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# A novel approach of combining isotopic and geochemical signatures to differentiate the sources of sediments and particulate nutrients from different land uses

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**Abstract**

Determining the source of sediments and associated nutrients from terrestrial to aquatic environments is critical for managing the detrimental impacts of soil erosion and loss of nutrients from terrestrial into aquatic environment. However, tracing the source of particulate nutrients from different land uses has not been adequately carried out due to methodological difficulties in separating sources, particularly in the Great Barrier Reef (GBR) catchment. The objective of this study was to develop a method to differentiate the sources of particulate nutrients from soils collected from different land uses (combination of beef and dairy grazing, sugarcane, forest and banana) using both geochemical and isotopic signatures. In order to select a discriminative group of signatures, all soil samples collected from each of the land use areas were fractionated to <63 μm size fraction and were analysed for both isotopic ($\delta^{13}C$, $\delta^{15}N$) and acid extractable geochemical properties (e.g. Zn, Pt and S). Considering the fact that the outcome of tracing models often depend on the type and robustness of the methods used, here we have employed a stable isotope mixing model (SIAR) to evaluate if the suite of selected elements could be used to estimate the relative contribution of different sources for a series of five virtually created sediment mixtures. For the five groups of virtual sediments, the SIAR model provided close estimates to the contribution values of sediment sources with the Mean Absolute Error (MAE) varying from 0.30 - 2.88%. Results from this study show for the first time that the combined use of isotopic and geochemical signatures enable the SIAR model to provide an accurate estimation of source apportionment where a variety of land uses needs to be investigated and shows promise as a valuable new sediment and particulate nutrient tracing tool.

**Keywords**: Sediment; Fingerprinting; Mixing models; Nitrogen; Stable isotopic abundance

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## 1. Introduction

Various issues of poor water quality in the Great Barrier Reef (GBR) lagoon have been identified as being due to increasing delivery of terrestrial sediments and associated particulate nutrients over the last century (Brodie et al., 2012). Particulate nitrogen (N) is considered the particulate nutrient of most concern and comprises the largest proportion of the total N load delivered to the GBR (Hunter and Walton, 2008, Joo et al., 2012, Brodie et al., 2017). In order to develop sound strategies to manage particulate nutrients discharge and its subsequent environmental impacts on the GBR lagoon, it is necessary to identify the main sources of sediments and associated nutrients delivered from the GBR catchment. The sediment fingerprinting technique utilises a combination of field sampling, biogeochemical analyses in laboratory and statistical modelling to allocate the contribution of each source for sediments and nutrients delivered to the rivers. In this technique, a number of biogeochemical properties are measured in both soil samples of potential sources within the upstream catchment and sediment mixtures collected at the river outlets (Haddadchi et al., 2013). A stepwise discriminant statistical analysis is used to select a suite of elements which distinguished between the sources, and then a mixing model is employed to determine the specific contributions from the discrete sources (Collins et al., 2017). However, the accuracy of these mixing models have rarely been tested (Haddadchi et al., 2014b). The accuracy and robustness of mixing model outputs highly depends on the discriminative power of selected tracers and the type of model used in fingerprinting techniques (Haddadchi et al., 2013, Collins et al., 1997).

All the potential signatures for fingerprinting techniques need to be accurately measurable and have a discriminative power in separating different sources. They also need to behave conservatively with respects to time and distance along the transport pathway from source to sink (Haddadchi et al., 2013). A variety of tracers such as colour (Grimshaw and Lewin, 1980), clay mineralogy (Bainbridge et al., 2016) and mineral magnetic characteristics (Motha et al., 2003, Hatfield and Maher, 2009), organic matter content (Walling and Amos, 1999) and radionuclide characteristics (Estrany et al., 2010, Wilkinson et al., 2015) have been used in recent studies. Few

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studies have also used compound- specific stable isotopes and biomarkers, especially aliphatic (saturated straight-chained) compounds such as nalkanes and n-carboxylic acids (fatty acids) for attribution of sediment and organic matter sources to specific land uses, such as forest, arable and pasture(Glendell et al., 2018, Alewell et al., 2016, Reiffarth et al., 2016, Blake et al., 2012). Sediment geochemistry has been widely used to quantitatively trace the source of sediments and nutrients on the catchment scale (Collins et al., 1997, Collins et al., 2010a, Collins et al., 2012, Walling et al., 2008, Davis and Fox, 2009, Furuichi et al., 2016). In this approach, different inorganic signatures such as major, trace and rare earth elements as well as stable and radioactive inorganic isotopes are employed to identify the spatial sources of sediments discharged to the rivers (Davis and Fox, 2009, Collins et al., 2010b, Haddadchi et al., 2014a). Moreover, the composition of stable isotopes of organic matter ($\delta^{13}C$ and $\delta^{15}N$) and elemental content of soil (e.g., carbon (C) and N) are also considered as a powerful combination of signatures in tracing the origin of sediments and associated nutrients (Coplen and Kendall, 2000). In that regard, they can specifically reflect different vegetation types across different land uses in the upstream catchment and hence have the ability to trace the source of particulate organic matter (Coplen and Kendall, 2000, Papanicolaou et al., 2003).

While there has been a rapid growth in studies undertaking sediment source fingerprinting in a range of environments and applications, there are still aspects of the approach that warrant further improvement in order to increase its robustness and acceptability particularly in cases where a number of different land uses in a large scale catchment need to be investigated and none of the above mentioned fingerprints can properly differentiate between sources (Owens et al., 2016, Guzmán et al., 2013)

The objective of this study was to develop a novel approach for combined use of isotopic ($\delta^{13}C$ and $\delta^{15}N$) and geochemical signatures to differentiate the sources of particulate nutrients from different land uses (e.g., grazing including beef and dairy, sugarcane, forest and banana) using soil samples from the Johnstone River catchment, Queensland as an example. Firstly, a discriminative combined

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group of fingerprints were selected using Kruskal–Wallis H-test and stepwise Discriminant Functional Analysis (DFA), and then Principal Component Analysis (PCA) was used to evaluate whether the selected fingerprints are able to distinguish between sediments and associated particulate organic matter originated from the four primary land uses. These sources were identified as the most likely to contribute to sediment and nutrient export during flow events in this area as they collectively comprise > 95% of the catchment area. Secondly, an analytical approach was used to test the accuracy and robustness of the novel methodology and widely used Stable Isotope Analysis in R (SIAR) mixing model by applying virtual mixtures of the four potential sources.

## 2. Background and theoretical consideration

To trace the sources of particulate organic matter in food webs in aquatic environments, a combination of stable isotopes such as $\delta^{13}C$ and $\delta^{15}N$ have been widely used (Bunn et al., 2003, Finlay, 2001, Hein et al., 2003). Similarly, they also have been used to determine the contribution of different sources of particulate organic matter (Garzon-Garcia et al., 2017, Cooper et al., 2015, McCorkle et al., 2016) and sediments (Garzon-Garcia et al., 2017, Mukundan et al., 2010, Laceby et al., 2015) in streams. The $\delta^{13}C$'s ability to discriminate between sources is based on the fact that different photosynthetic pathways result in distinct $\delta^{13}C$ fractionations. The majority of tree species follow the Calvin-Benson cycle ($C_3$) photosynthetic pathway with a mean $\delta^{13}C$ of −28‰ (Boutton, 1991, Fry, 2006). Some cropping plants and dominant grass species in warmer climates, on the other hand, mainly follow the Hatch-Slack cycle ($C_4$) pathway with a mean $\delta^{13}C$ of −13‰ (Coleman, 2012, Werth and Kuzyakov, 2010). Therefore, $\delta^{13}C$ can be considered as a signature to discriminate between the sources of organic matter derived from $C_3$ and $C_4$ plants in tropical and subtropical environments. Generally, $\delta^{15}N$ fractionation is much more complex than $\delta^{13}C$ due to multiple N sources and different potential internal transformations which can affect N isotopic ratios in derived organic matter from different plant materials. The atmospheric N ($N_2$) is the major form of N in the biosphere with $\delta^{15}N$ of 0‰ (Peterson and Fry, 1987). The majority of N in the rest

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of the biosphere also has $\delta^{15}N$ values between −10‰ and +10‰ (Evans, 2007, Finlay and Kendall, 2007). Several studies have used isotopic signatures to differentiate between subsoil and topsoil as the potential sources of sediments and particulate nutrients to the rivers (Garzon-Garcia et al., 2017, Laceby et al., 2016, Mukundan et al., 2010). However, these signatures are not able to differentiate the land uses covered with the vegetation that follows the same photosynthetic pathways.

The potential of geochemical signatures in separating sources is based on the theory that rock types can influence the geochemical properties of soils during the process of soil formation and development (Klages and Hsieh, 1975, Olley et al., 2001). Therefore, soils lying over different geological structures usually reflect a distinct group of geochemical fingerprints which is highly dependent on their source lithology (Douglas et al., 2009, Motha et al., 2002). As a result, the origin of discharged and transported sediments in a water way can be traced back using these distinct geochemical fingerprints, if they retain the distinguishable signatures (major, trace or rare earth elements) of their original rock parents (Hughes et al., 2009). Despite the popularity of geochemical fingerprinting, this technique is usually used to differentiate sources with different geological properties, and not able to distinguish between different land uses on the same geological structures. Therefore, it is necessary to have a combination of several diagnostic soil and sediment properties through which we can have a more discriminative approach in identifying the origin of sediments and associated nutrients, specifically when a great number of sources needs to be investigated (Collins and Walling, 2002), and if the objective of the study is to determine contributions from different land uses.

Figure 1 summarizes the basis for combining stable isotopes and geochemical properties of different land uses in cases when potential sources of sediments and associated nutrients cannot be completely separated on the basis of their geochemical or isotopic fingerprints alone. Then the same group of fingerprints can be measured in the mixture sediments originated from different land uses. In the end, a mixing model needs to be used to quantitatively determine the contribution of different sources to the mixture sediments.

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Using artificial mixtures with known contributions of sources has gained increasing popularity for testing the accuracy of the methods used to separate sources and mixing models prior to using them for field application (Haddadchi et al., 2014b). It provides an opportunity to test the robustness of widely used mixing models in estimating the relative contribution of sources in a mixture of sediments. This approach is also able to evaluate the strength of the final combination of fingerprinting properties in discriminating sources in cases where a wide range of sources needs to be investigated. Lees (1997) conducted one of the earliest studies on artificial mixtures to identify any non-linear additivity associated with the use of the frequently used mineral magnetic tracing properties in sediments. Following that, Small et al. (2004) used five artificial mixtures to explore the uncertainties related to source sampling in a Bayesian modelling approach. Recent studies have used synthetic mixtures based on Monte Carlo routines as an alternative to avoid laboratory work associated with generating and analysing specific properties of artificial source mixtures (Sherriff et al., 2015). Moreover, virtual sample mixtures have also recently been used to minimize uncertainties related to preparation and analysis of artificial mixtures (Palazón et al., 2015). In this study an analytical approach is used to evaluate the power of combined geochemical and isotopic signatures in differentiating sources and also to test the accuracy and robustness of the widely used Stable Isotope Analysis in R (SIAR) mixing model to determine the contribution of different sources to the virtually created mixtures.

## 3. Methods

### 3.1 Study region

The study was conducted in the Johnstone River catchment which is located in the wet tropical area of north-east Queensland and covers an area of 2624 $km^2$ (Innisfail; 17°31′S, 146°02′E). Two branches of this river, including south and north Johnstone, merge into a single stream at the Innisfail Township. The Johnstone River drains three main geographic sections of the catchment including upper, middle and lower sections. The upper section is composed of a mixture of different

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land-uses such as rainforest, cattle grazing pastures (including dairy and beef), horticulture, sugarcane farms and a minority urban input from the township in Malanda. The middle part is mainly covered by rainforest which is the dominant land use in the Johnstone catchment with 52.0% of the whole catchment area (Lewis and Brodie, 2011). The lower part is dominated by banana cropping (4.3% of total area) and sugarcane fields with a concentration of population in the townships of Innisfail and South Johnstone. While 15.4% of the whole catchment is covered by grazing pastures, sugarcane (14.0%) is the main intensive cropping land use in this area. Previous studies in the Johnstone Basin highlighted that increased erosion had occurred particularly after the 1970s (up to 3 fold increase in suspended sediment export) and coinciding with the expansion of the sugarcane industry(Kroon et al., 2010). Although this extra erosion caused more sedimentation in the main stream, analysis of sediments in the Johnstone River channel has shown that a mean suspended sediment load of 318,000 tonnes per year was exported out of the catchment into the Great Barrier Reef lagoon (Kroon et al., 2010, Lewis and Brodie, 2011). In this study sampling sites were selected to represent the dominant land uses of this catchment including: sugarcane, grazing (combination of beef and dairy), banana and forest (Figure 2). Land uses on the Johnstone catchment are located on different soil types and geological structures. The dominant part of upper catchment is comprised of basalt, while other geological units such as granite and alluvial sediments also can occur in different parts of the catchment. Red ferrosol, which is derived from basaltic rocks, comprises the main part of the upper catchment, while other soil types such as red dermosols (metamorphic rocks) and red kandosols (granite) are also considered to be the main soil type for steep to moderate slopes on the upper Johnstone catchment. Brown dermosols and redoxic hydrosols were observed to occur on the floodplain of this catchment. Agricultural farms are dominantly located on the basalt and alluvium soil units within the Johnstone catchment (Bain and Draper, 1997, Isbell, 2016, Hunter and Walton, 2008).

**3.2 Soil sampling**

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In this study, soil samples were collected from possible land use sources that may potentially contribute sediments and particulate nutrients into the river during rainfall events and transport them downstream. Four potential sources were identified and sampled in July 2016 including grazing (beef and dairy have been combined), sugarcane, forest and banana. These sources were selected after an extensive literature review (Lewis and Brodie, 2011, Hunter et al., 2001, Wallace et al., 2015) and field investigations. Considering the unequal distribution of land-uses along the Johnstone River, the whole river catchment was divided into two geographical sections including the upper and lower Johnstone in order to select sampling sites. Grazing of beef cattle occurred throughout the catchment, while dairy farming was restricted to the upper, more elevated areas, while sugarcane (except a few small farms in upper catchment) and bananas were grown only in the lower catchment (Hunter et al., 2001). To ensure the representativeness of sources within the study catchment, 20 sampling points were selected after an intensive literature review, taking the geological structures, soil erosion rate and also the accessibility of sampling sites into account, with a great help from local managers and researchers (Hunter and Walton, 2008)(Figure 2). Grazing and forest soil samples were exclusively collected from the upper catchment, while banana soil samples were collected from lower catchment. Sugarcane soil samples were collected from both sections including two samples from the lower and three samples from the upper Johnstone catchment. Sampling locations for different sources were selected using maps prepared by ArcGIS (10.0) (Desktop, 2011). Soil samples were collected from surface soil (0-10 cm) with an auger after vegetation was removed to ground level. Each source was sampled at five locations (Figure 2). At each location, a composite sample of five points was taken. All samples were taken using a stainless steel trowel which was regularly cleaned to avoid inter-sample contamination. All soil samples were packed in plastic bags and transported on ice to the laboratory for analysis. In total, 20 soil samples from different sources were analysed with preparation methods described below.

### 3.3 Sample preparation

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To ensure that collected samples represent the potential sources, physically visible organic matter (not bound to soil particles) were removed before passing soils through 4 mm sieve. Samples were air-dried and sieved (< 2 mm) to remove large roots, litter fragments and gravel. Then a subsample (20–30 g) was taken, gently disaggregated using a pestle and mortar and dry sieved through a 63 μm mesh to ensure sample consistency.

### 3.4 Virtual sediments

In this study the sediment mixtures were created virtually to avoid laboratory errors during the process of mixing and chemical analysis. Five source samples were selected from each of four land use sources of Johnstone catchment. For each group of mixtures (A, B, C, D and E), five individual mixtures were created and each individual virtual sample was derived as a simple proportional mixture using the tracer property data for the source categories (Palazón et al., 2015). Figure 3 shows diagrammatically the processes involved in preparing virtual sediments. Five groups of virtual mixtures of known source contributions were created: For group A, the same proportion of randomly selected soils from each land use were mixed to make five virtual sediment samples ($S_1$ to $S_5$). The four sources, grazing, sugarcane, forest and banana, each made a contribution of 25% to the five virtual sediments. Each of the sources had five subsamples. To create a virtual mixture, one randomly selected sample from each of the sources was mixed in the same proportion. For example, the same proportions of grazing soil from sample number grazing-2, sugarcane soil from sample number sugarcane-4, forest soil from sample number forest-3 and banana farm soil from sample number banana-5 were mixed together to make the $S_1$ virtual sediment. This mixing procedure was repeated five times to create the sample mixtures $S_1$ to $S_5$. The same process was used in creating the four other groups of virtual mixtures (B, C, D and E) with different contribution from the potential sources as described in the Figure3.

### 3.5 C and N stable isotope and elemental analysis

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In accordance with the procedure for measuring the stable isotope ratio of N ($\delta^{15}N$), all soil samples were pelletized in tin capsules. For $\delta^{13}C$, first inorganic carbonates were removed by shaking the small aliquot (2–5 g of each sample) with 2 ml of 10% hydrochloric acid (HCl) and allowing the suspension to stand overnight. More HCl was added to the samples until no further effervescence occurred. The sample was finely ground in a mortar and pestle after being dried at 60°C for 48 h. Then the samples were pelletized in silver capsules and weighed for analysis with a Sercon Hydra 20-22 Europa EA-GSL isotope-ratio mass spectrometer. Stable isotope ratios are reported in standard delta (δ) notation per mil (‰) as: $\delta_X = [(R_{sample}/R_{standard})-1]\times1000$ where X is $^{13}C$ or $^{15}N$ and $R=^{13}C/^{12}C$ or $^{15}N/^{14}N$, respectively. Standard reference materials were PDB limestone for C and air was the standard for N (Garzon-Garcia et al., 2017). In this study, in order to find the geochemical signatures, a total of 21 chemical elements (Na, K, Mg, Ca, Mn, Zn, Al, Cu, Sn, Ni,, Co, Cr, Pt, Pb, As, Hg, Fe, Ag, S, P and Au) were analysed in soils, using ICP-OES; Perkin Elmer; Optima 8300, after direct digestion with nitric and perchloric acid (Miller, 1998, Haddadchi et al., 2014b).

### 3.6 Statistical analysis and modelling

The most discriminative group of geochemical elements ( acid extractable Zn, Pt and S) were selected after a stepwise discriminant statistical analysis, and the discriminative power of isotopic signatures ($\delta^{13}C$, $\delta^{15}N$) were assessed using paired t-tests for the comparisons of data with equal means and variance (Garzon-Garcia et al., 2017, Collins and Walling, 2002). The principal component analysis (PCA) was used to separate the different land uses using geochemical or isotopic signatures alone or combined signatures. Then, for the first time a combination of isotopic and selected geochemical properties were modelled with SIAR V4 (Parnell et al., 2010) to evaluate this approach in differentiating the dominant land uses of the Johnstone River catchment by predicting the contribution of each land use to the virtual mixture of sources. SIAR was initially developed to infer the consumers' diet by isotopic analysis of sources. However, it has recently

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been widely used in sediment fingerprinting with omission of concentration dependency and the enrichment factor (set to 0) within the SIAR model (Dutton et al., 2013, Koiter et al., 2013). SIAR uses Bayesian mixing models and model fitting with Markov Chain Monte Carlo (MCMC) simulations of plausible values consistent with the data (n = 30,000) (Parnell et al., 2010). The uncertainty of this approach and the accuracy of the SIAR model were tested based on Mean Absolute Error (MAE) for different groups of virtual sediment mixtures:

$$\mathrm{MAE} = \frac{\sum_{j=1}^{m} |Xj - Yj|}{m} \quad (1)$$

Where, Xj is actual percentage of sources in virtual mixtures, Yj is the estimated contribution of each source (j) and m is the number of sources (m = 4).

## 4. Results

### 4.1 Source discrimination

#### 4.1.1 Stable isotopic properties

The discriminative power of isotopic signatures were tested prior to modelling. In combination, $\delta^{13}C$ and $\delta^{15}N$ discriminate between all the different sources (Table 1). The $\delta^{13}C$ discriminates between all sources ($p<0.001$), except grazing and sugarcane as both of them follow the Hatch-Slack cycle ($C_4$) photosynthetic pathway. In contrast, $\delta^{15}N$ was just able to discriminate between grazing and sugarcane ($p<0.05$). Principal components analysis (PCA) was also used to analyse the potential of $\delta^{13}C$ and $\delta^{15}N$, as isotopic properties, in discriminating between sources (Figure 4-A). The PCA plot highlights the distinctive source discrimination achieved for separating $C_4$ plants (grazing and sugarcane) and $C_3$ plants (forest and banana). However, it is obvious that isotopic signatures have not been able to completely separate sugarcane and grazing from each other. The score and loading plots were also used to examine which signature had the largest effect on variance of the data. The first principal component largely represents the difference between $C_4$ plants (grazing and sugarcane) from $C_3$ plants (forest and banana). Discrimination between these two vegetation types was dependent on the differences in $\delta^{13}C$ among these four land use sources (Table

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1). The second component tends to capture the difference between grazing and sugarcane sources, and largely corresponds with discrimination by $\delta^{15}N$, which has formed part of the fingerprint for this catchment. However, this component ($\delta^{15}N$) had a poor discrimination of grazing and sugarcane sources for this catchment (Figure 4-A). Therefore, these two isotopic signatures ($\delta^{13}C$ and $\delta^{15}N$) in combination provide a good discrimination amongst all the sources, however they are not able to completely separate $C_4$ plants (grazing and sugarcane) from each other and accordingly more fingerprint properties are required before sediment properties can be modelled in the SIAR (Tables S1 and S2).

### 4.1.2 Geochemical properties

Statistical analysis of geochemical signatures first involved using the nonparametric Kruskal–Wallis H test to identify those fingerprints that are able to significantly discriminate between different land uses (Collins and Walling, 2002). In this step, thirteen elements (P-values higher than 0.05) failed to exhibit significant differences between different sources (Table 2). Then, stepwise Discriminant Function Analysis (DFA) was used to identify an optimum group of geochemical fingerprints with the highest discriminatory power comprising the minimum number of geochemical signatures. The DFA indicated the most discriminative group of fingerprints based on the entry or removal of unique signatures from the analysis of sources. The selection of this discriminative group is based on the minimization of the variability within sources relative to the variability between sources and minimising Wilks' lambda (Collins and Walling, 2002). Results of the DFA are used to examine the proportion of samples that were accurately classified into the correct source groups. In this study Pt, S and Zn were able to assign 80% of the samples to their known sources (Table 3).

The PCA plot, demonstrates the first two principal components of geochemical properties in differentiating between the four studied sources (Figure 4-B). The first two components account for 94.8% of the total variance in the source fingerprinting data throughout the Johnstone River catchment. Moreover, the PCA score plot highlights that the first principal component largely

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represents the difference between banana and forest sources as well as it is responsible for discriminating between grazing and sugarcane land uses. Overall, discrimination between these four sources was mainly represented by Pt and Zn with a total variance of 62.4% in the first component. In contrast, the second component was not able to completely separate forest and grazing sources. This component largely corresponds with discrimination by S and Pt with a total variance of 32.3% (Figure 4-B and Tables S1 and S2).

### 4.1.3 Combined stable isotope and geochemical signatures

PCA results presented in the Figure 4-C shows that a combination of both geochemical and isotopic signatures are able to differentiate between all potential land use sources of sediments in the Johnstone River catchment. The PCA has revealed two principal components with a cumulative variance of 77.3 %. $PC_1$ was responsible for 46.7 % variance and is best represented by Pt, Zn and $\delta^{15}N$. These properties can be used to separate grazing and sugarcane as well as to discriminate between banana and forest land uses. $PC_2$ is best represented by $\delta^{13}C$ and S, accounting for 30.6% of total variance. These specific properties also had a notable role in differentiating between land uses covered with tree species (banana and forest) and other land uses on this catchment (Figure 4-C and Tables S1 and S2 ).

### 4.2 Accuracy of the combined isotopic and geochemical approach and SIAR modelling

The first group of virtual sediments (Figure 5-A), which were created from five randomly selected samples from each source with equal proportion of contribution, the SIAR model estimates were 24.5% for grazing, 25.5% for sugarcane, 25.1% for forest and 24.9% for banana sources with the MAE = 0.3%. In the 5 virtually made sediments with 40% proportion of grazing and sugarcane and 10% of forest and banana (Figure 5-B), the mixing model had an estimate of 38.9%, 40.6% 10% and 10.5% for grazing, sugarcane, forest and banana sources, respectively. These estimates are 1.1% lower than the actual contribution of grazing and 0.6% and 0.5% higher than the actual

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contribution from sugarcane and banana sources, respectively. The estimated contribution from forest soil is equal to its actual contribution in virtual sediments. The MAE for the second group of sediments was 0.55%. In group C including $S_{11}$ to $S_{15}$ virtual mixtures with 10% from grazing and sugarcane and 40% from forest and banana, the SIAR mixing model had an estimate of different source contribution to the virtual sediments (grazing = 9.8%; sugarcane = 11.5% forest= 40.5% and banana=38.2%) with the MAE=1% (Figure 5-C). The estimated contribution for each source in group D ($S_{16}$ to $S_{20}$; grazing=10%; sugarcane = 40% forest = 10% and banana=40%) was 10.8% for grazing; 40.3% for sugarcane, 11.4% for forest and 37.5% for banana with the MAE=1.25% (Figure 5-D). . In the last category, group E, created mixture of sediments with 40% proportion of grazing and forest and 10% of sugarcane and banana (Figure 5-E), the mixing model has an estimate of 36%, 13.2%, 38.4% and 12.4% for grazing, sugarcane, forest and banana land uses, respectively. This model underestimated the actual contribution of grazing and forest, while the estimated contribution of sugarcane and banana were 3.2% and 2.4% higher than the actual contribution of these sources, respectively. In this group of sediments the MAE of estimates was 2.8%. Details of modelling outputs are provided in the supplementary documents (Figures S1 to S5).

The accuracy of the combined isotopic and geochemical approach and SIAR modelling allowed us to use this approach in tracing the sources of sediments to the Johnstone River. The preliminary results showed that forest with 83.4% was the largest contributor to the river bed sediments in the upper Johnstone catchment. Grazing with 9.4% and sugarcane with 7.2% were the second and the third contributors to this part of river, respectively, while bandanna farms had no contribution in sediments delivered to the upper Johnstone River (Table S3).

## 5. Discussion

Results from this study have highlighted the possibility of using combined isotopic and geochemical properties for tracing sediments and nutrients sources from catchments containing different land uses.

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While it was possible to distinguish between land uses with different photosynthetic pathway ($C_4$ vs $C_3$ plants) by isotopic signatures, it was not possible to differentiate between land uses covered by vegetation with the same photosynthetic pathway. However, the combined use of isotopic and geochemical signatures allowed us to distinguish between the main sediment sources on the Johnstone catchment, which has not been previously possible with the use of other fingerprints. Results from this study can be used for the source catchments modelling framework in estimating pollutant loads and determining the quantitative contribution of different sources. It can be a useful tool for the GBR authorities to fulfil their catchment management targets in reducing non-point source pollution and minimising the risk to the reef from a decline in the quality of water entering the reef from adjacent catchments.

**5.1 Isotopic and geochemical signatures in different land uses**

In this study, $\delta^{13}C$, $\delta^{15}N$ and acid extractable Zn, Pt and S were successfully used as complementary signatures in discriminating potential sources of sediments and nutrients from different land uses (grazing, sugarcane, forest and banana) in the Johnstone River catchment. Results have shown that Zn, Pt and $\delta^{15}N$ are the key elements that clearly discriminates between the land uses covered by the plants with the same photosynthetic system (Figure 4-C). It is assumed that a combination of both geological properties and management systems on each land use has led to such discriminative power for these key elements. For example, a substantial amount of different metals (e.g., Cu, Cd, Zn, Pb and Mn) are being transferred into soils by farmers through application of chemical fertilisers (Wong, 1985) and pesticides which may be present as impurities (Omwoma et al., 2010). For instance, phosphorus fertilisers are considered as the main source of metals and metalloids (e.g. Cd, Mo, Cu, Sr, Th, Ni, and Zn) in soils due to the presence of such active compounds in the phosphate rocks which are the original materials used for producing phosphate fertilisers (McBride and Spiers, 2001, Lottermoser, 2009, Carnelo et al., 1997, Nziguheba and Smolders, 2008). The enrichment of trace metals such as Zn in sugarcane and banana land uses (Table 4) in north

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Queensland could be due to the high rate of fertiliser application on these intense agricultural farms over time (Lottermoser, 2009, Omwoma et al., 2010, Lin et al., 2010).

The abundance of $\delta^{15}N$ reflects the effect of management practices of each land use on the N cycle processes. For instance, the long term application of different types of fertilisers is considered as an effective factor in altering $\delta^{15}N$ patterns in different land uses (Robinson, 2001, Choi et al., 2003, Antil et al., 2005, Bol et al., 2005). Moreover, this pattern reveals more details about the quantitative importance of the main N transformation processes and N losses from different land uses. Indeed, the processes, through which the different forms of N (e.g. $NH_3$, $N_2$, NO, $N_2O$, $NO_3$ ) are lost to the environment, eventually leading to the enrichment of $\delta^{15}N$ in the residual pool (including $NH_4^+$, $NO_3^-$ and organic N) that remain in the soil (Robinson, 2001, Högberg, 1997). Although $\delta^{15}N$ has been widely used in different studies as a discriminative factor in isotope modelling approaches, it has always been complicated to interpret the abundance of $\delta^{15}N$ in different land uses (Zhou et al., 2013). It is due to the fact that the discriminative power of this signature highly depends on the type and the amount of N input or in other words, the N input-output balance in different land uses (Högberg and Johannisson, 1993). Researchers have recently examined the effect of long-term application of different fertilisers on the $\delta^{15}N$ abundance of soil and plant materials (Choi et al., 2003, Nakano et al., 2003, Bateman et al., 2005). It has been reported that soil and plant tissues in the farms with application of composts and other organic fertilisers are more enriched in $\delta^{15}N$ compared to those in the farms treated with urea and inorganic fertilisers such as ammonium nitrate (Choi et al., 2003, Nakano et al., 2003, Bateman et al., 2005).

Platinum plays a key role in differentiating between land uses in this study (Table 4 and Figure 4-C). Concentration of Pt group elements in soils mainly depend on geology and parent materials, while other biogeochemical factors can also affect the concentration of Pt in soils (Mudd, 2012). Microbial communities play a key role on transformation, concentration and movement of Pt on the soil surface in different environments (Reith et al., 2016). In fact, studies have shown that the soil microbial community composition and biodiversity is highly affected by management practices

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applied on different land uses due to the fact that microorganisms have a complex interaction with the environment that they reside, and they play a critical role in most of the soil ecological processes (Tian et al., 2017).

Table 4 also shows that land uses covered with trees (banana and forest) are more enriched in S compared to other land uses. Figure 4-C demonstrates that S (and $\delta^{13}C$) are responsible for separating banana and forest land uses from sugarcane and grazing. It could be attributed to the critical role of S in nutrition of tree species (Johnson, 1984). In fact, S is required in larger quantity for trees, as they need it for the synthesis of amino acids. It is reported that there is a strong correlation between S and N in tree tissue, and more than 80% of S in tree tissues is used for producing amino acids such as cysteine, and methionine (Johnson, 1984). In fact, trees can capture and pump up nutrients by enlarging the soil volume exploited by their roots. It is a basic tool for trees to have access and incorporate nutrients from the horizons beyond the rooting depth of crops and accumulate them on soil surface particularly when they have a high demand for nutrients (Buresh et al., 1996).

### 5.2 Source discrimination and uncertainties in mixing model

A limitation of fingerprinting research is the difficulty in developing a robust and widely applicable source tracing technique by selecting independent properties, that are able to properly differentiate between sources, followed by a mixing model (Collins and Walling, 2002). Therefore, the use of artificial mixtures of known contribution of sources has gained increasing popularity in recent years and represents an important component for the development of the fingerprinting techniques (Haddadchi et al., 2014b, Palazón et al., 2015). Previous studies have shown that with the uncertainties within the process of selecting the proper fingerprints and modelling output, it is recommended to test the accuracy and robustness of methods in differentiating among sources and employing mixing models prior to applying them to field samples (Brosinsky et al., 2014,

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Haddadchi et al., 2014b). A study on artificial laboratory mixtures where source contributions were known revealed high levels of uncertainty in discriminating sources thus suggesting a better selection of fingerprinting properties to achieve a better and more robust estimation of source contributions by mixing models. (Brosinsky et al., 2014). Moreover, Haddadchi et al. (2014b) reported high uncertainties in predicting the contribution of different sources to the artificially-made sediments using different mixing models. In their study the modified Hughes and Collins models were evaluated as the most robust and the weakest source contribution predictor with the MAE= 5.4% and 28.3%, respectively (Haddadchi et al., 2014b).

In this study the mixing model results are consistent with the PCA results in terms of source discrimination. It indicates that the SIAR model is able to give reliable outputs based on the new approach in discriminating among different land uses. The relative changes in the accuracy of the SIAR model in estimating the contribution of sources to the different group of virtual mixtures highlight the importance for selecting the most discriminative group of fingerprints in cases when different land uses need to be investigated (Figure 5). The most accurate estimation by the model was given to the group of mixtures with the same contribution from each source (MAE= 0.3%) (Figure 5-A). While the SIAR had the lowest accuracy in predicting the contribution of sources to the group E of virtual mixtures (40% contribution from Grazing and forest with 10% contribution from sugarcane and banana) with MAE= 2.8% due to the high contribution of grazing and forest land uses to this mixture (Figure 5-E). Because, on the one hand there is a similarity between isotopic signatures of grazing and sugarcane land uses (Table 1), and on the other hand geochemical fingerprints were not able to clearly separate forest and grazing sources from each other (Figure 4-B).

## 6. Conclusions

This study for the first time demonstrated that a combination of both geochemical (acid extractable Zn, S and Pt) and isotopic signatures ($\delta^{13}C$, $\delta^{15}N$) are able to differentiate the sources of sediments

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and particulate nutrients among grazing, sugarcane, forest and banana land uses from the samples collected from the Johnstone River catchment. Zn, Pt and $\delta^{15}N$ are the key fingerprints contributing to the discrimination between the vegetation with the same photosynthetic systems. Results have also highlighted that S and $\delta^{13}C$ are responsible for separating banana and forest from sugarcane and grazing land uses. The $\delta^{13}C$ is considered as a discriminative signature in separating $C_4$ plants (grazing and sugarcane) from $C_3$ plants (forest and banana) and S provides another key signature in separating tree species (banana and forest) from sugarcane and grazing. This study has also demonstrated that SIAR mixing model is able to provide accurate source attributions (MAE= 0.3%-2.8%) for virtual mixtures of sources with known contributions of each source applying the selected group of fingerprinting properties. For future researches, it is also necessary to make sure that the selected group of signatures, in a sediment tracing study, behave conservatively along transport pathways throughout the catchment and potentially in the interfaces of freshwater-marine environment to ensure the robustness of the selected signatures in tracing the source of sediments and nutrients to the marine environment.

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**Table 1**
Paired T-Tests results for $\delta^{13}C$ and $\delta^{15}N$ signatures of the sources (grazing, sugarcane, forest and banana).

| Source | | n | SD | Grazing | Sugarcane | Forest | Banana |
|---|---|---|---|---|---|---|---|
| | $\delta^{13}C$ (‰) | | | | | | |
| Grazing | -15.74 | 5 | 0.46 | | | | |
| Sugarcane | -15.35 | 5 | 0.65 | - | | | |
| Forest | -27.42 | 5 | 0.40 | *** | *** | | |
| Banana | -23.61 | 5 | 0.94 | *** | *** | *** | |
| | $\delta^{15}N$ (‰) | | | | | | |
| Grazing | 6.66 | 5 | 0.97 | | | | |
| Sugarcane | 5.17 | 5 | 0.84 | * | | | |
| Forest | 6.26 | 5 | 1.48 | - | - | | |
| Banana | 5.48 | 5 | 1.33 | - | - | - | |

(−) not significant, (*) significant at $p < 0.05$, (**) significant at $p < 0.01$, (***) significant at $p < 0.001$

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**Table 2**

Kruskal–Wallis H-test for identifying significant differences between sources.

| Tracer | H-value (Chi-square) | P-value |
|---|---|---|
| Na | 9.58 | 0.022* |
| K | 13.88 | 0.003* |
| Mg | 15.55 | 0.001* |
| Ca | 13.75 | 0.003* |
| Mn | 15.44 | 0.001* |
| Zn | 16.23 | 0.001* |
| Al | 6.74 | 0.081 |
| Cu | 5.03 | 0.170 |
| Sn | 4.78 | 0.190 |
| Ni | 3.06 | 0.383 |
| Co | 4.66 | 0.198 |
| Cr | 0.33 | 0.954 |
| Pt | 12.77 | 0.005* |
| Pb | 3.95 | 0.267 |
| As | 13.27 | 0.004* |
| Hg | 5.25 | 0.154 |
| Fe | 1.22 | 0.747 |
| Ag | 3.73 | 0.292 |
| S | 16.97 | 0.001* |
| P | 7.45 | 0.059 |
| Au | 1.59 | 0.662 |
| Pd | 1.35 | 0.717 |

*Statistically significant at $P < 0.05$.

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**Table 3**

Stepwise Discriminant Function Analysis (DFA) for selecting the most discriminant group of elements.

| Step | Tracer | Wilk's lambda | % of sources classified correctly | Cumulative % of sources classified correctly |
|---|---|---|---|---|
| 1 | Pt | 0.278 | 50 | 50 |
| 2 | S | 0.121 | 60 | 75 |
| 3 | Zn | 0.065 | 60 | 80 |

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**Table 4**

Paired T-Tests results for geochemical signatures of sources (grazing, sugarcane, forest and banana).

| Source | | n | SD | Grazing | Sugarcane | Forest | Banana |
|---|---|---|---|---|---|---|---|
| | Zn ($mg.kg^{-1}$) | | | | | | |
| Grazing | 95.34 | 5 | 32.77 | | | | |
| Sugarcane | 143.86 | 5 | 15.09 | * | | | |
| Forest | 72.58 | 5 | 14.60 | - | *** | | |
| Banana | 183.60 | 5 | 46.14 | ** | - | *** | |
| | Pt ($mg.kg^{-1}$) | | | | | | |
| Grazing | 7.88 | 5 | 2.32 | | | | |
| Sugarcane | 1.20 | 5 | 1.06 | *** | | | |
| Forest | 8.02 | 5 | 3.27 | - | ** | | |
| Banana | 2.04 | 5 | 1.48 | *** | - | ** | |
| | S ($mg.kg^{-1}$) | | | | | | |
| Grazing | 309.04 | 5 | 65.61 | | | | |
| Sugarcane | 240.28 | 5 | 22.39 | - | | | |
| Forest | 415.40 | 5 | 103.06 | - | ** | | |
| Banana | 405.60 | 5 | 54.29 | * | *** | - | |

(−) not significant, (*) significant at $p < 0.05$, (**) significant at $p < 0.01$, (***) significant at $p < 0.001$

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**Highlight**

- Tracing the source of sediments and nutrients is critical for aquatic ecosystems
- A method developed to differentiate the source of sediments from different land uses
- Both isotopic ($\delta^{13}C$, $\delta^{15}N$) and geochemical fingerprints (e.g. Zn, Pt and S) were used
- Combined fingerprint and the SIAR model can predict the source of nutrients

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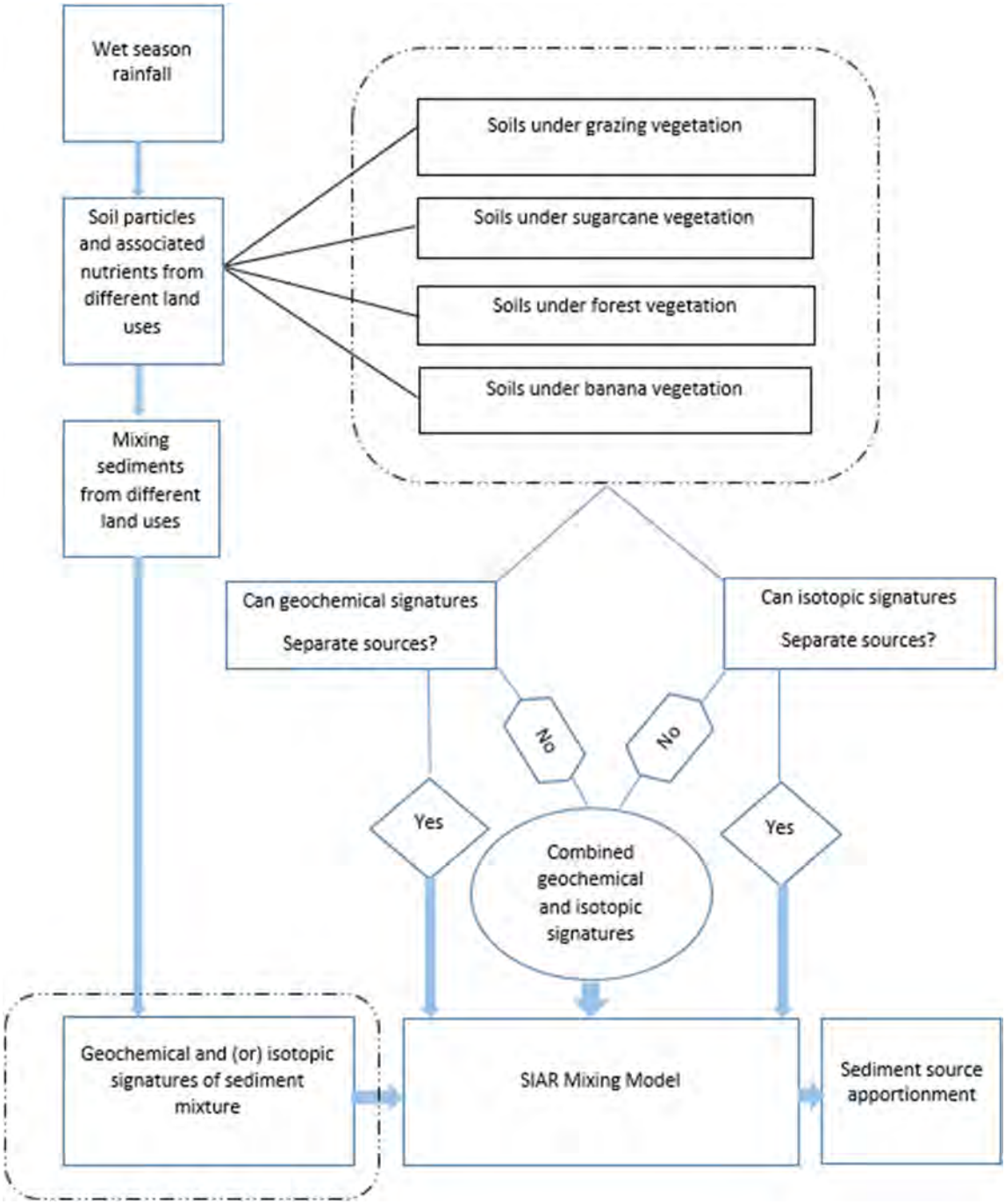
Wet season rainfall
Soil particles and associated nutrients from different land uses
Soils under grazing vegetation
Soils under sugarcane vegetation
Soils under forest vegetation
Soils under banana vegetation
Mixing sediments from different land uses
Can geochemical signatures Separate sources?
Can isotopic signatures Separate sources?
No
No
Yes
Yes
Combined geochemical and isotopic signatures
Geochemical and (or) isotopic signatures of sediment mixture
SIAR Mixing Model
Sediment source apportionment

Figure 1

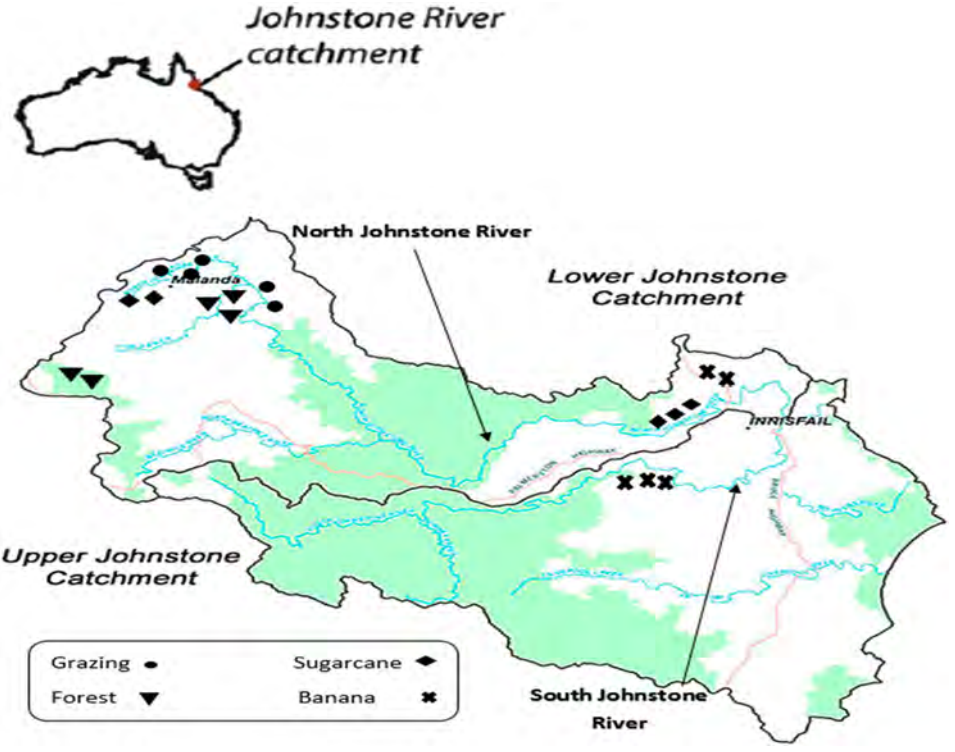
Johnstone River catchment
North Johnstone River
Lower Johnstone Catchment
Upper Johnstone Catchment
Malanda
INNISFAIL
South Johnstone River
Grazing
Forest
Sugarcane
Banana

Figure 2

| | Random selection of samples from each source | | | | Virtual sediment | |
|---|---|---|---|---|---|---|
| | Grazing | Sugarcane | Forest | Banana | Individual sediment | Group sediment |
| Group A | 25% 2 | 25% 4 | 25% 3 | 25% 5 | $S_1$ | Grazing=25% |
| | 25% 5 | 25% 1 | 25% 4 | 25% 2 | $S_2$ | Sugarcane=25% |
| | 25% 3 | 25% 5 | 25% 2 | 25% 4 | $S_3$ | Forest=25% |
| | 25% 1 | 25% 3 | 25% 5 | 25% 3 | $S_4$ | Banana=25% |
| | 25% 4 | 25% 2 | 25% 1 | 25% 1 | $S_5$ | |
| Group B | 40% 2 | 40% 4 | 10% 2 | 10% 5 | $S_6$ | Grazing=40% |
| | 40% 4 | 40% 1 | 10% 3 | 10% 2 | $S_7$ | Sugarcane=40% |
| | 40% 1 | 40% 3 | 10% 1 | 10% 4 | $S_8$ | Forest=10% |
| | 40% 5 | 40% 5 | 10% 5 | 10% 3 | $S_9$ | Banana=10% |
| | 40% 3 | 40% 2 | 10% 4 | 10% 1 | $S_{10}$ | |
| Group C | 10% 2 | 10% 5 | 40% 1 | 40% 3 | $S_{11}$ | Grazing=10% |
| | 10% 4 | 10% 2 | 40% 2 | 40% 1 | $S_{12}$ | Sugarcane=10% |
| | 10% 5 | 10% 1 | 40% 4 | 40% 2 | $S_{13}$ | Forest=40% |
| | 10% 1 | 10% 4 | 40% 5 | 40% 4 | $S_{14}$ | Banana=40% |
| | 10% 3 | 10% 3 | 40% 3 | 40% 5 | $S_{15}$ | |
| Group D | 10% 2 | 40% 2 | 10% 3 | 40% 5 | $S_{16}$ | Grazing=10% |
| | 10% 1 | 40% 3 | 10% 5 | 40% 4 | $S_{17}$ | Sugarcane=40% |
| | 10% 3 | 40% 4 | 10% 4 | 40% 2 | $S_{18}$ | Forest=10% |
| | 10% 5 | 40% 1 | 10% 2 | 40% 1 | $S_{19}$ | Banana=40% |
| | 10% 4 | 40% 5 | 10% 1 | 40% 3 | $S_{20}$ | |
| Group E | 40% 5 | 10% 1 | 40% 5 | 10% 1 | $S_{21}$ | Grazing=40% |
| | 40% 4 | 10% 5 | 40% 1 | 10% 3 | $S_{22}$ | Sugarcane=10% |
| | 40% 3 | 10% 4 | 40% 2 | 10% 2 | $S_{23}$ | Forest=40% |
| | 40% 2 | 10% 2 | 40% 3 | 10% 5 | $S_{24}$ | Banana=10% |
| | 40% 1 | 10% 3 | 40% 5 | 10% 4 | $S_{25}$ | |

Figure 3

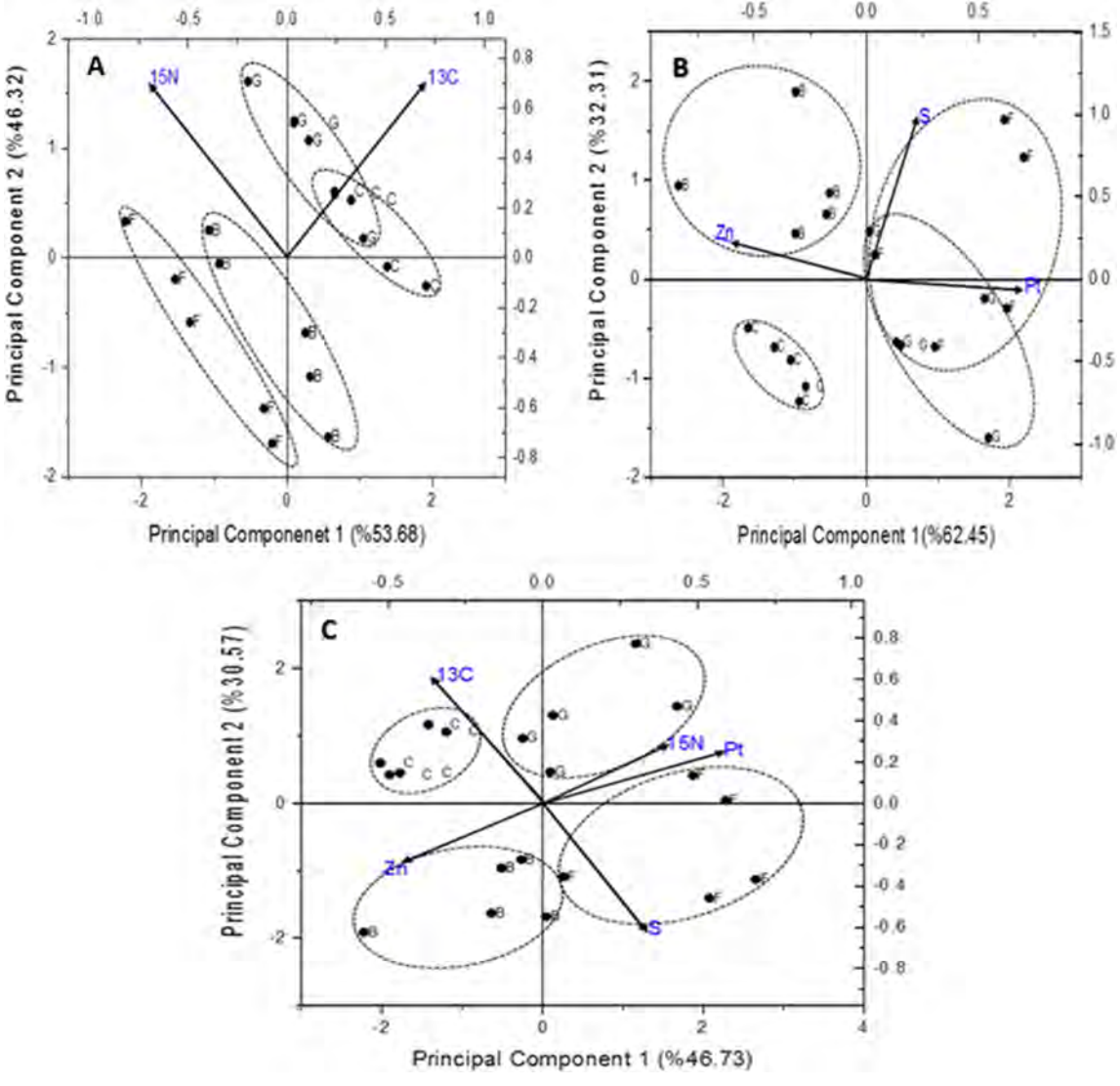
A
15N
13C
Principal Componenet 1 (%53.68)
Principal Component 2 (%46.32)
B
S
Zn
Pt
Principal Component 1(%62.45)
Principal Component 2 (%32.31)
C
13C
15N
Pt
Zn
S
Principal Component 1 (%46.73)
Principal Component 2 (%30.57)

Figure 4

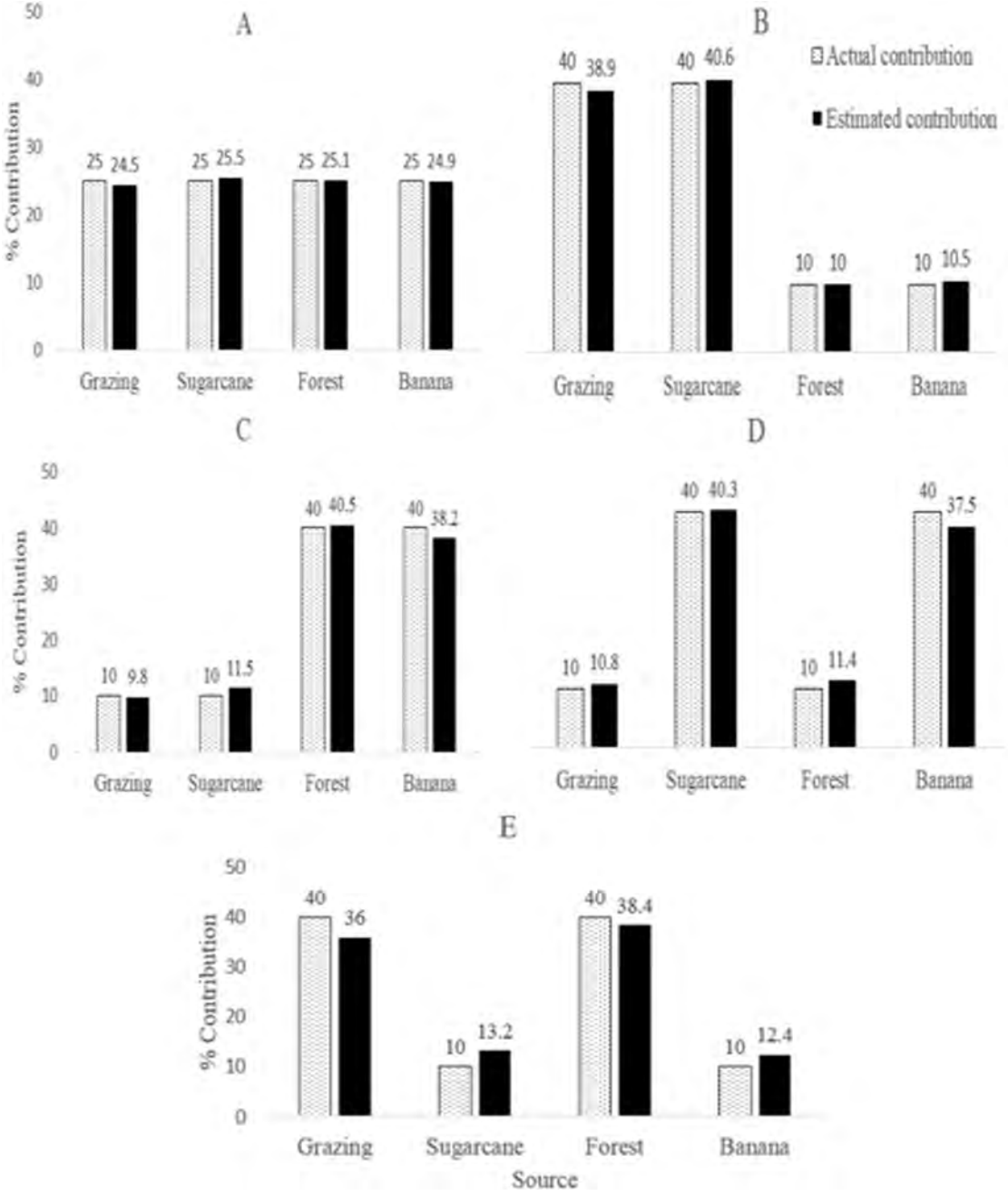
A
% Contribution
50
40
30
20
10
0
25 24.5
25 25.5
25 25.1
25 24.9
Grazing
Sugarcane
Forest
Banana
B
Actual contribution
Estimated contribution
40 38.9
40 40.6
10 10
10 10.5
Grazing
Sugarcane
Forest
Banana
C
% Contribution
10 9.8
10 11.5
40 40.5
40 38.2
Grazing
Sugarcane
Forest
Banana
D
10 10.8
40 40.3
10 11.4
40 37.5
Grazing
Sugarcane
Forest
Banana
E
% Contribution
40 36
10 13.2
40 38.4
10 12.4
Grazing
Sugarcane
Forest
Banana
Source

Figure 5

Accepted Manuscript

# A novel approach of combining isotopic and geochemical signatures to differentiate the sources of sediments and particulate nutrients from different land uses

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