Cooperative Research Centre for Coastal Zone, Estuary & Waterway Management

Technical Report No. 13

Identification of Sediment Sources in the Fitzroy River Basin and Estuary, Queensland, Australia

February 2005

G. Douglas, P. Ford, M.Palmer,
R. Noble and R. Packett

Queensland Government
Natural Resources and Mines

CSIRO

CRC for Coastal Zone Estuary & Waterway Management

Nutrient and carbon cycling in subtropical estuaries (Fitzroy) – FH1
Technical Report No 13

Identification of sediment sources in the Fitzroy River Basin and Estuary, Queensland, Australia

G. Douglas[1], P. Ford[2], M. Palmer, R. Noble[4] and R. Packett[4]

1. CSIRO Land and Water, Centre for Environment and Life Sciences, Floreat, WA
2. CSIRO Land and Water, Canberra, ACT
3. CSIRO Mathematical and Information Sciences, Centre for Environment and Life Sciences, Floreat, WA
4. Queensland Department of Natural Resources and Mines and, Rockhampton, Qld.

February, 2005

Acknowledgements

PF managed the project and conducted field sampling in the Fitzroy River Basin and Estuary. MP constructed the mixing model used to interpret sediment sources. GD interpreted geochemical, mineralogical and statistical data and mixing model output and wrote the final report. RN provided invaluable information on the nature of the Fitzroy Basin and Estuary as the Fitzroy Study Area Coordinator. RP collected a number of field samples and provided catchment information. All authors provided critical comment on the final report.

Table of Contents

Abbreviations used in this Report

Localities

FRB	Fitzroy River Basin
FRE	Fitzroy River Estuary
GBR	Great Barrier Reef

Rock/soil types

BB	Bowen Basin
SB	Surat Basin
NEFB	New England Fold Belt
TB	Tertiary Basalt
TFB	Thomson Fold Belt

Phosphorus

FRP	Filterable Reactive Phosphorus
TP	Total Phosphorus

List of Figures

List of Tables

Summary

The reduction of sediment deliveries into Keppel Bay region of the Great Barrier Reef (GBR) is a key measure in the conservation of the GBR with the enhanced delivery of sediment and nutrients to coastal and reef zones having the potential to profoundly influence fundamental ecological processes in this natural icon. Recently, major reductions (50%) in the sediment and nutrient deliveries from the FRB have been mandated. Considerable funds are now being applied through the National Action Plan to ameliorate the major catchment sources of sediments. Bilateral agreements between the Australian and Queensland governments, the Reef Water Quality Protection Plan and the National Action Plan for Salinity and Water Quality include imperatives for improved water quality within Great Barrier Reef (GBR) catchments and for reduced loads of sediments, nutrients and contaminants to be delivered to the GBR lagoon.

To lower loads of sediments and nutrients reaching the coast from the FRB an understanding of the sources of these sediments is essential. This research has provided important regional scale information on the sources of sediments entering the FRE and together with sediment modelling tools will help to inform cost-effective investments in reduction of sediment loads to the GBR. The significance of this project to stakeholders is in the improved management of land and water resources required within the FRB to achieve these objectives which will be included as targets in the regional Natural Resource Management Plan being developed by the Fitzroy Basin Association Inc. The findings from this work also have generic relevance to other large sub-tropical agricultural catchments.

The project aim was to identify and characterise the principal processes and spatial and temporal relationships involved in suspended solid transport and transformations within the estuary, and identify source and sink areas. An integrated geochemical, mineralogical, statistical and modelling approach has been used to identify the major sources of catchment sediment in weirs and dams in the FRB and FRE. Based on a reconnaissance soil sampling survey of major soil types, a purpose-built Bayesian mixing model was applied to estimate actual proportions of major catchment soil types in weirs, dams and floods in the FRE.

Weir and dams provide an insight, albeit based on limited sampling and influenced by a range of factors, into the origin, transport and (temporary) storage and deposition of sediment within the FRB. Three spatial sediment associations exist within the FRB:

- The Dawson River in the southern and central FRB carries only a small basaltic component with inputs dominated by soil inputs from the Surat and Bowen Basins.
- Rivers from the central FRB carry variable amounts of basaltic material, predominantly transported during flood events. Soils from the Surat Basin form a minor component, while soils of the Bowen Basin contribute very little fine sediment in local weirs and dams on the MacKenzie River despite the fact that they constitute the majority of the central FRB. Soils from the Thompson Fold Belt, located in the west of the FRB, constitute a substantial proportion of the sediment transported by, and retained in, impoundments in the central FRB.
- Rivers from the western FRB predominantly carry sediment derived from the Thompson Fold Belt that may constitute (*ca.* 70-80%) of the fine sediment source.

Flood events sampled in this study, in contrast to weir and dam samples, are dominated by basaltic material. It is estimated that flood events have an estimated average enrichment of *ca.* 7 over the mapped distribution of basalt within the FRB catchment.

In the FRE, soils from the Bowen Basin, Surat Basin, and, to a lesser extent the basaltic soils, display a distinct longitudinal variation along the FRE with both Bowen Basin and basaltic soils progressively enriched towards the ocean. In contrast, soils of the Surat Basin display an opposite trend. The estimated abundance of these soil types also varies widely. Bowen Basin soils range between 0 and 50% (mean 22 ± 13%), while the Surat Basin soils range between 0 and 40% with a lower mean abundance of 15 ± 10%. Basaltic soils deposited within Keppel Bay have a higher mean abundance from *ca.* 0-13km upstream (13± 5%) relative to samples further upstream within the FRE (9± 4%). Soils derived from the

Thompson Fold Belt and New England Fold Belt do not display a longitudinal trend, but differ in abundance and variability. Thompson Fold Belt soils are confined to a relatively narrow range between *ca.* 20-40% with a mean abundance of 30 ± 7%. Soils from the New England Fold Belt have a wider range of between 0 and 50%, but lower mean abundance of 23 ± 14%.

Relative to their abundance in the FRB catchment, soils of the Bowen Basin display the greatest depletion factor (0.5), while soils from the Surat Basin (0.8), New England Fold Belt (1.2) and basaltic soils (1.1) are not significantly different from their FRB abundance. Thompson Fold Belt soils are the most enriched within the FRE (4.3 times) despite these soils, which are located in the western-most portion of the FRB catchment, being amongst the most distant from the FRE. The low and uniform concentration of basaltic materials, especially in comparison to the high basaltic content of the flood events, suggests that this material is preferentially exported from the FRE.

Basaltic soils in the FRB have, on average, *ca.* 2.5 to 3.4 times less total phosphorus (TP) than comparable basaltic soils from the Moreton Bay and Johnstone River catchments. Furthermore, they have similar TP concentrations to most other soils within the FRB. Thus, in considering the flux of TP from the catchment, it is the total sediment flux which is of major importance, rather than the flux of individual catchment soils. It is likely, however, that the bioavailability of the phosphorus may differ particularly where substantial amounts of P are incorporated into Fe-oxide phases which are potentially available for release under anoxic conditions arising from deeper burial within de-oxygenated estuarine sediment.

This study has been undertaken during a period of well below average flood flows. Consequently sediment deliveries from the various catchments may be atypical. Nonetheless, this study has allowed us to identify factors which can modify sediment geochemistry in transit through the FRB and cause changes post-arrival in the FRE. Based on this data we have drawn conclusions about the processes and sources of the sediment deliveries to the FRE. These conclusions can be made more robust through additional research which should focus on three areas:

(a) Because of cost and logistic constraints a number of key sub-catchments within the FRB were not sampled in this initial study. The Sandy Creek catchment in the westernmost FRB, which drains the largest area of basaltic soils in the FRB, is now of particular interest. The research reported here has identified this area as potentially the most significant source of basaltic material to the MacKenzie River, and the Bedford and Bingegang Weirs. Similarly, the granitic soils present within the TFB remain unsampled and are likely to be a substantial source of sediment within the Theresa Creek catchment. With a relatively small effort, it would be possible to build substantially on the work reported here.

(b) The highly variable hydrology of flood events within the FRB have the inherent capacity to transport large amounts of suspended sediment. This sediment may be derived from a variety of sources such as by direct entrainment of catchment soils, resuspension of riverine sediments in temporary storages (*e.g.* riparian zones or overbank deposits) or scouring of accumulated sediment in dams and weirs. Modelling, particularly at major river catchment scales using weirs and dams as sampling points, will allow an estimate of the mass balance of sediment from major soil types during floods. In addition, isotopes of Sr and Nd, which have been used in similar sediment tracing studies, could be used to provide an independent estimate of catchment sediment sources. It is likely that these flood events transport the majority of sediment delivered into the FRE. Thus, major flood events should be monitored to assess changes in the composition and suspended sediment load over the entire hydrograph within the FRE. This will allow quantitative estimates of sediment sources using the mixing model. In particular, quantitative measurements on the composition, and load, of sediment being deposited within the FRE and Keppel Bay should be made a high priority.

1. Background

The enhanced delivery of sediment and nutrients to coastal and reef zones has the potential to profoundly influence fundamental ecological processes in these highly valued environments. In the specific context of land management in the Fitzroy River Basin (FRB) the removal of sediments and nutrients from the FRB catchments is a matter of on-going concern. In addition, reduction of sediment deliveries into Keppel Bay region of the Great Barrier Reef (GBR) (Fig. 1) is seen as a key measure in the conservation of the GBR with major reductions (50%) in the sediment and nutrient deliveries from the FRB now mandated. In addition, considerable funds are now being applied through the National Action Plan to ameliorate the major catchment sources of sediments.

Effective remediation, amelioration, or reduction of sediment deliveries from the catchment to the GBR involves, in part, the identification and effective management of catchment sediment sources and associated nutrients. Furthermore, even semi-quantitative identification of the principal sediment source regions provides a powerful "reality test" for the various numerical models used to predict regional sediment sources and sinks and to prioritize the remedial work. In this study, a multi-disciplinary approach, integrating geochemistry, mineralogy, and statistics, has been applied to make a preliminary identification of the principal sources of sediment, and their delivery to, and processing within, the Fitzroy River Estuary (FRE). Similar sediment tracing studies using a geochemical and isotopic approach have been used in other aquatic systems in Queensland such as the Moreton Bay estuary (Douglas *et al*., 2003a), major water supply dams (*e.g.* Douglas *et al.,* 2002, Douglas *et al*., 2003b, accepted, Douglas *et al.,* 2003c) in southeast Queensland, and in elsewhere in the world in major river basins (*e.g.* Allegre *et al.,* 1996).

2. Need

The Fitzroy estuary is characterised by significant flows of freshwater from the large agriculturally based catchment during summer, with extended periods of low flow for most of the year. Large loads of sediments and nutrients and unknown amounts of agricultural chemicals are transported through the estuary and further offshore during the major flow events. The upper estuary also receives urban runoff from Rockhampton and during the extended periods of low flow the main sources of freshwater for the estuary are probably those (approx. 20 ML/day) from the three sewage treatment plants at Rockhampton some of which are due for upgrading.

There are limited data for water quality and estuarine health indicators. In the upper estuary where tidal velocities are low, primary production (algal biomass) can be high and blooms are probably limited by the usual turbidity of the water.

The impact of these significant inputs to the estuary from the upper catchment and from within the estuarine area itself on the ecological health of the estuary and adjacent marine areas is poorly understood. Whether the system is sustainable under current management strategies is also in doubt. The Task FH1 will produce the fundamental knowledge on the spatial and temporal dynamics of sediments, nutrients, carbon, pesticides and primary (algal) production for the system enabling more sustainable management in the future. This information will be of primary importance as an input to biophysical modelling of the system (CM) and to improving understanding both at scientific and stakeholder (CS) levels. The data and sampling activities of FH1 were closely linked to those of the other Tasks in project FH especially to FH3 (impacts of changed freshwater flows on fisheries production) and FH4 (influence of habitat distribution and quality on abundance and biodiversity of fish and crustaceans). The findings from this work have generic relevance to other large sub-tropical agricultural catchments.

3. Objectives

Objective as stated in the original proposal:

- To identify and characterise the principal processes and spatial and temporal relationships involved in nutrient, carbon and suspended solid transport and transformations within the Fitzroy River Estuary (FRE), and identify source and sink areas.

4. Geography, geomorphology and geology of the Fitzroy River Basin

4.1 Geography and geomorphology

The FRB catchment is the second largest seaward-draining catchment in Australia (Fig. 1). It covers an area of *ca.* 144,000 km^2 and ranges from the Carnarvon Gorge National Park in the west to the major regional city of Rockhampton (population *ca.* 65,000) in the east, approximately 25km from the Southern Pacific Ocean. The FRB catchment has quite limited coastal lowland areas around Rockhampton, with a more extensive lowland wetland area immediately surrounding and down to the mouth of the FRE. Moving inland, the land rises gently to a series of low ranges separated by large areas of very low gradient especially in the northern and central parts of the catchment. Originally, much of the catchment was covered by brigalow scrub but this was removed in two episodes of intense land clearing in the 1960s and the 1970s. The predominant land use is cattle grazing (>80%) but considerable areas (~10%) are also used for dryland cropping. Irrigated horticulture and cotton growing is limited to areas around Emerald (in the central west) and Theodore (in the south). Coal mining is the most important economic activity, but occupies only a very small portion of the catchment.

Five major rivers combine to form the Fitzroy (Fig. 1) which drains the catchment into Keppel Bay. These are: the Nogoa rising in the far west of the catchment which flows through Emerald and is then joined by Theresa Creek coming from the northwest around Clermont. The Comet drains the south-central part of the catchment and after joining with the Nogoa forms the Mackenzie River. The Connor-Isaac, draining the northern part of the catchment, joins the MacKenzie just upstream of Tartrus weir. The Dawson joins the MacKenzie further downstream. It drains the southern part of the catchment with the Don and Dee as its major tributaries. The combined stream now known as the Fitzroy enters the southern Pacific Ocean about 60 km downstream of Rockhampton.

The rivers which drain the FRB are low gradient streams incised into the landscape. Small floods remain within the banks, but overbank flows are common and connect the river to the adjacent floodplains. The FRB is located at the boundary between the temperate and tropical convergence zones and can receive rain during both summer and winter. Summer monsoonal rainfall remains the dominant driver of the highly episodic river flows. Annual average suspended sediment transport at Rockhampton is estimated to 4.3 million tonnes based on sampling 3 minor floods in 1994, 1996, and 1997, and the flow record from 1964-1997 (Horn *et al.,*1998). Kelly and Wong (1994) conclude for the 30 years 1964-1995 that 264 million tonnes of material have been exported by the Fitzroy past Rockhampton. This implies an annual average sediment yield double that of Horn *et al*., (1998).

An unknown portion of this sediment is transported through the complex river/floodplain environment and its associated sediment storages. There is a clear need to quantify the source, amount, and quality of sediment generated across the catchment, the pollutants carried with it, and the effects of the practical management options. This CRC Coastal Zone (CRCCZ) project contributes to understanding these issues. Further information is available at: www.coastal.crc.org.au.

4.2 Catchment geology

More than 100 rock types are present in the FRB catchment. A summary of major catchment rocks/alluvium and their distribution in the FRB catchment are given in Table 1 and Fig. 1. The geology of the FRB can be organised according to the major structural units:

- Cambrian-Ordovician metamorphic rocks and the Devonian-Carboniferous siliciclastic rock and calc-alkaline volcanics of the Thomson Fold Belt (TFB) which occupy the westernmost portion of the FRB catchment,
- Devonian-Carboniferous calc-alkaline volcanics, Permian volcaniclastic and siliciclastic rocks, calc-alkaline volcanics and pillow basalts and Carboniferous-Cretaceous granitoids of the New England Fold Belt (NEFB) which dominate the easternmost area within the FRB catchment,
- Permian-Triassic siliciclastic rocks, limestone, andesite and coal of the Bowen Basin (BB) and the Jurassic-Cretaceous siliciclastic rocks and coal of the Surat Basin (SB)

which occupy the majority of the central and southern FRB catchment respectively, and

- Tertiary siliciclastic rocks, oil shale, lignite and basalt of the Duaringa Formation and the mudstone, oil shale, sandstone and lignite of the Biloela Formation (collectively referred to as DBF) which occur within or bordering, and sub-parallel to the strike of the NEFB.

Overlying the major structural units is an extensive and varied Tertiary weathering sequence which may include laterite, duricrust, local gravel scree and clastic sediments and extensive soil formation. The most important aspect of the Tertiary geology in the FRB is the presence of extensive, principally basaltic, volcanics, (Tertiary Basalts – TB) which cover large areas of the western catchment, mostly overlying Bowen Basin sediments particularly in the catchments of the Nogoa and Comet Rivers and a lesser extent in the vicinity of the Theresa and Retreat Creeks (Fig. 1). More isolated occurrences of Tertiary basalts also occur in the headwater catchments of the Isaac and in feeder tributaries to the Dawson River upstream of Biloela. Numerous isolated patches of basalt within the FRB catchment, particularly within the Connors, Isaac and Comet River catchments are probably remnants of previously much more extensive basaltic volcanism that have been weathered and transported to other parts of the catchment or into the FRE/South Pacific Ocean as mixed basaltic soils.

5. Evaluation of Approach and Methods

5.1 Sample collection and preparation

A catchment reconnaissance sampling program was devised for the FRB which incorporated prior knowledge of the abundance of major rock types and sediment generation and delivery from specific sub-catchments to obtain 106 geochemically representative soils. All FRB soil sample locations were recorded using GPS. Fitzroy River estuarine samples were collected using an Eckmann grab at the mouth, and along the length of the estuary up to the barrage at Rockhampton. FRB weir sediments were obtained as grab samples. Flood samples were collected in plastic containers, allowed to settle over a number of weeks with the supernatant decanted. All FRB catchment soil and Fitzroy River estuarine samples and flood samples were wet sieved to <63 µm and settled in water columns in the laboratory to obtain a <10 µm fraction. The <10 µm fraction was then dried and ground in a WC mill to homogenize the sample.

5.2 Major and trace element analysis

The <10 µm fraction of sediment and catchment soil samples were analysed by CSIRO using X-ray fluorescence (XRF) for major (SiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5) and trace elements (Ba, Ce, Cl, Cr, Co, Cu, Ga, La, Ni, Nb, Pb, Rb, S, Sr, V, Y, Zn, Zr) on fused glass discs on a Phillips PW1480 instrument, using the methods of Norrish and Chappell, (1977) and Hart (1989) and by neutron activation analysis (NAA) by Becquerel Laboratories, Australia, for major (Ca, Fe, Na and K) and trace elements (Ag, As, Au, Ba, Br, Ce, Co, Cr, Cs, Eu, Hf, Ir, La, Lu, Mo, Nd, Rb, Sb, Sc, Se, Sm, Ta, Tb, Te, Th, U W, Yb, Zn, Zr) using methods described in Potts (1987).

5.3 Statistical analysis

Canonical variate analysis (CVA) was used to examine for differences between the FRB catchment rock types and estuarine sediments using the function lda from the MASS library (Venables and Ripley, 2002) in the R statistical package (Hornik, 2004).

Canonical variate analysis was used on a subset of elements (where elements were selected to highlight contrasts between catchment soil types) to ascertain if linear combinations of the geochemical data could be used to effectively separate or discriminate between different sources. The derived linear coefficients were then used to predict the canonical scores for the geochemical data collected from the Fitzroy River Estuary sediments, and these predicted scores were then overplotted on the catchment soil scores.

5.4 Bayesian mixing model

The Bayesian statistical model used to determine the proportions of sediment sources in this study was first used in the Moreton Bay study (Douglas *et al*., 2003a), and has been used also to determine proportions of catchment sediment in Lake Samsonvale, Douglas *et al*., 2003b, Palmer and Douglas, submitted) and Lake Wivenhoe (Douglas *et al.,* 2003c).

Each of the Fitzroy weir, dam and estuary sediment samples can be considered to be comprised of varying proportions of source material, originating from different parts of the catchment. The problem is to estimate the relative proportions of various sources within a sample. The approach taken is to model the contribution of the sources as contributing in a linearly additive manner. Mathematically, for the $j'th$ sample, the model can be written

$$y_j = Az_j$$

where A is a p x k matrix, where each column of A corresponds to the elemental composition of an endmember (a specific soil type with a unique geochemical signature), and the elements of the vector z_j correspond to the proportions of various endmembers in the sample. The concentrations of various major elements (as wt% oxides) and trace elements (as µg/g), characterizes each dam sediment sample. At each site j, there corresponds a p column of observations y_j and a k-column vector of unknown proportions z_j of the catchment geologies (soils). It is postulated that the sample measurements follow a multivariate normal distribution, conditional on the proportions z_j. The distribution is

$$p(y_j \mid z_j, A, \Gamma) = (2\pi)^{-\frac{\nu}{2}} |\Gamma|^{-\frac{1}{2}} \exp\left\{-0.5\left(y_j - Az_j\right)' \Gamma^{-1}\left(y_j - Az_j\right)\right\}.$$

The distribution of the unknown z_j is modelled by assuming that the additive log-ratio transformation (alr) of the proportions follows a multivariate-normal distribution; *i.e.* the k-part composition vector z_j has a logistic normal distribution

$$p(z_i \mid \mu, \Sigma) = \left(\frac{1}{2\pi}\right)^{\frac{k-1}{2}} |\Sigma|^{-\frac{1}{2}} \left(\frac{1}{\prod z_i}\right) \exp\left(-\frac{1}{2}(\theta_i - \mu)' \Sigma^{-1} (\theta_i - \mu)\right)$$

and where

$$\theta = alr(z) = \log\left(\frac{z_{-k}}{z_k}\right) = \left(\log\left(\frac{z_1}{z_k}\right), \log\left(\frac{z_2}{z_k}\right), \ldots, \log\left(\frac{z_{k-1}}{z_k}\right)\right)'$$

A Bayesian approach, similar to that described in Billheimer (2001), which allows for the derivation of a joint posterior probability distribution of the parameters, and Monte Carlo Markov Chain (MCMC) algorithms (Gilks *et. al*., 1966) are used to derive estimates of the unknown parameters. This approach not only provides estimates of the composition of the endmembers, but can be used to estimate the unknown mixing proportions. In the present study, the mixing model MCMC sampler was generally run for 10000 iterations, with a “burn-in” of 500 iterations after which every tenth sample was retained, thus yielding 9500 model values. Examination of plots of a range of variables was made to check convergence of the samplers.

Over 100 individual rock, and hence derivative soil types are present in the FRB catchment. As it was not practical to model the contributions of all of the individual soils derived from the rock types, endmembers for the mixing model were aggregated into five groups (also see Table 1). These groups comprise the Bowen Basin soils (BB - 28 samples), the Surat Basin soils (SB - 10 samples), the Thomson Fold Belt soils (TFB - 6 samples), the New England Fold Belt soils (NEFB - 21 samples) and the Tertiary Basaltic soils (TB - 16 samples). This gave a total of 81 catchment soil endmembers used in the mixing model.

Modelling of the contribution of catchment endmembers to weirs, dams and to the Fitzroy River Estuary (FRE) used a subset of major elements (SiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5 expressed as wt% oxide) and trace elements (Ba, Ce, Co, Cr, La, Ni, Pb, Rb, Sc, Sr, Th, V, Y, Zn, Zr expressed as µg/g) which were selected to highlight differences in the geochemistry of catchment endmember soils and thus improve discrimination when used in the Bayesian mixing model. In the specific case of FRE samples the major elements MgO, CaO, Na_2O, K_2O and trace elements Ba, Rb and Sr were omitted due to the potential for exchange during mixing with seawater.

5.5 Seawater exchange of weir and dam sediments

Approximately 3g of weir or dam sediment was added to 300mL of 35 ppth filtered (GF/C) seawater in an acid-washed plastic container sealed, and mixed for three days on a bottle roller. The sediment was then centrifuged at 10,000 rpm, the supernatant discarded and washed three times with 300mL of distilled water to remove any remaining salts. The weir and dam sediment samples were then dried (105^{o}C) and manually ground (agate mortar and pestle) before being analysed by XRF and NAA (Section 3.2).

6. Results

6.1 Major and Trace Element Geochemistry

Major and trace element geochemistry may be used to distinguish between different sources of sediment (soils) delivered from the FRB to the Fitzroy River Estuary (FRE), in addition to sediment stored in weir and dams and that carried during flood events. Interpretation of major and trace element variation diagrams and identification of catchment sediment sources in estuarine sediments is subject to constraints due to three factors:

- during soil formation, particularly in a system such as the FRB which is exposed to episodic and often extreme rainfall events, it is likely that mixing of soils derived from different catchment rock types will occur, producing soils whose composition is not representative of any original rock type,
- for certain elements, in particular the alkalis and alkaline earths (*e.g.* Na, K, Ca and Mg), there is modification of catchment soil cation chemistry by exchange with seawater cations during sediment transport and deposition into the FRE. The effects of seawater leaching on the composition of FRE sediments are discussed in more detail in Section 6.1.4,
- within the estuary, detrital (shell) carbonate is frequently incorporated into the bottom sediment during deposition, burial and, in the case of a high energy estuary such as the Fitzroy, physical reworking of the sediments.

In addition, the estuarine sediment samples were collected over a very limited time span. One of the major themes of this research project is the highly dynamic character of sediment transport in the estuary. Much of the sediment material is highly mobile and is being continuously reworked and relocated. This sampling of the estuary is thus very much a "snapshot" of the distribution of sediment materials at a single time and is dominated by the characteristics and sediment sources of the last flood preceding our sampling together with material which is delivered by purely local processes such as bank erosion. Active bank erosion can be seen going on in parts of the estuary and this has the effect of adding "old" sediments to the recently delivered material. In addition there is active deposition in the "Cut-through" removing material and, in retrospect, this area has been under sampled. Our study has taken place during an abnormally dry period for the whole catchment and, as a consequence, the sediment transport has been by relatively small events coming from limited zones of the catchment rather than by widespread inputs. Despite the modification of the primary geochemical characteristics which has occurred due to factors outlined above, useful information on physical and geochemical processes can be obtained.

Relatively less mobile elements (*e.g.* La, Th, Douglas *et al*., 2002) have been used primarily in the geochemical analysis to identify catchment sediment sources and in particular discriminate between basaltic and non-basaltic sediment sources. This is discussed in the next section.

6.1.1 Fitzroy River Estuary sediments

The relationship between La and Th is particularly useful in differentiating Tertiary basaltic and non-basaltic soils and sediments in eastern Australia. Typically, Tertiary basalts weather to a consistent La/Th ratio of *ca.* 8-10 over a wide range of chemical index of alteration (CIA – McLennan *et al.,* 1990) from 60-90, with soils or sediment derived from sedimentary (TFB, SB, BB, DB) and/or predominantly granitic/acid volcanic (NEFB) soils having a distinctly lower range of ratios from *ca.* 2-5. Intermediate ratios in some FRB catchment soil samples are indicative of a mixed source. In particular, some soils from the BB, NEFB and TB (Table 1) have a composition that suggests a degree of contamination by (mixing with) basaltic soils (see fields defined in Fig. 2). This is not surprising, recalling Section 2.2, that basaltic flows were far more extensive as evidenced by the existence of isolated remnants and that there would be substantial entrainment mixing with non-basaltic soils and re-deposition within the FRB during flood events. As can be seen from Fig. 1 and Table 1 different geological units are concentrated in different parts of the catchment (though there are some overlaps). We use the geological structural name as a short hand for the region where it is the dominant unit.

The geochemical signature of the FRE sediments suggests that they are derived from a predominantly sedimentary (non-basaltic) source with La/Th ratios typically <4. This is consistent with derivation from soils derived from the BB, SB, TFB or NEFB (Table 1). Importantly, the FRE sediments are clearly differentiated from a La-Th mixing line defined by Tertiary basalts from the FRB catchment and similar basalts from the Moreton Bay catchment (Douglas *et al*., 2003) suggesting that the Tertiary basalts are not a major component of the sediments deposited (remaining) within the FRE. Importantly, however, the FRE sediments lie near the basaltic end of the group of predominantly granitic/acid volcanic of the NEFB and sedimentary FRB catchment sources. This composition is not consistent with any one FRB catchment soil, but rather suggests the presence of a small basaltic component in the sediments of the FRE.

Sediments from the FRE define a small array with little variation relative to other sedimentary catchment soil sources. This absence of substantial geochemical variation in estuarine sediments has been noted in other studies (Douglas *et al.,* 2003) also and may reflect homogenisation during fluvial transport and subsequent tidal reworking and bioturbation within the FRE (Fig. 2a).

The inference from La-Th compositions that the sediments of the FRE are predominantly derived from sedimentary (TFB, SB, BB, DB) and/or predominantly granitic/acid volcanic (NEFB) sources with a lesser basaltic component is also supported by other geochemical relationships. Plots of K_2O versus TiO_2 (Fig. 3) and P_2O_5 versus Fe_2O_3 (Fig. 4), all suggest a predominantly sedimentary and/or granitic sources with a lesser basaltic component with the FRE sediments plotting within the broad envelope of soil compositions defined by the BB, SB, TFB, NEFB and DB (Table 1), but in general closest to the Tertiary basaltic soils (Fig. 2). The relationship between MgO + K_2O and CaO (Fig. 5) suggests little or no basaltic component in the FRE sediment, however, this relationship, which is strongly influenced by cation-exchange with seawater, is discussed in greater detail in Section 4.1.4.

6.1.2 Fitzroy River Basin weirs and dams

Sediment samples from weirs and dams from the FRB catchment display greater geochemical variation than that observed in the FRE sediments. The likely reasons for this are three-fold: firstly there is less homogenization of the sediments within weirs and dams rather than in a tidal estuary with a large daily and seasonal tidal range. Secondly, many of the weir and dam sediment samples represent subcatchments with distinctive geology and hence, geochemical signatures. Lastly, surface or suspended sediment collected from weirs or dams may not be indicative of the entire (sub) catchment but may merely reflect temporal or spatial factors such as recent local bank collapse or the most recent sediment input from a sediment-laden tributary.

Some weir or dam samples have geochemical signatures indicative of almost no basaltic contribution, other have a composition more consistent with that of the FRE sediments. The wide range of geochemical variation is particularly apparent in a sample from Theresa Creek Dam and two sediment samples from Fairbairn Dam which have elevated K_2O, consistent with rocks from the TFB (Table 1) which forms a substantial portion of the upper catchment of both dams (Fig. 1). In contrast sediments from Comet, Bingegang and Bedford Weirs have the lowest K_2O, TiO_2, and highest Fe_2O_3 and P_2O_5 concentrations, consistent with derivation from a higher proportion of the basaltic soils which constitute a substantial portion of the Comet River catchment. This catchment is known to transport a large suspended sediment load (Horn *et al*., 1998).

6.1.3 Fitzroy River Basin flood events

Samples of sediment from three flood events from the Comet and Bedford Weirs and the Fitzroy River Motor Boat Club downstream of the barrage provides an insight into the variation in composition of suspended sediment transported in high flow events, relative to the composition of bottom sediments in the FRE. In addition, the composition of sediments transported during flood events is of particular importance, as this material will not only be deposited within the FRE, but presumably transported into Keppel Bay and beyond.

Flood event sediments have a La-Th composition consistent with a substantially higher basaltic component as they plot intermediate between the La-Th mixing line for Tertiary basaltic soils and the sedimentary (TFB, SB, BB, DB) and/or predominantly granitic/acid volcanic (NEFB) soils (Fig. 2, Table 1). Similarly, these samples are enriched in Fe_2O_3, although not P_2O_5, relative to the sedimentary and/or granitic soils but are also substantially more depleted in K_2O, have lower MgO + K_2O and may be marginally higher in CaO and TiO_2 (Fig.s 3-5). All these features are consistent with a higher basaltic component. Mineralogical analysis (Section 4.2) also suggests a higher basaltic component in the flood sediments. The sediments from the Comet and Bedford Weirs were collected from the same flood event and their close geochemical relationship suggests a common derivation, that of a mixed basaltic and sedimentary source over the central portion of the FRB.

6.1.4 Cation exchange during estuarine mixing - seawater exchange of weir and dam sediments

A geochemically-diverse subset of seven FRB weir and dam (freshwater) sediments were mixed with seawater to explore possible modifications of the sediment cation chemistry that would be likely to occur during sediment advection into the FRE (seawater) mixing zone. This information is not only important in understanding the influence of estuarine mixing on clay mineral chemistry, but also will influence the selection of elements in a mixing model that will be used to estimate proportions of different catchment soils types being generated from the FRB catchment. In addition, changes in clay mineral cation chemistry may influence clay mineral flocculation and possible changes in Sr isotopic composition, this latter process already noted in other studies of estuarine sediments (Douglas *et al.,* 2003a).

The most substantial change that occurs in the major cation chemistry is the loss of Ca (63% ± 6% - mean ± 1 std dev) with corresponding increases in Mg (18% ± 10%) and K (7% ± 4%). In terms of trace elements, there was substantial loss of Sr (20% ± 14%) and, while there was variability in individual samples, there was no net gain or loss in Ba (0% ± 8%). This latter result is in contrast to other studies which suggest substantial Ba desorption during estuarine mixing (Douglas *et al.,* 2002, McCulloch *et al.,* 2003), however, the relatively short period of exchange (*ca.* 72 hours) and/or differences in sediment mineralogy and particle size, even within the <10µm fraction, may explain the discrepancy.

Interestingly, proportionately more Ca was lost relative to increases in the concentrations of other cations. While it is expected that a substantial proportion of the cation exchange would occur in clay minerals, another phase, perhaps pedogenic or other carbonates, may undergo selective dissolution on mixing with seawater, giving rise greater than expected losses of Ca.

A plot of MgO (%) + Na_2O (%) versus CaO (%) displays the net changes in cation chemistry that occur upon mixing a subset of weir and dam sediments with seawater (Fig. 5). Point A represents the mean composition of the subset of weir and dam samples, while point B is their final composition after exposure to seawater in the laboratory. This mixing line is of a similar trajectory and magnitude to the mixing line for weir and dam samples (freshwater (starting) point C) and the mean composition of all FRE (seawater) samples (point D) implying that the major changes that occur in cation–exchange are rapid (<72 hours) and that the laboratory simulation of cation exchange provides a realistic representation of the process after weir or dam sediments are transported into the FRE.

Selected samples of both the FRE sediments and flood sediments have anomalous CaO concentrations relative to other samples with a linear trend defined between the majority of FRE sediments and the CaO-enriched outliers. A similar linear trend also exists for the flood sediments where the one anomalous flood sediment is higher in Ca than all catchment soils and even the Tertiary basaltic soils which are enriched relative to the rest of the sample group. Mineralogical analysis of the FRE sediment (sample 67) and the flood sediment (sample FMBC) indicates that they contain small amounts of calcite ($CaCO_3$) *ca.* 2% ± 1% and 3% ± 1% respectively. Recalculation of the CaO contents based on the removal of $CaCO_3$ yields CaO concentrations compatible (within an error in the estimated abundance of $CaCO_3$ of ± 1%) with other FRE sediments (line E-F) and flood sediments (line G-H, Fig. 5). Other minor enrichments in the CaO concentration of FRE, particularly between *ca.* 1-1.5% CaO may indicate the presence of small amounts of calcite.

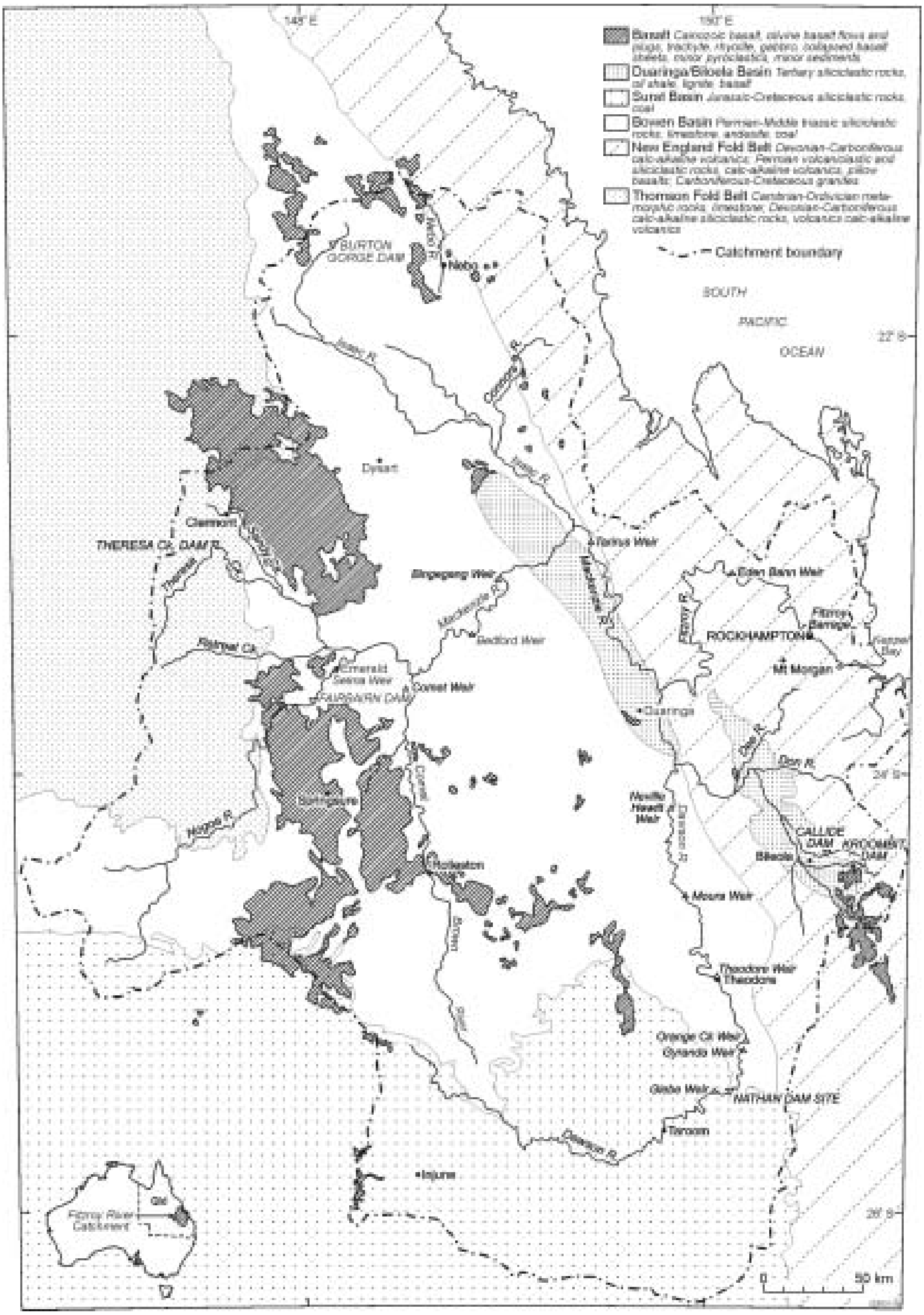


Figure 1. Geology and major river systems in the Fitzroy River Basin catchment

Table 1. Summary of Fitzroy River Basin catchment geology.

Age	*Unit*	*Tectonic unit*	*Location in Fitzroy Basin*	*River sub-catchment*	*Rock types*	*Cainozoic cover*
Tertiary	*Biloela Formation (Tb)*	*DB equiv. ?*	*East/Central around Biloela*	*Dawson/Don*	*silty, sandy mudst, oil shale, sandst, lignite*	1
Tertiary	*Duaringa Formation (Td)*	*DB*	*East/Central near Duaringa*	*MacKenzie/Dawson*	*mudst, sandst,cong, siltst, oil shale, lignite, basalt*	2
Cretaceous	*Un-named (Kut)*	*NEFB*	*W of Rockhampton*	*Fitzroy*	*trachyte flows, minor rhyolite*	3
Cretaceous	*Un-named (Kub)*	*NEFB*	*W of Rockhampton*	*Fitzroy*	*basalt*	4
Jurassic	*Evergreen Formation (Je)*	*SB*	*Southern*	*Dawson/Comet*	*siltst, mudst, sandst, oolitic, ironstone, coal*	1
Jurassic	*Hutton Sandstone (Jh)*	*SB*	*Southern*	*Dawson/Comet*	*sandst, siltst, mudst, minor cong*	1
Jurassic	*Injune Creek Group (Ji)*	*SB*	*Southern*	*Dawson/Comet*	*sandst, siltst, mudst, coal, cong*	
Triassic	*Clematis Group (Re)*	*BB*	*Central/southern*	*Dawson/Comet*	*sandst, cong, mudst, siltst*	1
Triassic	*Moolayember Formation (Rm)*	*BB*	*Central/southern*	*Dawson/Comet*	*mudst, sandst, carbonaceous shale, cong*	1
Triassic	*Rewan Group (Rr)*	*BB*	*Central/southern*	*Dawson/Comet*	*sandst, mudst, siltst, cong*	1
Permian-Triassic	*Permian Granitoids (Prgy/i)*	*NEFB*	*Southeastern*	*Dawson*	*leucocratic biotite adamellite*	1
Late Permian	*Rangal Coal Measures (Pwj)*	*BB*	*Central/southern*	*Comet*	*sandst, siltst, mudst, coal, tuff, cong*	1
Late Permian	*Gyranda Formation (Pwy)*	*BB*	*Central/southern*	*Dawson/MacKenzie*	*siltst, sandst, mudst, cong, tuff*	
Late Permian	*Collinlea Sandstone (Po)*	*BB*	*Central/southern*	*Nogoa*	*sandst, cong, siltst, mudst*	1
Permian	*Back Creek Group (Pb)*	*BB*	*Central and western*	*Connors/Isaac*	*mudst, sandst, cong, limest*	1
Permian	*Lizzie Creek Volcanics (Pv)*	*NEFB*	*Northeastern*	*Connors*	*andesite crystal/lithic tuffs, agglom, black siltst*	1
Permian	*Moah Creek beds (Ps)*	*NEFB*	*Central-eastern*	*Fitzroy*	*conglomeratic mudst, mudst, cong, sandst*	1
Permian	*Bedserker Beds (Pt)*	*NEFB*	*Coastal/Rockhampton*	*Fitzroy*	*acid-int volcanics, tuff-mudst, mudst, sandst, siltst*	4
Permian	*Un-named (Px)*	*NEFB*	*Coastal/Rockhampton*	*Fitzroy*	*serpentinite*	2
Carboniferous	*Ducabrook Formation (Cu)*	TFB	*Central-western*	*Nogoa*	*sandst, mudst, shale, limest, tuff*	5
Carboniferous	*Un-named (C)*	*NEFB*	*Eastern/lower Fitzroy*	*Fitzroy*	*siltst, sandst, cong, limest, mudst*	4
Carboniferous	*Glandore Granodiorite (Cgl)*	*NEFB*	*Southeastern*	*Dawson*	*granodiorite, diorite, tonalite, adamellite*	6
Devonian-Carb	*Connors Volcanics (DC)*	*NEFB*	*Central-northern*	*Connors*	*andesite, dacite, rhylt, tuff, agglom/breccia/cong, sandst*	1

Tectonic Unit *DB - Duaringa Basin, NEFB - New England Fold Belt, SB - Surat Basin, BB - Bowen Basin, TFB - Thomson Fold Belt*

Tertiary/Cainozoic cover *1- TB - basalt +/- olivine, trachyte, rhyolite, gabbro, seds, sandst, siltst, congl, laterite, soil, alluvium, gravel, scree, sand, duricrust, 2- as per 1, but no basaltic or other volcs, coast seds*
3 - alluvium, gravel, scree, sand, duricrust, 4 - alluvium, coastal sediments, 5 - soil, alluvium, gravel, scree, sand, duricrust, 6 - laterite, soil, alluvium, gravel, scree, sand, duricrust

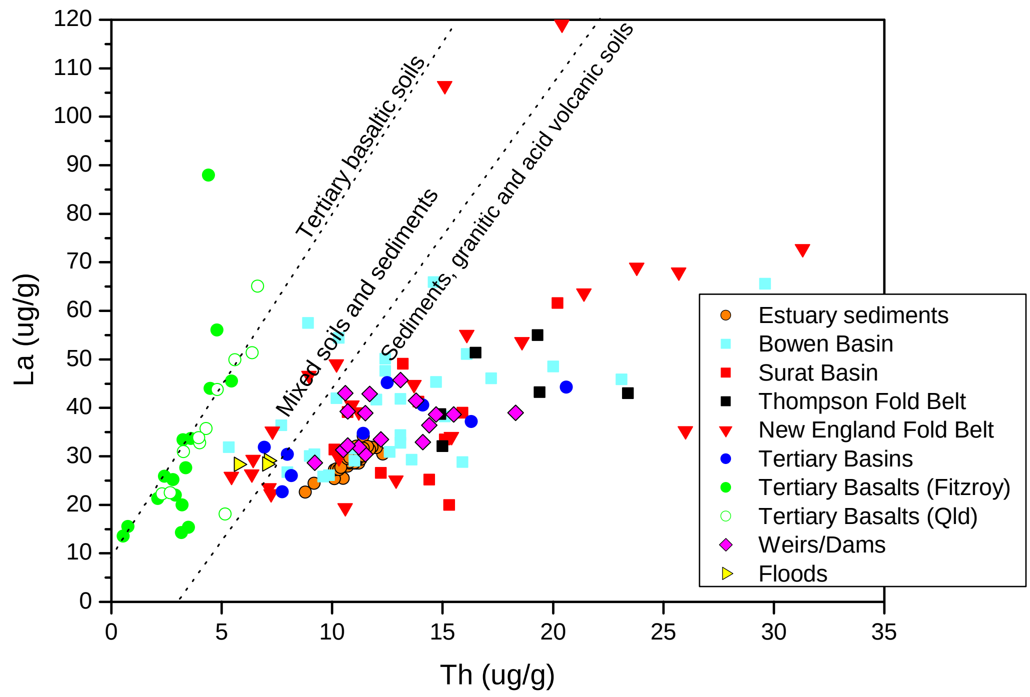


Figure 2. Concentrations (µg/g) of La vs Th for Fitzroy River Estuary sediments, Fitzroy River Basin soils, weir, dam sediments and flood event sediments. Tertiary Basalts (Qld) from the Moreton Bay catchment, SE Queensland and also plotted (see text).

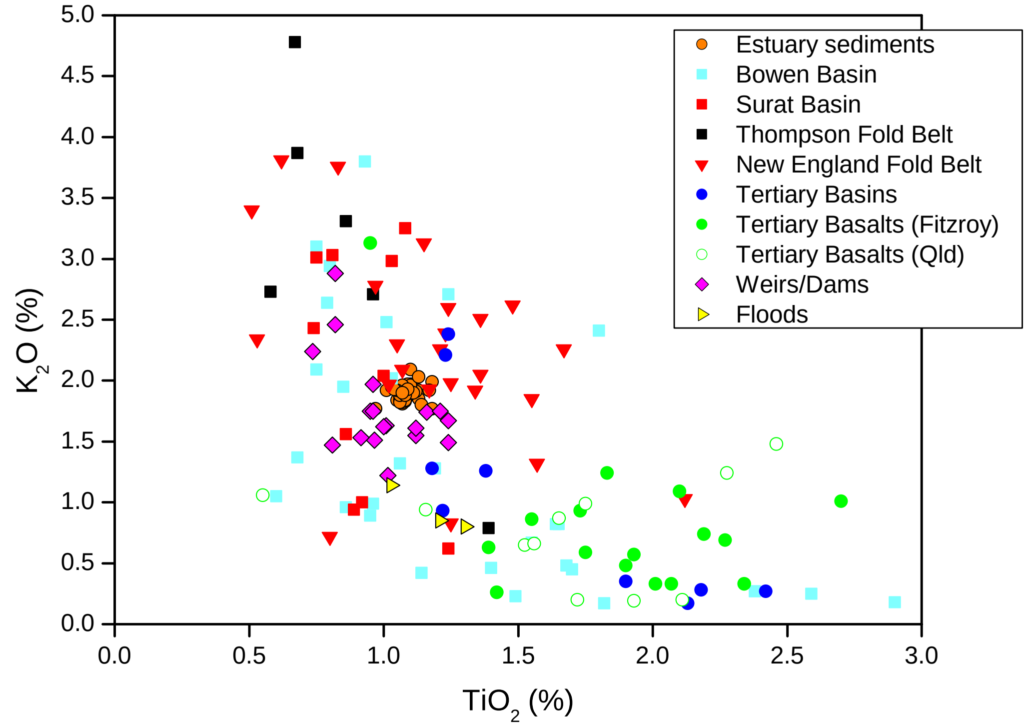


Figure 3. Concentrations (%) of K_2O versus TiO_2 for Fitzroy River Estuary sediments, Fitzroy River Basin soils, weir, dam sediments and flood event sediments. Tertiary Basalts (Qld) from the Moreton Bay catchment, SE Queensland and also plotted (see text).

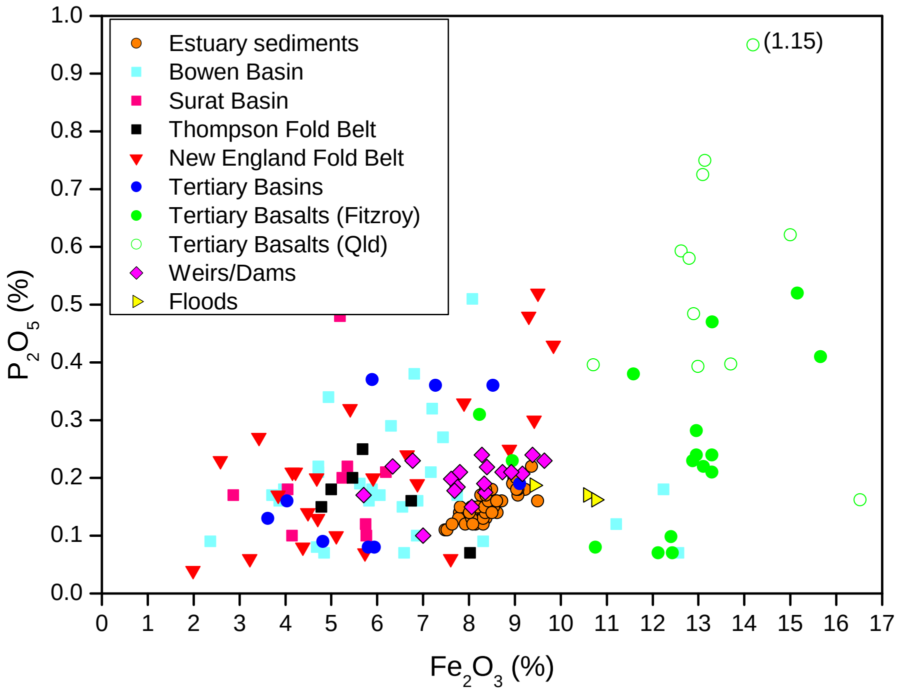


Figure 4. Concentrations (%) of P_2O_5 versus Fe_2O_3 for Fitzroy River Estuary sediments, Fitzroy River Basin soils, weir, dam sediments and flood event sediments. Tertiary Basalts (Qld) from the Moreton Bay catchment, SE Queensland and also plotted (see text).

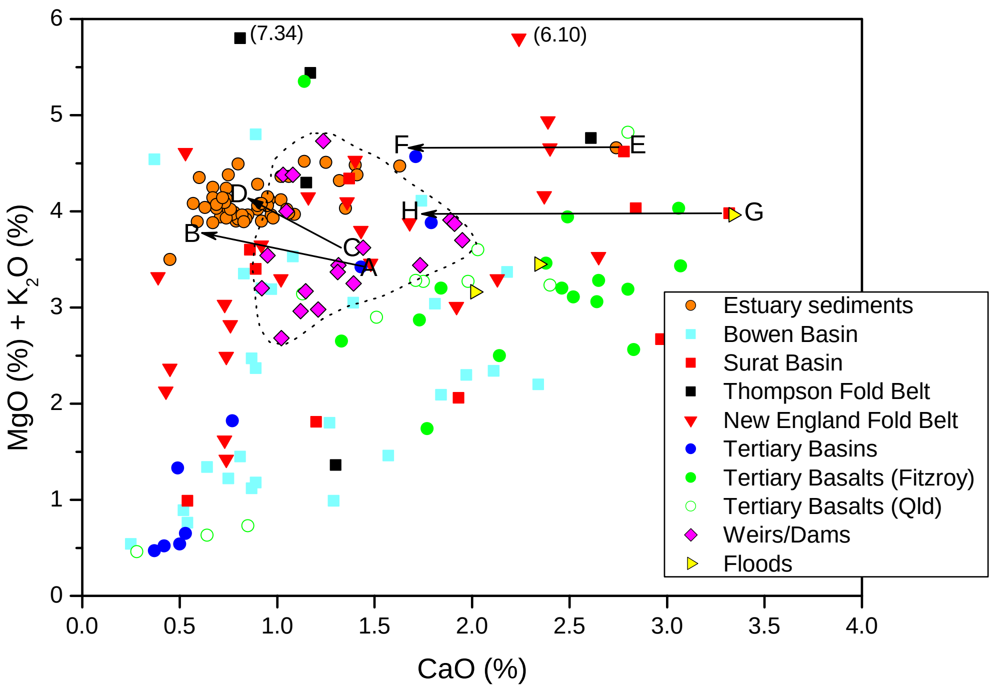


Figure 5. Concentrations (%) of MgO + K_2O versus CaO for Fitzroy River Estuary sediments, Fitzroy River Basin soils, weir, dam sediments and flood event sediments. Tertiary Basalts (Qld) from the Moreton Bay catchment, SE Queensland and also plotted (see text). Dotted line encompasses weir and dam sediments. Points A to F represent mixing lines (see text).

6.2 Mineralogy

Mineralogical analysis of FRE, weir and dam and flood event sediments (Table 2) support the general observations made on the basis of major and trace element geochemistry. Sediments from the FRE have low smectite concentrations of 42% ± 12% relative to both weir (*ca.* 70%) and flood samples (*ca.* 80%) derived from the MacKenzie River and its western tributaries, in particular the Comet and Nogoa Rivers and Theresa Creek, implying a lower basaltic content in the estuarine sediments. Similarly, illite to illite + smectite ratios (I/I+S), frequently used as a measure of basaltic to non-basaltic sources, are higher in the FRE sediments (12 ± 4) than in the weir and dam and flood samples from the central and western FRB (Table 2). In addition, quartz, kaolinite and feldspars (albite and orthoclase) are also higher in the FRE suggesting a greater relative contribution from the BB and SB sediments and/or granitic/acid volcanic material derived from the NEFB. It is important to note, however, that the Theresa Creek Dam which exclusively drains the TFB (Fig. 1) is comparatively enriched in quartz, feldspar and mica/illite (the latter in accordance with its enriched K_2O – Section 4.1.2, Fig. 3). Thus, a greater proportion of sediment derived from the TFB may also be responsible for some of the observed enrichment of quartz and felspars in the FRE.

The relative paucity of smectite in the FRE sediments, a mineral primarily derived from the breakdown of basalt in (sub-) tropical conditions, is also consistent with the process of mineralogical fractionation, even within the <10µm size fraction used in this study. Clay mineral fractionation has frequently been observed in the aquatic environment (*e.g.* Griggs and Hein, 1980, Gibbs, 1977), with illites, which generally have a larger particle size (in addition to quartz, and feldspars and sometimes kaolinite), settling more rapidly than smectite. There may be a general fining of the sediment with depth and the preferential focussing (*e.g.* Likens and Davis, 1975, Hakanson, 1997, Blais and Kalff, 1995), of the finest (smectite-rich) sediment particularly in temporary sediment storage zones such as the weirs and dams that occur in the FRB. Furthermore, once the sediment is remobilized during flood events, it is usually enriched in smectite due to the lower energy required to entrain this mineral due to its particle size, and thus it is preferentially transported. This pattern is apparent within flood samples collected from within the FRB with these samples the most enriched in smectite, having the lowest I/(I+S) values and also being relatively depleted in quartz, feldspar and kaolinite.

A direct consequence of the preferential entrainment and transport of smectites relative to other minerals, due to the inherently small particle size, is that smectite-rich material of basaltic origin, will be transported further into the Keppel Bay and the South Pacific Ocean within the freshwater plume generated during major flood events in the FRB. In addition, the average tidal range in the FRE is 4 to 5m which creates high velocity tidal flows (see later), leading to sediment sorting and re-working between flood events. Thus, it is likely that any smectite deposited in the FRE due to settling and/or coagulation after mixing with seawater is likely to be preferentially removed from the estuarine mixing zone. The importance of the fractionation of sediment during flood events and estuarine mixing within the FRE leading to preferential enrichment of smectite and its transport is discussed further in Section 5.

6.3 Statistical analysis

The relationship between the sediments of the FRE, those of weirs and dams and the soils of the FRB has been examined using canonical variate analysis (CVA). The CVA scores for the sediments from the FRE, in general do not appear to cluster around any particular FRB catchment soil (Fig. 6). As observed in the analysis of the geochemistry (Section 4.1.1) the sediments from the FRE show little variation relative to the catchment soils of the FRB and are mostly contained within the field defined by the sedimentary and/or granitic/acid volcanic soils but at the end closest to the Tertiary basaltic (TB) soils. As observed in the geochemical analysis of the weir and dam sediments (Fig. 2-5), there is generally a wider range of compositions than in the sediments of the FRE indicating both relatively basaltic-rich and basaltic-poor sediment. Flood samples plot intermediate between the sediments of the FRE and weirs and dams and the Tertiary basaltic soils of the FRB again suggesting a higher basaltic component is being transported in flood events in this study.

In essence, the sediments of the FRE, weir and dam sediments and flood event sediments are bound by three endmembers in canonical variate space; the sedimentary soils of the TFB, the sedimentary soils of the SB and BB and the basaltic soils of the TB (Fig. 6). The mostly granitic/acid volcanic soils of the NEFB form a more diffuse pattern in CVA space, however, it likely that they also contribute to the sediments contained within the FRE.

Geochemical variation of the weir and dam samples from the FRB can be further analysed by ranking from negative to positive the first CVA score (LD1, Fig. 6, Table 2). In general those with the most negative LD1 score are associated with the Dawson River and are primarily derived from SB sediments. The presence of substantial smectite in the Theodore and Gyranda Weirs (Table 2) in spite of very isolated occurrences of TB in the Dawson catchment also indicates a hitherto unidentified source of basaltic material which may reflect more extensive weathering and mixing of basaltic and non-basaltic soils.

The Therese Creek Dam is distinctive within the FRB in that it probably contains little or no basaltic component within its catchment (Fig. 1). The Therese Creek Dam sediments also have a large negative LD2 score typical of TFB sediments (Fig. 6) which occupy the majority of its catchment along with Cainozoic soils and alluvium.

The Tartrus Weir, Fairbairn Dam, Comet Weir, MacKenzie and Fitzroy River samples have intermediate LD1 scores indicative of a more substantial basaltic component. One of the Fairbairn Dam samples, and the Cuthrough in the Fitzroy Estuary have high negative LD2 scores also suggestive of a substantial contribution from the TFB sediments and/or a possible NEFB component in the latter. This association between Fairbairn Dam samples and the TFB sediment is also supported by high K_2O which is generally enriched in TFB soils (Fig. 3).

Sediment from one of the Comet Weir samples and the Bingegang and Bedford Weirs, all of which capture the Comet and Nogoa Rivers have the most strongly expressed basaltic signature with the highest LD1 scores of all of the weirs. This is not unexpected given the extensive Tertiary basaltic occurrences in the western portions of the FRB catchment (Fig. 1). Thus, the Comet, Bingegang and Bedford Weirs may be considered as important repositories for sediment enriched in basaltic material. A distinctly negative LD2 score for one Bedford Weir sediment sample may be indicative of a contribution from the TFB.

Flood event sediments from the Fitzroy Motor Boat Club (FMBC), Bedford and Comet Weirs have the highest (most positive) LD1 and intermediate LD2 scores. These scores are compatible with a substantial contribution from Tertiary basaltic soils and are in agreement with mineralogical and geochemical evidence.

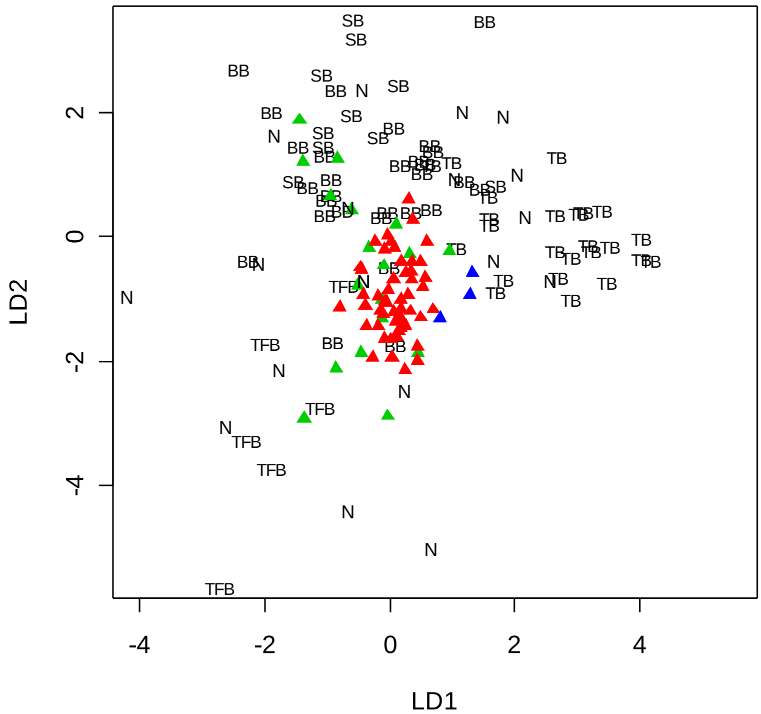


Figure 6. Canonical variate scores for selected Fitzroy River Basin catchment soils, Fitzroy River estuary, weir and dam and flood sediments (TFB – Thomson Fold Belt, SB – Surat Basin, BB – Bowen Basin, N – New England Fold Belt, TB – Tertiary Basalts, red triangle – Fitzroy River Estuary sediments, green triangle – weir sediments, blue triangles – flood sediments).

Table 2. Weirs,dams and flood events in the Fitzroy River Basin catchment ranked according to the first canonical variate (LD1). Associated rivers (with the principal FRB catchment geology indicated by the colour-code) and the catchment abundance of rock types are also listed.

Weirs or dams	LD1	LD2	River	Rock types* (decreasing abundance)
Gyranda Weir	-1.45	1.87	Dawson	SB
Glebe Weir Boat Ramp	-1.39	1.2	Dawson	SB
Theresa Creek Dam	-1.37	-2.92	Theresa Ck	TFB+ BB
Theodore Weir	-0.95	0.65	Dawson	SB + BB
Fairbairn Dam	-0.87	-2.12	Nogoa	TFB + BB+ TB + SB
Glebe Weir Dam Wall	-0.84	1.26	Dawson	SB
Tartrus Weir	-0.61	0.42	MacKenzie	SB + BB + NEFB + TFB + TB
Fairbairn Dam	-0.51	-0.78	Nogoa	TFB + BB + TB + SB
Comet Weir	-0.47	-1.85	Comet	BB + TB +SB
Bingegang Weir	-0.12	-1.31	MacKenzie	SB + BB + TFB + TB
Comet Weir	-0.12	-1.01	Comet	BB + TB +SB
MacKenzie River above Tartrus Weir	-0.1	-0.47	MacKenzie	SB + BB + TFB + TB
Fitzroy Est. Cuthrough near Centre Is.	-0.03	-2.88	Fitzroy	BB + NEFB + SB + TFB + TB
Fitzroy above Barrage	0.1	0.19	Fitzroy	BB + NEFB + SB + TFB + TB
Bingegang Weir	0.32	-0.28	MacKenzie	SB + BB + TFB + TB
Bedford Weir	0.45	-1.87	MacKenzie	SB + BB + TFB + TB
Bedford Weir	0.95	-0.24	MacKenzie	SB + BB + TFB + TB
Flood events	**LD1**	**LD2**	**River**	**Rock types* (decreasing abundance)**
Fitzroy Motor Boat Club 13/01/02	0.81	-1.31	Fitzroy	BB + TB + NEFB + SB + TFB
Comet Weir Flood 8/1/02	1.28	-0.93	Comet	BB + TB + SB
Bedford Weir Flood 8/1/02	1.32	-0.57	MacKenzie	BB + TB +SB + TFB

*SB – Surat Basin, BB – Bowen Basin, TFB – Thomson Fold Belt, NEFB – New England Fold Belt, TB – Tertiary Basalts

Table 3. Mineralogy (%) of Fitzroy River Estuary (FRE) bottom sediment, Fitzroy River Basin (FRB) weir sediment and flood sediment samples.

Estuary sample No.	**Quartz**	**Kaolinite**	**Mica/Illite**	**Smectite**	**Albite**	**Orthoclase**	**Hematite**	**Anatase**	**Amphibole**	**Calcite**	**I/(I+S)**[1]
5	18	25	4	43	6	2	0	0	0	0.5	9
6	17	9	8	49	7	2	0.5	1	0	0	14
10	13	24	3	51	4	2	0.5	0	0	0	6
12	15	32	6	38	4	1	0.5	0	0	0	14
21	22	24	4	40	7	2	0.5	0	0.5	0	9
23	24	22	3	38	8	2	0.5	0	2	0	7
26	34	15	4	32	13	2	0	0	0	0	11
37	17	33	7	36	4	2	0.5	0	0	0	17
58	19	27	8	40	5	2	0.5	0	0	0	17
63	25	21	3	40	9	2	0.5	0	0.5	0	7
64	13	29	6	46	3	1	0.5	0	0	0	12
67	13	13	11	56	3	0	0	0	0	2	16
Mean ± 1 std dev	*19 ± 6*	*23 ± 7*	*6 ± 3*	*42 ± 7*	*6 ± 3*	*2 ± 1*	*0 ± 1*	*0 ± 0*	*0 ± 1*	*0 ± 1*	*12 ± 4*
Weir sample	**Quartz**	**Kaolin**	**Mica/Illite**	**Smectite**	**Albite**	**Orthoclase**	**Hematite**	**Anatase**	**Amphibole**	**Calcite**	**I/(I+S)**
Bedford Weir	8	9	8	74	0	0.5	0	0	0	0	10
Theodore Weir	12	23	2	50	6	4	1	1	0	0	4
Theresa Creek Dam	20	22	22	25	8	3	0.5	0	0	0	47
Gyranda Weir	13	14	6	66	0	0.5	0.5	0	0	0	8
Flood sample	**Quartz**	**Kaolin**	**Mica/Illite**	**Smectite**	**Albite**	**Orthoclase**	**Hematite**	**Anatase**	**Amphibole**	**Calcite**	**I/(I+S)**
Bedford Weir	6	7	4	82	0	0.5	0.5	0	0	0	5
Comet Weir	5	8	8	78	0	0.5	2	0	0	0	9
FMBC[2]	4	5	2	84	0	0.5	0.5	0	0	3	2

1 [%Illite/(%Illite + %Smectite)]*100

2 Fitzroy River Motor Boat Club

6.4 *Model estimates of proportions of catchment soils in weirs, dams and Fitzroy Estuary sediments*

6.4.1 *Model estimates of proportions of catchment soils in weirs and dams*

A summary of model estimates of the proportions of five catchment endmember soil types (Bowen Basin – BB, New England Fold Belt – NEFB, Surat Basin – SB, Tertiary Basalts – TB and Thomson Fold Belt – TFB) for weirs, dams and flood events and the associated river system in the Fitzroy River Basin (FRB) are presented in Table 4. A number of general trends are evident in the distribution of catchment endmember soils in impoundments or flood events:

(i) Southern Fitzroy River Basin impoundments (Dawson River catchment)
Model estimates indicate that Gyranda, Theodore Weir, and Glebe Boat ramp and Dam Wall sediment samples are dominated by soils derived from the SB (57-75%) with a lesser proportion of BB soils (1-25%). Only a small proportion of TB soils are present (1-14%). Similarly, only a small proportion of NEFB soils are present (1-2%) except for Theodore Weir where there is an estimated that 27%. The latter enrichment may reflect the contribution of a number of small tributaries (*e.g.* Boam and Oxtrack Creeks) which drain the NEFB and join the Dawson River directly above Theodore Weir. The presence of TFB soils in the uppermost Glebe Weir (Fig. 1) may reflect aeolian input or an ancient connection of the upper Dawson River to the most western portion of the FRB.

(ii) Western Fitzroy River Basin impoundments (Nogoa River and Theresa Creek catchments)
Theresa Creek Dam and both Fairbairn Dam sediment samples strongly reflect the presence of TFB soils which range in abundance from 34-61% (Table 4). Model estimates suggest that SB sediments constitute between 16% and 39% delivered via the Nogoa River to Fairbairn Dam (24-39%), or possible aeolian input or via former tributaries to Theresa Creek Dam (16%). TB material is low (6-18%) in both dams reflecting that the majority of the catchment is located above the large expanses of basaltic soils in the mid-west of the Fitzroy Basin (Fig. 1). BB soils are virtually absent in the Theresa Creek and Fairbairn Dams (1-3%), whilst NEFB soils are low in the Fairbairn Dam sediments (6%), but elevated in the Theresa Creek dam sediment sample (20%). The enrichment of NEFB soils in the Theresa Creek Dam sample may reflect the flow (for *ca.* 50km) of Theresa Creek through a large outcrop of Devonian granite and lesser acid volcanics. These are likely to be similar in composition to Permian granitoids which constitute a large proportion of the NEFB. The contribution of the Devonian granite and/or acid volcanics is also strongly indicated by the mineralogy of the Theresa Creek Dam sediment sample which is enriched relative to other impoundment sediments in feldspar and mica/illite (Table 3). A moderate illite to illite + smectite ratio (I/(I+S)) is also characteristic of a granitic or other felspathic input.

(iii) Central Fitzroy River Basin impoundments (Comet and MacKenzie River catchments)
The majority of samples from the central FRB are noteworthy in that model estimates suggest that they contain almost no sediment derived from the BB (1-10%). Similarly, abundances of NEFB soils are also generally low except for Tartrus Weir (23%) which is located close to and may be influenced by tributaries draining the NEFB and/or sediment delivered by the Connors River via the Isaac River (Fig. 1). The presence of a NEFB contribution to both Comet River Weir samples (13-19%) in addition to that of TFB soils (32-57%) may be indicative of:

- *The presence of the Devonian Granite (as a geochemical surrogate of NEFB soils) in the Theresa Creek catchment*
  This possibility is discussed in (ii) above and is supported by close examination of relevant geological maps (*e.g.* Bowen Basin Solid Geology, 1:500,000) which shows large areas of alluvium and soils largely confined to, and hence likely to be principally derived from, this unit.

- *Deposition of sediment from the western Fitzroy Basin catchment via backflow events into the Comet River*
  Historical evidence indicates that after heavy rainfall in the western catchment sediment-laden water may flow from the Nogoa upstream into the Comet River, and that this may have been more extensive prior to the construction of the Fairbairn Dam

on the Nogoa in the early 1970's. Given the proximity of the Comet River catchment to the TFB dominated region, aeolian inputs may also be important in the delivery of fine-grained soil material.

- *The capture of the Nogoa River or pre-existing fluvial systems*
  Geomorphological studies of the FRB suggest that high energy river systems existed prior to the present day fluvial regime. In particular, some fluvial sediment has been noted to contain cobble-sized rocks indicative of a very high energy system (B. Finlayson, Univ. Melb. *pers. comm*.). Given the proximity of the Comet and Nogoa (the latter river draining the TFB) it is possible that other drainage networks may have been present, possibly prior to the deposition of the floodplain TB in the central west of the FRB.

- *Regional aeolian inputs of TFB material*
  A possibility exists that aeolian inputs of TFB soils to the central FRB may be an important component in the sediment budget of the Comet River. In particular, it is likely that the Aeolian inputs will be fine, and thus mostly incorporated into the <10µm fraction of sediment analysed in this study.

Model estimates of the contributions of soils from the SB indicate that it may vary substantially from 5-60% with major variation even in sediment samples from the same weir (e.g. Bedford Weir – 5-32%, Bingegang Weir – 14-35%, Table 4). Similarly TB soils may also vary widely in absolute abundance (6-45%) and within individual weirs (e.g. Bedford Weir – 22-45%). The highest TB occurs on the MacKenzie River within the Bedford and Bingegang Weirs (10-45%, ave. *ca.* 29%).

(iv) Eastern Fitzroy Basin sediments (Fitzroy River)
Model estimates of catchment soil abundance in the eastern FRB sediment samples (Fitzroy Estuary Cuthrough near Centre Island within the actual FRE and Fitzroy above the barrage) vary widely. The sediment sample from the Cuthrough contains an abundant NEFB soil component which may reflect the selective separation of the less mobile material. Recycling of sediments from influence of local tributaries and the main stem due to the widely observed bank collapse which is a common feature of the estuary (see also Section 4.4.2). The only other abundant soil type in the Cuthrough sample is from the TFB which has been recognised as an important source of sediment to weirs and dams in the central and western areas of the Fitzroy Basin.

The presence of a TFB soil component in the Cuthrough sediment sample is the only common feature with the Fitzroy sediment sample from above the barrage with both samples containing a similar abundance (24% versus 31% respectively). In contrast, the sample of Fitzroy River sediment from above the barrage is the only sample to contain a substantial BB component (40%) in addition to some SB (16%) and TB (18%) soils.

(v) Flood events (Fitzroy, Comet and MacKenzie Rivers)
The modelled estimate of the composition of suspended sediment samples from the flood events sampled in this study differ substantially from the weir and dam samples. Flood events are dominated by TB soils (63-81%) with minor proportions of most other catchment soil endmembers including BB (0-12%), NEFB (0-6%), SB (8-14%) and TFB (2-15%). This indicates that during flood events that basaltic material is preferentially transported in the fine (<10µm) fraction investigated in this study relative to other soil types.

Table 4. Estimated proportions of catchment soil endmembers in bottom sediment samples and flood events in the Fitzroy River Basin. Ranking of weirs, dams and floods and colour-coding as per Table 2.

Weirs or dams	**BB**	**NEFB**	**SB**	**TB**	**TFB**	**River**
Gyranda Weir	0.23	0.01	0.75	0.01	0.01	Dawson
Glebe Weir Boat Ramp	0.25	0.02	0.60	0.04	0.09	Dawson
Theresa Creek Dam	0.01	0.20	0.16	0.09	0.54	Theresa Ck
Theodore Weir	0.01	0.27	0.57	0.14	0.01	Dawson
Fairbairn Dam	0.03	0.06	0.24	0.06	0.61	Nogoa
Glebe Weir Dam Wall	0.19	0.02	0.61	0.03	0.15	Dawson
Tartrus Weir	0.01	0.23	0.60	0.06	0.10	MacKenzie
Fairbairn Dam	0.03	0.06	0.39	0.18	0.34	Nogoa
Comet Weir	0.05	0.13	0.15	0.09	0.57	Comet
Bingegang Weir	0.06	0.05	0.35	0.37	0.16	MacKenzie
Comet Weir	0.06	0.19	0.24	0.19	0.32	Comet
MacKenzie River above Tartrus Weir	0.08	0.09	0.29	0.09	0.44	MacKenzie
Fitzroy Est. Cuthrough near Centre Is.	0.01	0.58	0.06	0.03	0.31	Fitzroy
Fitzroy above Barrage	0.40	0.02	0.16	0.18	0.24	Fitzroy
Bingegang Weir	0.09	0.04	0.14	0.10	0.62	MacKenzie
Bedford Weir	0.10	0.15	0.05	0.22	0.48	MacKenzie
Bedford Weir	0.07	0.09	0.32	0.45	0.06	MacKenzie
Flood events	**BB**	**NEFB**	**SB**	**TB**	**TFB**	Comet
Fitzroy Motor Boat Club 13/01/02	0.00	0.06	0.11	0.81	0.02	Fitzroy
Comet Weir Flood 8/1/02	0.00	0.00	0.14	0.70	0.15	Comet
Bedford Weir Flood 8/1/02	0.12	0.03	0.08	0.63	0.14	MacKenzie

6.4.2 Model estimates of proportions of catchment soils in the Fitzroy Estuary

A longitudinal plot of model estimates of the proportions of five catchment endmember soil types (Bowen Basin – BB, New England Fold Belt – NEFB, Surat Basin – SB, Tertiary Basalts – TB and Thomson Fold Belt – TFB) for the sediment samples collected in the Fitzroy River Estuary (FRE) is presented in Fig. 7. The estimated average proportions of the five FRB catchment endmembers are given in Table 6. A number of general trends are evident in the distribution of catchment endmember soils in impoundments or flood events.

Soils from the BB, SB, and, to a lesser extent, TB, display longitudinal variation along the FRE with both the BB and TB progressively enriched towards the ocean (Keppel Bay, Fig. 7). In contrast, soils of the SB display an opposite trend being most enriched immediately below Rockhampton. The estimated absolute abundance of these soil types also ranges widely with BB ranging between 0 and 50% (mean 22 ± 13%) and the SB ranging between 0 and 40% with a lower mean abundance of 15 ± 10% (Table 5). Noteworthy is the higher mean abundance of TB soils within Keppel Bay ca. 0-13km upstream (13± 5%) relative to samples further upstream which have both a lower mean abundance (9± 4%).

Soils derived from the TFB and NEFB do not display any longitudinal trend but differ in abundance and variability. TFB soils are confined to a relatively narrow range between *ca.* 20-40% with a mean abundance of 30 ± 7%. Those from the NEFB have a wider range of between 0 and 50%, but lower mean abundance of 23 ± 14% (Table 5).

The abundance of catchment soil endmembers retained within the FRE varies widely relative to their areal abundance in the FRB catchment (Table 5). Soils of the BB display the greatest depletion factor (0.5), while the SB soils are less depleted (0.8). Soils derived from TB (1.1) and NEFB (1.2) both display marginal enrichment. Given the large variability in the average FRE abundance, however, it is unlikely that soils of the SB, TB and NEFB are significantly different from their FRB abundance. Soils of the TFB are clearly the most enriched within the FRE (4.3 times) with these soils being amongst the most distant from the FRE (Fairbairn

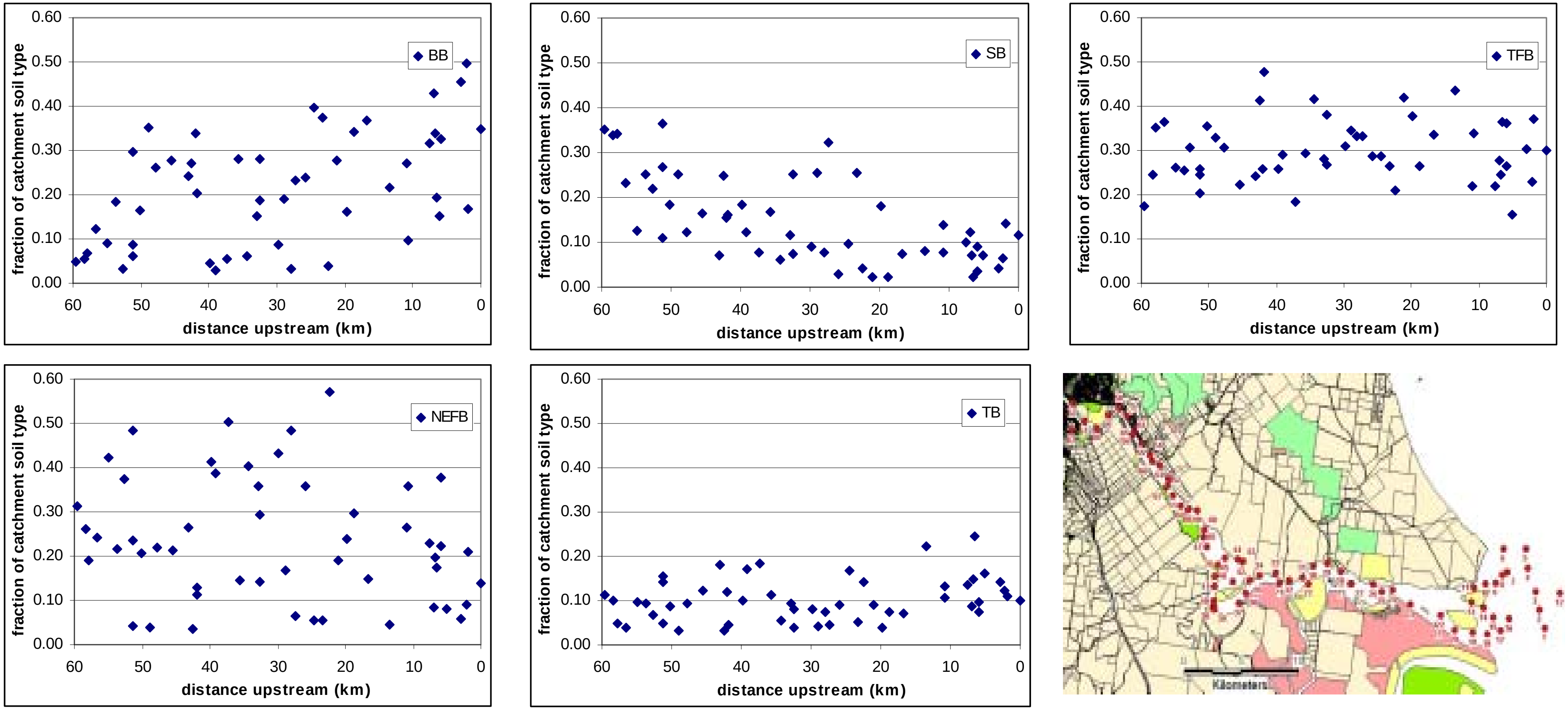
Dam, and to a lesser extent, Theresa Creek Dam, are the only impoundments with the potential to trap soils transported from this upper FRB catchment source (Fig. 1). The low and uniform concentration of TB derived materials, especially in comparison to the high TB content of the flood events, suggests that this material is preferentially exported from the estuary.

Table 5. Modelled estimates of the percentage of catchment soil endmembers in the Fitzroy River Estuary.

Catchment Endmember	Bowen Basin	New England Fold Belt	Surat Basin	Tertiary Basalt	Thomson Fold Belt
Estuary Abundance (1)	22 ± 13	23 ± 14	15 ± 10	10 ± 5	30 ± 7
Catchment Abundance (2)	46.0%	19.0%	18.6%	9.5%	6.9%
Enrichment Factor	0.5	1.2	0.8	1.1	4.3

(1) estimated μ ± 1 ů calculated using the Bayesian mixing model
(2) relative abundance calculated in absence of Duaringa and Biloela Basins (Fig. 1)

Figure 7. Longitudinal plots of modelled estimates of the fraction of catchment soil types (Bowen Basin soils – BB, Surat Basin soils – SB, Thomson Fold Belt soils – TFB, New England Fold Belt soils – NEFB and Tertiary Basaltic soils – TB) in the Fitzroy River Estuary bottom sediments from the most eastward sample location (site 12) upstream towards Rockhampton.



7. Discussion

A synthesis of geochemical, mineralogical and statistical analysis and geochemical modelling of weir and dam sediments, suspended material collected from flood events, discussed in the previous sections, allows us to make associations between the major sediment types, and different areas in the FRB. The three major sources of sediment and their spatial associations are:

- (i) Tertiary basaltic soils derived from the western and central FRB and delivered via the Comet and Nogoa Rivers and potentially Theresa and Sandy Creek.
- (ii) Soils derived predominantly from the BB sediments and southern FRB from the SB which are delivered by the Dawson.
- (iii) Soils derived from the western FRB, and in particular those derived from the TFB

7.1. Inferred sources from weir and dam sediment investigations

Geochemical, mineralogical statistical analysis and geochemical modelling of the weir and dam sediments allows general statements to be made about the dominant sources of sediment in specific river catchments. It is these materials that are ultimately delivered to the FRE. Within the westernmost catchment, Theresa Creek Dam strongly reflects the influence of the TFB from which its sediment is primarily derived (Fig. 1). Similarly, two samples from Fairbairn Dam also have a strong TFB geochemical signature, although one sample also has a significant basaltic character (estimated at 18% TB, Table 4) reflecting the influence of basaltic soils in the lower catchment of the Nogoa River. This heterogeneity in sediment composition, even within one dam, is discussed in detail later. Elsewhere within the western FRB, the strongly basaltic character of the Comet Weir sediments reflects the presence of large exposures of basaltic soils over much of its catchment. Thus, the Comet River appears to be a major source of basaltic material within the central FRB. Model estimates suggests only a small to moderate amount of TB (9-18% Table 4) is actually retained within the weir. This is consistent with the radionuclide data indicating highly efficient transfer of material through the system. Analysis of floods in this system (Section 5.3) suggests a much higher proportion of TB is carried during these events. This leads to the conclusion that the post flood weir sediment samples are an imperfect representation of the actual flood event materials.

Within the central FRB, the MacKenzie River is intersected by two weirs, the Bedford and Bingegang (Fig. 1). These weirs have the strongest basaltic composition of all the weirs within the FRB catchment (10-45% from model estimates, Table 4). This reflects not only the contribution of sediment from the Comet River, but also the Nogoa River, Theresa Creek and other western catchment tributaries although none of the upstream weirs sediments are sufficiently basaltic to explain the enrichment observed in sediments from Bedford and Bingegang Weirs. At present the relative contribution and composition of sediment from Theresa Creek below the Theresa Creek Dam is unquantified. Importantly, one of its main tributaries, Sandy Creek near Clermont, drains another large area of basaltic soils immediately to its north and east (Fig. 1) and thus, may be a source of sediment substantially enriched in basaltic material.

The sediments of the Tartrus Weir are substantially less basaltic than the upstream Bedford and Bingegang Weirs. This is consistent with dilution by basalt-poor sediment delivered by the Connors and Isaac River systems which contain only isolated occurrences of basaltic soils in their catchments (Fig. 1).

The three weirs situated along the Dawson River contain substantially less basaltic material relative to weirs on the Comet, Nogoa and MacKenzie River systems. This is not surprising given the relative paucity of basaltic material, particularly within the southernmost portion of the FRB catchment which is occupied predominantly by SB soils (Fig. 1, Table 1).

Sediments from the Fitzroy River from above the barrage at Rockhampton contain a relatively high proportion of TB (Table 2, 5). This is consistent with the MacKenzie River and its tributaries being a major source of fine sediment (defined as <10μm in this study) to the lower Fitzroy River. Sediment from near Centre Island with the FRE has a substantially lower TB component which may reflect preferential transport of basaltic soils from the estuary (see

Section 5.4). Flow dynamics may also play a part in the differences between the samples collected from above the Fitzroy Barrage and at the Cuthrough. The Barrage samples were collected from a large backwater in the barrage (the river/barrage itself is scoured clean after every flood event) where the flow effects are minimal, and thus settling of the finest particles can take place here. The Cuthrough is subject to tidal variations but since it is a loop with a nodal point at the distal end, the flows (and water velocity) are reduced relative to the main channel. There are also velocity gradient along the estuary with the highest being at the mouth. Because of the asymmetry these are highest on the inflows so it is conceivable that a large proportion of the undifferentiated material deposited during a flood event could be resuspended on an inflow with the non-basaltic material settling and/or being sorted upstream while the more slowly settling TB (smectite-dominated) material transported back down the FRE and out into Keppel Bay where it is then propagated north.

The analysis of the composition of impoundments within the FRB allows a number of general statements to be made about sources of sediment to the FRE estuary:

- The Dawson River in the southern and central FRB carries only a small TB component and the inputs from this area are dominated by soil inputs from the SB and BB.

- Rivers from the central FRB carry variable amounts of TB, with much of this transported during flood events. Soils from the SB form a minor component with little contribution from soils of the BB despite the fact that they constitute the majority of the central FRB. Soils from the TFB constitute a substantial proportion of the sediment transported by, and retained in, impoundments in the central FRB.

- Rivers from the western FRB predominantly carry sediment derived from the TFB and may even carry a greater proportion (*ca* 70-80%) than that suggested by model estimates if the NEFB component (as a surrogate for granitic material within the TFB in the western FRB) is also considered.

7.2. Inferences from flood-delivered sediments

As in the case of weirs and dams in the FRB catchment, analysis of sediment delivered in flood events also gives an insight into the geochemical and mineralogical heterogeneity as a function both catchment soil type and hydrology. Flood event sediments are composed of the higher proportion of basaltic material compared to both weir and dam sediments and the FRE sediments (Tables 2, 3, 5). Because of the drought there have been only a very limited number of flood events which we have been able to sample, and these have been mainly in the Comet and Dawson catchments thus our conclusions regarding the geochemical characteristics of the flood events necessarily reflect the limited distribution of floods across the whole catchment. Thus the flushing by high flow events of rivers in the central and western FRB (due to increasing connectivity) which have the highest proportion of basalt in their catchments, in addition to the ability of high flows to increasingly entrain the fine-grained basaltic (smectitic) soils inevitably leads to high TB outputs reflected in our observations. Furthermore, there are anecdotal accounts that most flood events scour weirs such as the Bedford and Bingegang which have the most basaltic-rich sediments sampled in the FRB.

7.3. Selective retention of catchment sediments in the Fitzroy River Estuary

Within the FRE, the retention of sediment from different FRB catchment soil endmembers will be primarily dependant on three factors. These are as follows:

(i) The influence of sub-catchments

It is clear from analysis of impoundments within the FRB that rivers from the western and central FRB will primarily deliver soil materials derived from TB, SB and TFB. In the case of the TFB this will be disproportionately represented by a factor of *ca.* 4 (TB, SB) to *ca.* 8 (BB) relative to all other catchment endmembers. The Dawson River, in contrast to the central and western rivers of the FRB, will primarily deliver SB and BB soils with potentially some less abundant contributions from NEFB and TB soils. Thus, during major hydrological events, and depending on the flow of individual rivers and the magnitude and relative order of flow maxima substantially different proportions of catchment soil endmembers may be deposited within the FRE.

(ii) Flocculation and resuspension

The rate of flocculation and settling of suspended sediment within estuaries is dependent on a number of factors including salinity, particle surface charge (zeta potential) mineralogy and particle size. The salinity front slowly propagates upstream post flood so at the same time sediments in different parts of the river are exposed to quite different salinities. During large flood events scouring of the FRE will occur leading to resuspension, as well as transport of material offshore within the freshwater plume. Due to the inherently smaller particle size of the TB particles (being primarily composed of smectite (see flood samples – Table 3) and in the event of flocculation, they are likely to settle as a slower rate relative to other sediment types, and thus, it is likely that these will be transported further within the freshwater plume. It is likely that difference in particle characteristics may also explain the differential distribution of BB- and SB-derived sediments in the FRE. The preferential export of basaltic material in flood events and the retention of more granitic or other more siliceous sediments within the estuary has been advocated by McCulloch *et al* (2003) in a study of the nearby Johnstone River. In this study it was demonstrated that the majority of fine-grained sediment (which contained a substantial basaltic component) were transported and deposited a number of kilometres offshore.

(iii) Flood event magnitude

Analysis of limited flood events within the FRB clearly indicates that a propensity to the transport of finer-grained TB soils. If it is assumed that the average proportion of TB in a flood event is *ca.* 70% (Table 4) and this catchment abundance is approximately 10% (Table 5) this represents an enrichment factor of *ca.* 7 as opposed to the enrichment factor of *ca.* 1 estimated for the present-day FRE sediments. As described above, however, it is likely that during a flood event of sufficient magnitude that the majority of TB-laden sediment would be carried within the freshwater plume into Keppel Bay and potentially beyond. During our study period all the flood flows have been well below the median size.

(iv) *Role of weirs and dams*

The weirs and dams sampled in this study constitute temporary storage zones for catchment sediment and highlight both the spatial heterogeneity of sediment being transported by the major rivers systems and the influence of catchment geology. The utility of weirs and dams in identification of sediment sources is that they integrate (sub) catchment sediment inputs, albeit with varying fidelity. The extent to which weir sediments truly represent catchment sources depends on as the predominance of flow and/or suspended sediment load from particular sub-catchments. Purely local effects such as bank collapse on the declining limb of the hydrograph may also distort the composition of the weir sediments. Although these factors may result in spatial heterogeneity of bottom sediment (*e.g.* Douglas *et al.,* 2003b), sediment from impounded water bodies provide a useful first-order representation of sediment sources. The compositional variation of weir and dam sediments in the FRB is discussed below.

(v) *Local erosion and deposition*

The FRE estuary is highly dynamic and we have noted zones of active erosion as well as zones of active deposition (and colonisation by mangroves) in different parts of the river. These processes are occurring on a range of time scales and will lead to the addition of previously stored material as well as the removal of new material from the estuary. Thus the estuary sediments are an imperfect sample of the material which passes through the estuary during flood events, but they remain predominantly our best way of sampling the inputs.

7.4 Phosphorus content of catchment soils and the Fitzroy River Estuary sediments

Identifying the relative proportions of catchment soils being delivered into riverine, estuarine, and coastal systems places us in a good position to estimate the relative flux of P from each source also. This has direct application in focussing catchment management aimed at reducing nutrient deliveries on those soils which deliver the highest fluxes of P. In similar studies of sediment transport into Queensland coastal waters, basaltic soils, despite often constituting only a relatively small proportion of the sediment being delivered, have been identified as the major contribution to the P flux, due to their inherently high P concentration (Douglas *et al.,* 2003a, McCulloch *et al.,* 2003a, b).

Average total phosphorus (TP) concentrations and TP concentration ranges for FRB soils, weir and dam sediment and flood sediment, in addition to Johnstone River catchment basaltic soils (McCulloch, 2003b) and Moreton Bay basaltic soils (Douglas *et al.,* 2003a) are presented in Table 6. In contrast to the studies above, Tertiary basaltic soils in the FRB have, on average, approximately 2.5 to 3.4 times less TP than comparable basaltic soils from the Moreton Bay and Johnstone River catchments respectively (Table 6). It is unlikely that the fractionation of the soil samples to <10µm is responsible for these differences, as the Moreton Bay soils, as well as all the soils, weir and dam, and flood event samples (Section 3.1), were fractionated in an identical manner. Furthermore, fractionation to a smaller size fraction generally results in an increase in trace element concentrations due to the loss of quartz, albeit to a lesser extent from basaltic rather than granitic or other soils. In any case, analyses of unfractionated soils yield similar TP concentrations. In addition, tests of P-desorption in P-free water from similar Johnstone River flood sediments indicated little or no P-loss(McCulloch *et al.,* 2003b) thus, implying little or no P-loss during wet sieving and settling used to separate the <10µm size fraction used in this study.

A direct consequence of the substantially lower TP concentrations contained within the Tertiary Basaltic soils of the FRB catchment is that the TB derived materials do not differ in phosphorus concentration from all the other soils types within the FRB catchment (Table 6). Thus, in considering the flux of TP from the catchment, it is the total sediment flux which is of major importance, rather than the individual catchment soil components. Nonetheless, where particular catchments preferentially deliver a particular soil type, as in the case of basaltic soils in the Comet, it is still important to know the proportions, and source locations of these soil types being delivered if effective remedial measures are to be undertaken. An additional factor to consider is the bioavailability of TP contained within each soil type. During the weathering process and pedogenesis, it is likely that substantial amounts of P are incorporated into Fe-oxide phases which are potentially available for release under anoxic conditions arising from burial within transiently or permanently anoxic catchment impoundments or estuarine sediment.

Table 6. Average total phosphorus (TP) concentrations and concentration ranges in Fitzroy River Estuary sediments, Fitzroy River Basin catchment soils, weir and dam sediments, flood event sediments and other Tertiary basalts from the Burdekin River catchment and Moreton Bay catchment (SE Qld).

Sediment/soil type	**Average TP (µg/g) ± 1ů**	**TP concentration range (µg/g)**
Estuary sediments	657 ± 106	480 - 960
Bowen Basin	969 ± 784	305 - 4277
Surat Basin	1139 ± 993	436 - 3622
Thomson Fold Belt	735 ± 261	305 - 1091
New England Fold Belt	938 ± 738	131 - 3666
Tertiary Basins	883 ± 550	349 - 1615
Tertiary Basalts (Fitzroy)	985 ± 551	305 - 2051
Tertiary Basalts (SE Qld)	2480 ± 1121	707 - 5014
Tertiary Basalts (Johnstone)	3334 ± 1174	1615 - 4248
Weirs/Dam sediment	863 ± 153	436 - 1047
Flood sediment	755 ± 56	707 - 816

8. Benefits and Outcomes

Under the bilateral agreements between the Australian and Queensland governments, the Reef Water Quality Protection Plan and the National Action Plan for Salinity and Water Quality include imperatives for improved water quality within Great Barrier Reef (GBR) catchments and for reduced loads of sediments, nutrients and contaminants to be delivered to the GBR lagoon. The Fitzroy Basin is a major contributor to the loads of these materials reaching coastal areas in the southern GBR. Cost-effective investment in improved land, vegetation and water management to lower these loads from the Fitzroy Basin requires an understanding of the sources and movement of sediments within the basin.

This scientific study has provided new, relevant and timely information on the sources and movement of sediment by:

- Identification of the principal sources of sediment from the Fitzroy River Basin (FRB) to both weirs and dams on many sub-catchment river systems and quantitative estimates of the contribution of major catchment soil types.
- Identification of the principal sources of sediment to the Fitzroy River Estuary (FRE) and quantitative estimates of the contribution of major catchment soil types.
- Identification of longitudinal variation of catchment sediments retained within the FRE.
- Recognition of total sediment flux, rather than individual soil types as the main determinant of total phosphorus flux to the FRE.
- Importance of floods in the delivery of suspended material dominated for floods studied by contributions from basaltic soils, much of which does not appear to be retained within the FRE.
- Identification of the Bowen Basin as a minor contributor to sediment retained within the FRE despite constituting almost 50% of the FRB soils.
- Identification of soils of the Thompson Fold Belt as a disproportionately large contributor to sediment retained within the FRE.

This research on sediment sources and movement complements other Coastal CRC research within Task FH1 which has investigated sediment, nutrient and contaminant dynamics in the Fitzroy estuary and Keppel Bay and sediment modelling tools being developed in the region by the NR&M science group and Catchment Hydrology CRC. Thus this research has provided crucial new regional scale information on the sources of sediment entering the Fitzroy estuary. This information will inform cost-effective investment by Governments through the Fitzroy Basin Assoc Inc. into changes to land management practices so that sediment, nutrient and potentially contaminant loads reaching the coast from the Fitzroy Basin can be reduced.

9. Further Development

As we noted earlier, this study has taken place at a time of well below average flood flows. Consequently sediment deliveries from the various catchments have been very uneven. The data has allowed us to identify factors which can modify the geochemistry in transit through the river system and cause changes post-arrival in the estuary. Based on this data we have drawn conclusions about the processes and sources of the sediment deliveries to the estuary. These conclusions can be made more robust through additional research which should focus on three areas:

(a) Because of cost and logistic constraints, a number of key sub-catchments within the FRB were not sampled in this initial study. The Sandy Creek catchment in the westernmost FRB, which drains the largest area of basaltic soils in the FRB, is now of particular interest. The research reported here has identified this area as potentially the most significant source of basaltic material to the MacKenzie River, and the Bedford and Bingegang Weirs. Similarly, the granitic soils present within the TFB remain unsampled and are likely to be a substantial source of sediment within the Theresa Creek catchment. With a relatively small effort, it would be possible to build substantially on the work reported here.

(b) The highly variable hydrology of flood events within the FRB floods have the inherent capacity to transport large amounts of suspended sediment. This sediment may be derived from a variety of sources such as by direct entrainment of catchment soils, resuspension of riverine sediments in temporary storages (*e.g.* riparian zones or overbank deposits) or scouring of accumulated sediment in dams and weirs. Modelling, particularly at major river catchment scales using weirs and dams as sampling points, will allow an estimate of the mass balance of sediment from major soil types during floods. In addition, isotopes of Sr and Nd, which have been used in similar sediment tracing studies, could be used to provide an independent estimate of catchment sediment sources. It is likely that these flood events transport the majority of sediment delivered into the FRE. Thus, major flood events should be monitored to assess changes in the composition and suspended sediment load over the entire hydrograph within the FRE. This will allow quantitative estimates of sediment sources using the mixing model. In particular, quantitative measurements on the composition, and load, of sediment being deposited within the FRE and Keppel Bay should be made a high priority.

10. Conclusions

An integrated geochemical, mineralogical, statistical and modelling approach has been used to identify the major sources of catchment sediment in weirs and dams in the FRB and FRE. Based on a reconnaissance soil sampling survey of major catchment soil types, a purpose-built Bayesian mixing model was applied to estimate actual proportions of catchment soil endmembers in the weir, dam and estuary samples.

Weir and dams within the FRB provide an insight, albeit based on limited sampling and influenced by a range of factors, into the origin, transport and deposition of sediment within the Fitzroy Basin. Three spatial sediment associations exist within the Fitzroy River Basin. Firstly, the Dawson River in the southern and central FRB carries only a small TB component with inputs dominated by soil inputs from the SB and BB. Secondly, rivers from the central FRB carry variable amounts of TB, predominantly transported during flood events. Soils from the SB form a minor component, while soils of the BB contribute very little fine sediment in local weirs and dams on the MacKenzie River despite the fact that they constitute the majority of the central FRB. Soils from the TFB constitute a substantial proportion of the sediment transported by, and retained in, impoundments in the central FRB. Lastly, rivers from the western FRB predominantly carry sediment derived from the TFB that may constitute (*ca* 70-80%) of the fine sediment source.

Flood events, in contrast to weir and dam samples, are dominated by basaltic material. It is estimated that flood events have an estimated average enrichment of TB of *ca.* 7 over the mapped distribution of TB within the FRB catchment.

In the FRE, soils from the BB, SB, and, to a lesser extent the TB component, display a distinct longitudinal variation with both BB and TB progressively enriched towards the ocean. In contrast, soils of the SB display an opposite trend. The estimated absolute abundance of these soil types also displays substantial variation. The BB material ranges between 0 and 50% (mean 22 ± 13%), while the SB ranges between 0 and 40% with a lower mean abundance of 15 ± 10%. TB soils deposited within Keppel Bay have a higher mean abundance from *ca.* 0-13km upstream (13 ± 5%) relative to samples further upstream within the FRE (9 ± 4%). Soils derived from the TFB and NEFB do not display any longitudinal trend, but differ in abundance and variability. TFB soils are confined to a relatively narrow range between *ca.* 20-40% with a mean abundance of 30 ± 7%. Those from the NEFB have a wider range of between 0 and 50%, but lower mean abundance of 23 ± 14%.

Relative to their areal abundance in the FRB catchment, soils of the BB display the greatest depletion factor (0.5), with SB soils less depleted (0.8). Soils derived from TB (1.1) and NEFB (1.2) both display marginal enrichment, however, it is unlikely that soils of the SB, TB and NEFB are significantly different from their FRB abundance. TFB soils are the most enriched within the FRE (4.3 times) despite these soils being amongst the most distant from the FRE. The low and uniform concentration of TB derived materials, especially in comparison to the high TB content of the flood events, suggests that this material is preferentially exported from the estuary.

Tertiary basaltic soils in the FRB have, on average, approximately 2.5 to 3.4 times less TP than comparable basaltic soils from the Moreton Bay and Johnstone River catchments respectively. Furthermore, they are similar in TP concentration to most other soils within the FRB. Thus, in considering the flux of TP from the catchment, it is the total sediment flux which is of major importance, rather than the flux of individual catchment soil components. It is likely, however, that the bioavailability of the phosphorus may differ particularly where substantial amounts of P are incorporated into Fe-oxide phases which are potentially available for release under anoxic conditions arising from deeper burial within de-oxygenated estuarine sediment.

11. References

Allegre, C.J., Dupre, B, Negrel, P. and Gaillardet, J., (1996). Sr-Nd-Pb isotope systematics in the Amazon and Congo River systems: Constraints about erosional processes. *Chem. Geol*., 131, 93-112.

Billheimer, D. (2001) Compositional Receptor Modelling. *J. Environmetrics* 12, 451-467

Blais, J.M. and Kalff, J., (1995). The influence of lake morphometry on sediment focussing. *Limnol. Oceanogr*., 40, 582-588.

Douglas, G.B., Caitcheon, G. G., Pinchand, G. T., Adeney, J. A. and Orr, P.T., (2002). Sediment sourcing in Lake Wivenhoe: Stage 1 – Reconnaissance lake sediment sampling survey. *CSIRO Land and Water* Report, June, 2002. 35pp.

Douglas, G.B. Palmer M.J. and Caitcheon, G., (2003a). The provenance of sediments in Moreton Bay, Australia: A synthesis of major, trace element and Sr-Nd-Pb isotopic geochemistry, modelling and landscape analysis. *Hydrological Processes*, 494, 145-152.

Douglas, G.B., Ford, P.W., Jones, G.J. and Palmer, M.J., (2003b). Identification of sources of sediment to Lake Samsonvale (North Pine Dam), south east Queensland, Australia. *Intl. Assoc. Hydrol. Sci*. Sp. Publ. Red Book 279 (accepted).

Douglas, G.B., Caitcheon, G. G., Pinchand, G. T., Adeney, J. A. and Orr, P.T., (2003c). Sediment sourcing in Lake Wivenhoe: Stage 2 – Identification of Lake Sediment Sources. *CSIRO Land and Water* Report, June, 2003. 44pp.

Gibbs, R.J., (1977). Clay mineral segregation in the marine environment. *J. Sed. Petrol*., 47, 237-248.

Gilks, W.R., Richardson, S. & Spiegelhalter, D.J., (1996). *Markov Chain Monte Carlo in practice*. London, Chapman and Hall.

Griggs, G.B. and Hein, J.R., (1980). Sources, dispersal, and clay mineral composition of fine-grained sediment off central and northern California. *J. Geol*., 88, 541-566.

Hakanson, L., (1977). The influence of wind, fetch and water depth on the distribution of sediments in Lake Vanern, Sweden. *Can. J. Earth Sci.,* 14, 397-412.

Hart, M., (1989). Analysis for total iron, chromium, vanadium and titanium in varying matrix geological samples by XRF, using pressed powder samples. Standards in x-ray analysis. Aust. X-ray Anal. Assoc. (W.A. Branch). Fifth State Conf.: 117-129.

Horn, A., Joo, M., and Poplawski, W., (1998). Queensland riverine sediment transport rates: A progress report. Water Quality Group report 2/98, Dept. Natural Res., Qld.

Hornik (2004), "The R FAQ" http://www.ci.tuwien.ac.at/~hornik/R/

Kelly, J. N., and Wong, W. T. (1996). Sediment transport in the Fitzroy River during flood events. Proc. First Aust. Stream Management Conf.: Stream Management '96 ,pp 19-21, 19 -23 Feb. 1996, Merrijig, Victoria (Eds I.D. Rutherfurd and M. Walker). CRC for Catchment Hydrology, Clayton, Victoria.

Likens, G. E. and Davis, M. B., (1975). Post-glacial history of Mirror Lake and its watershed in New Hampshire, USA: An initial report. *Int. Ver. Theor. Angew. Limnol. Verh*., 19: 982-993.

McCulloch, M.T., Fallon, S., Wyndham, T, Hendy, E., Lough, J. and Barnes, D., (2003a). Coral record of increased flux to the inner Great Barrier Reef since European settlement. *Nature*, 421, 727-730.

McCulloch, M.T., Pailles, C., Moody, P. and Martin, C.M., (2003b). Tracing the source of sediment and phosphorus into the Great Barrier Reef lagoon. *Earth Plant. Sci. Lett*., 210, 249-258.

McLennan, S.M., Taylor, S.R., McCulloch, M.T. and Maynard, J.B., (1990). Geochemical and Nd-Sr isotopic composition of deep-sea turbidites: Crustal evolution and plate tectonic associations. *Geochim. et Cosmochim. Acta*, 54, 2015-2050.

Norrish, K. and Chappell, B., (1977). X-ray fluorescence spectrometry. In J. Zussman (ed) Physical methods in determinative mineralogy. Academic Press, London: 201-272.

Potts, P., (1987). A handbook of silicate rock analysis. Blackie.

Venables, W. and Ripley, B., (1999). Modern Applied Statistics with S-PLUS. Third Edition. NewYork: Springer-Verlag.

Appendix 1: Intellectual Property

CSIRO Background IP

CSIRO background IP comprises the following: Data know-how and copyright in the computer modelling program used in the project This Background IP is not required to be used in conjunction with Project IP and is not licensed on this occasion.

An enclosed CD contains the following information:

Major and trace element geochemistry for
- (i) weir and dams within the Fitzroy River Basin
- (ii) soils within the Fitzroy River Basin
- (iii) sediments from within the Fitzroy River Estuary