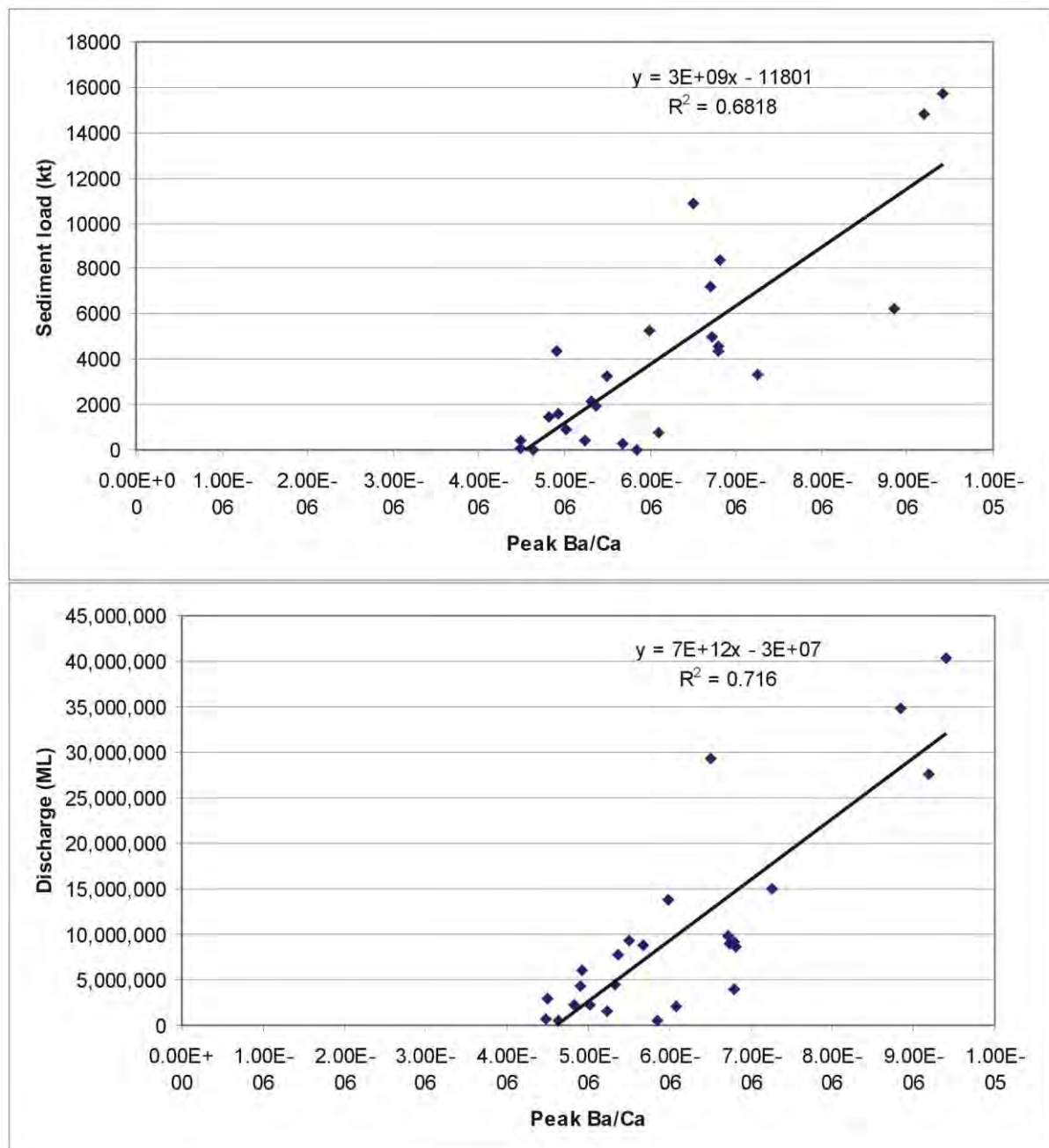


Figure 7: Correlation plots of the annual peak Ba/Ca ratio with sediment load (top graph) and with total Burdekin discharge (bottom graph) for the HAV32A core.

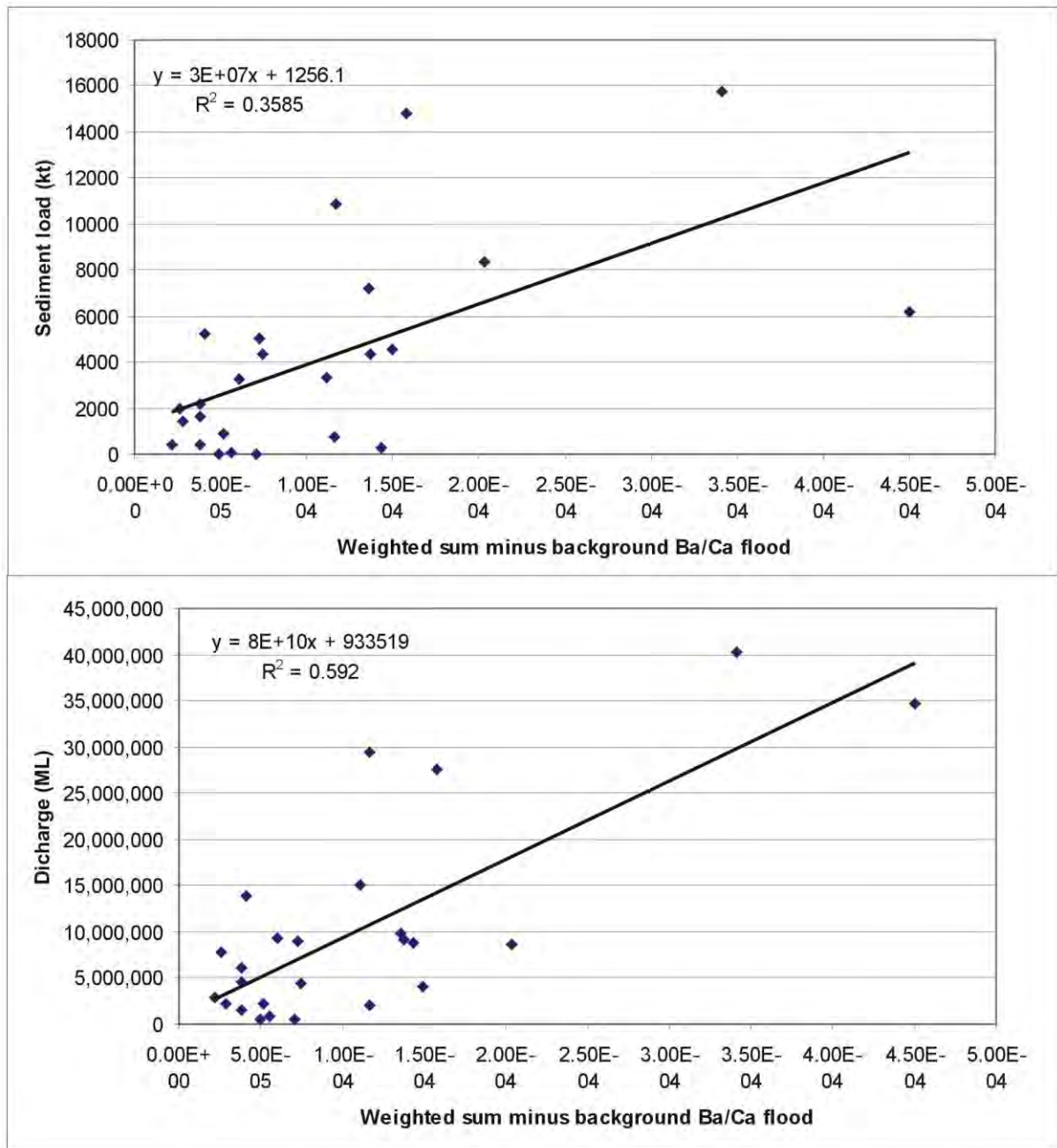


Figure 8: Correlation plots of the annual weighted sum (minus background ratio) Ba/Ca ratio with sediment load (top graph) and with total Burdekin discharge (bottom graph) for the HAV32A core.

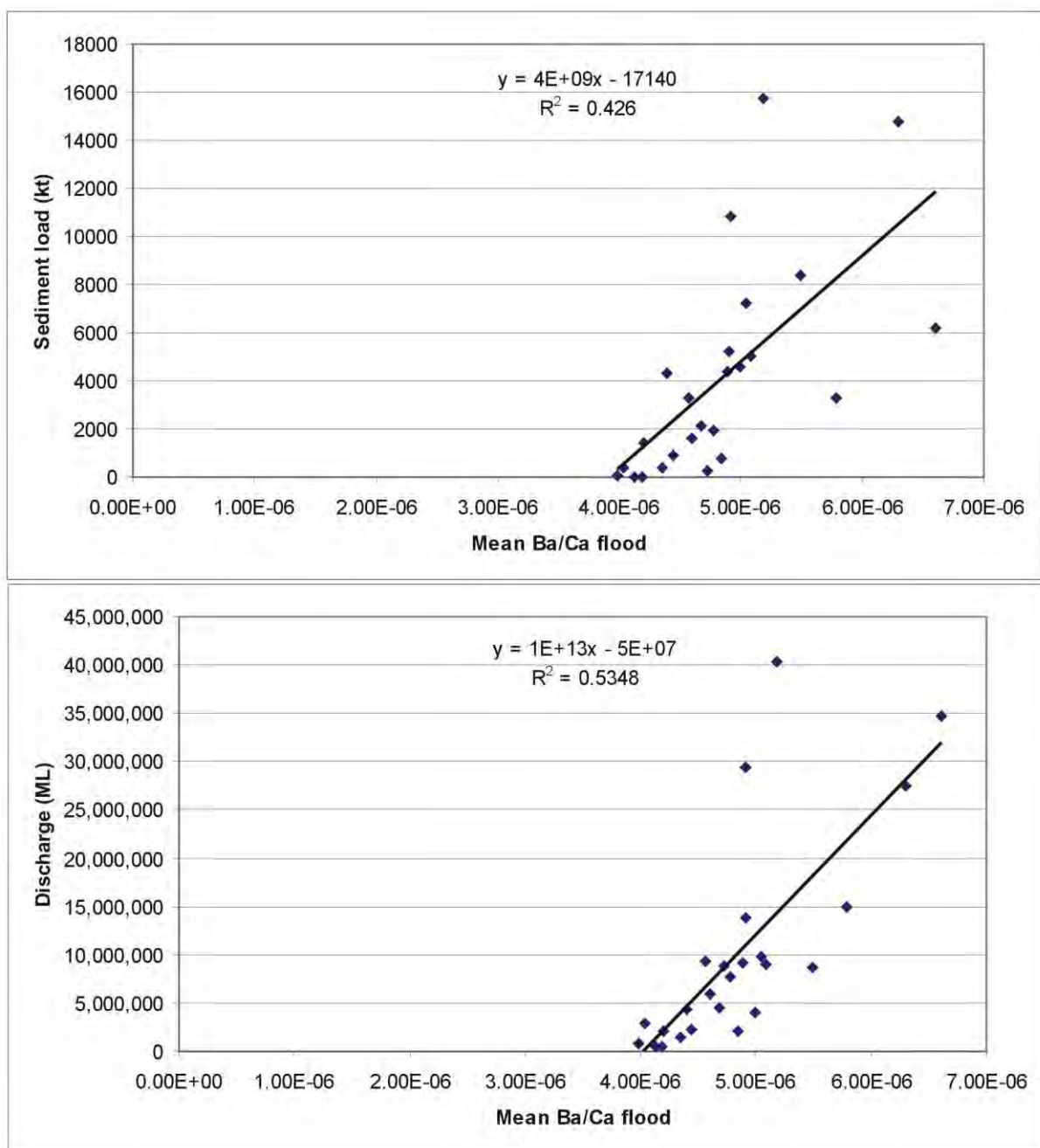


Figure 9: Correlation plots of the mean flood Ba/Ca ratio with sediment load (top graph) and with total Burdekin discharge (bottom graph) for the HAV32A core.

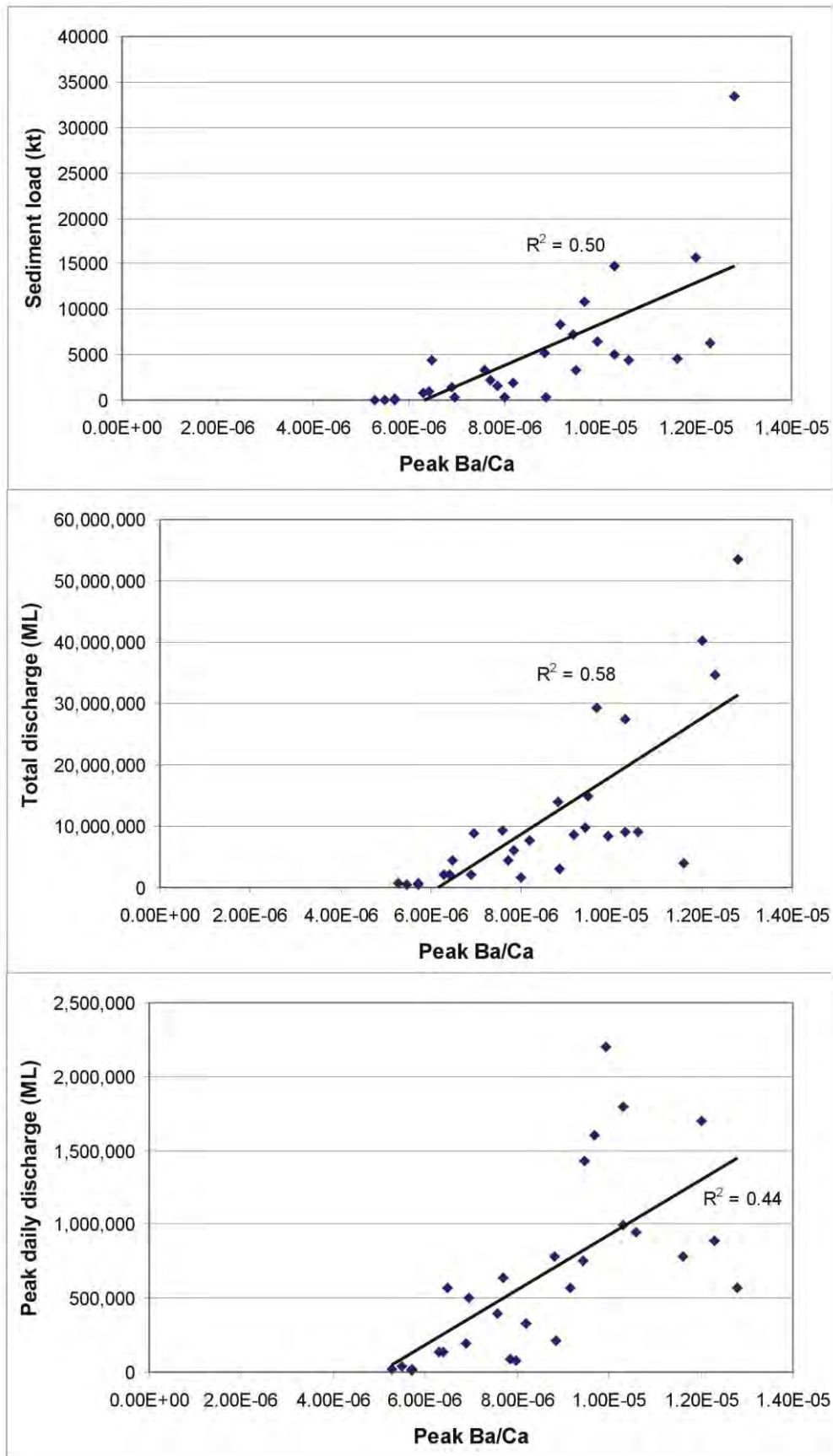


Figure 10: Correlation plots of the annual peak Ba/Ca ratio with sediment load (top graph) and with total Burdekin discharge (middle graph) and Burdekin peak daily discharge for the NEL29A core.

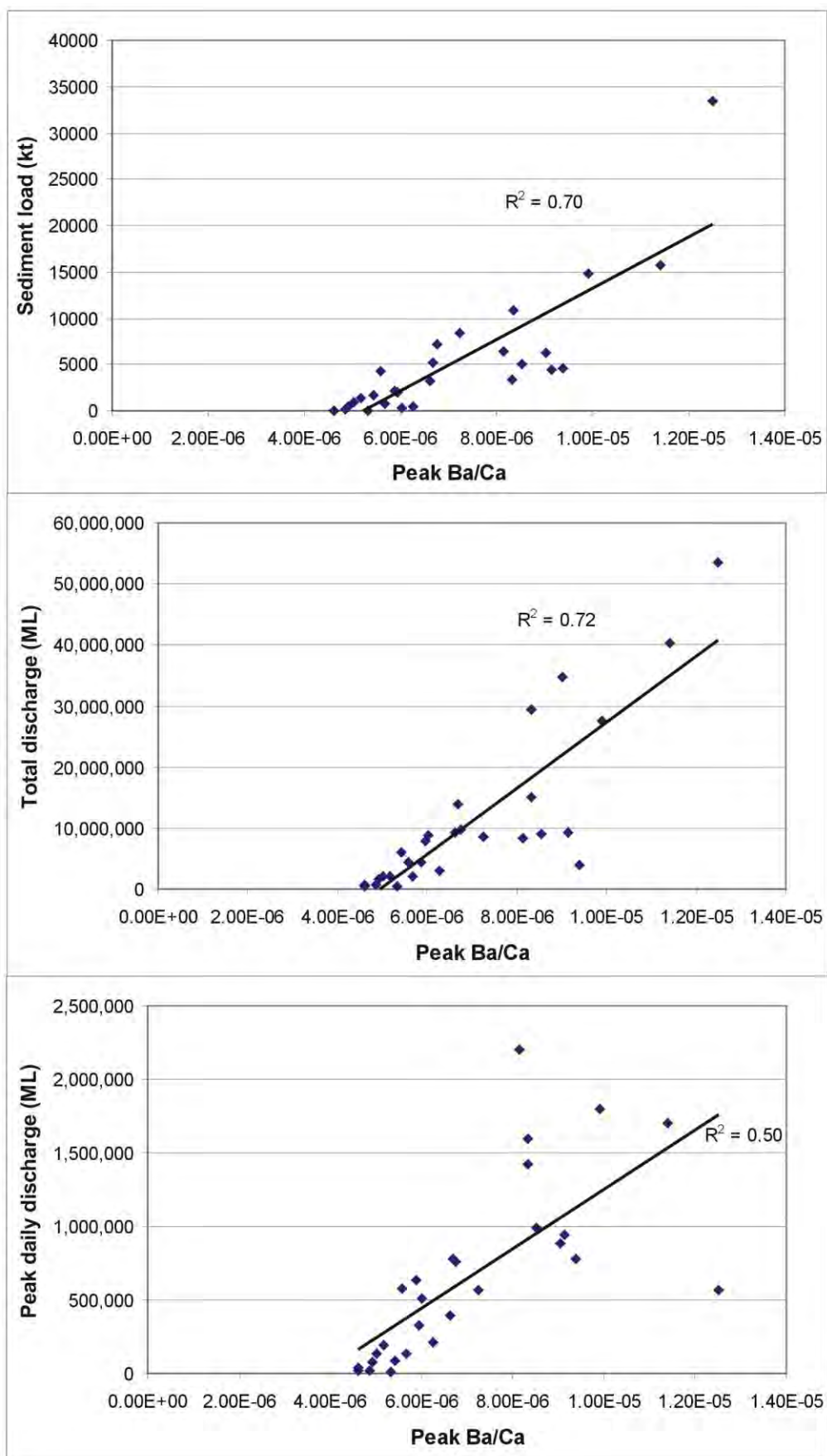


Figure 11: Correlation plots of the annual peak Ba/Ca ratio with sediment load (top graph) and with total Burdekin discharge (middle graph) and Burdekin peak daily discharge for the PAN31B core.

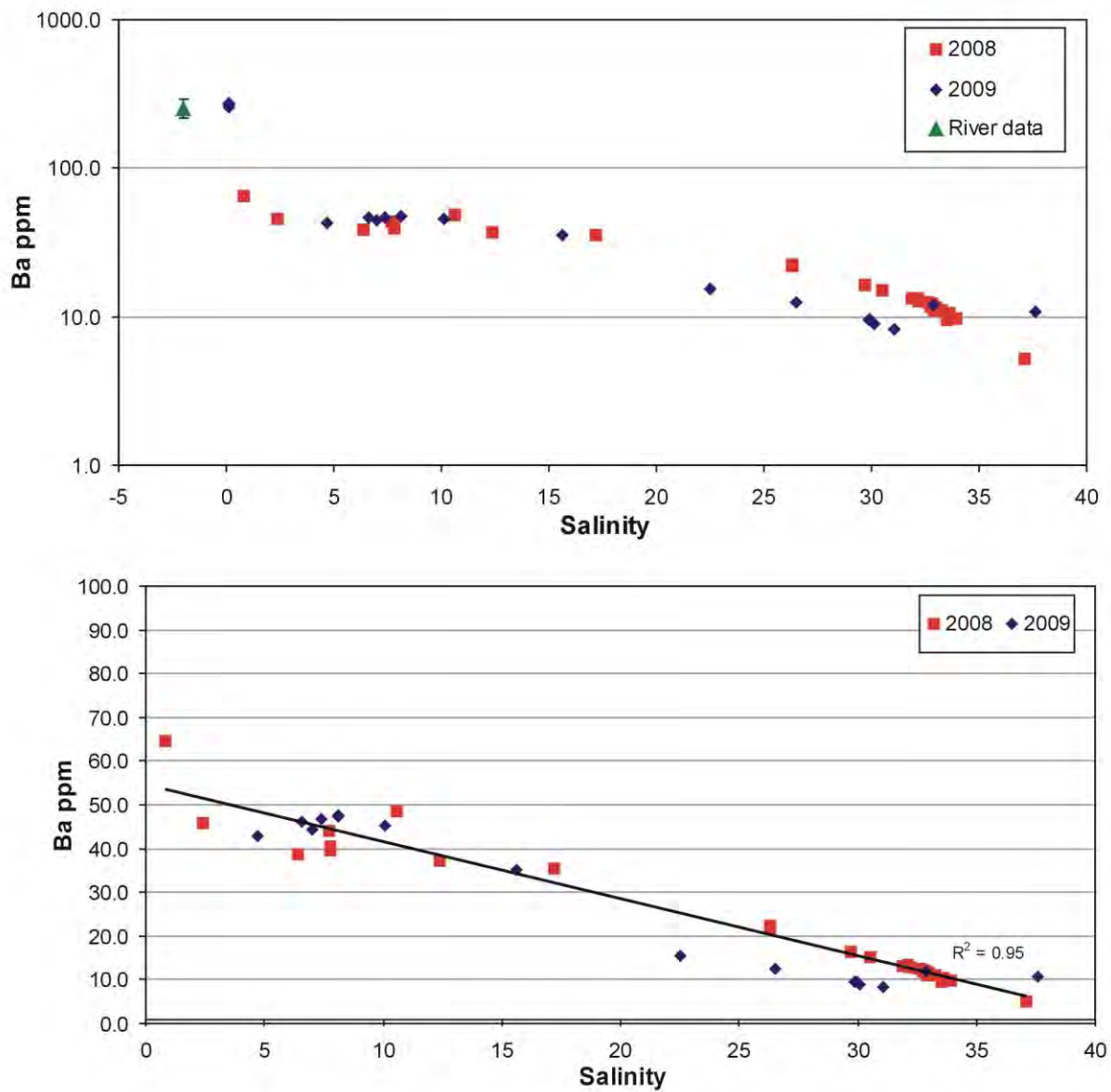


Figure 12: Graphs showing the mixing of barium concentration over the salinity gradient in the 2008 and 2009 flood plumes.

4.0 RECOMMENDATIONS AND CONCLUSION

We examined the validity of the coral Ba/Ca ratio as a proxy for sediment load in 10 coral cores collected along a gradient of the influence of Burdekin River discharge. The data show that only four of the cores displayed trends consistent with river discharge variability. Examination of these cores revealed that while a reasonable correlation with sediment load and Ba/Ca ratio could be established, the relationship with total river discharge was stronger. Further analysis of the data coupled with measurements of barium in flood plumes suggest that in fact the river discharge variation better accounts for the coral Ba/Ca ratio, although an reanalysis of the full Havannah Island coral core (previously analysed by McCulloch et al., 2003) would be required to confirm our finding. Based on our findings a critical review of literature from other locations around the World that have applied the coral Ba/Ca ratio to show changes in sediment load should also be conducted.

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