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Fingerprinting the contribution of quarrying to fine-grained bed sediment in a mountainous catchment, Iran

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Abstract

The contribution of quarrying in the context of multiple catchment sources of fine-grained sediment has rarely been investigated. This study assessed the relative importance of quarrying as a sediment source alongside rangeland surface soils and channel banks in a mountainous catchment in northern Tehran, Iran, using fingerprinting. Eight geochemical tracers were measured on 24 potential sediment source samples and four fine-grained sediment samples. Statistical analysis to select three different composite fingerprints for discriminating the potential sediment sources comprised: (1) the Kruskal–Wallis H test (KW-H), (2) a combination of KW-H and discriminant function analysis (DFA), and (3) a combination of KW-H and principal components & classification analysis (PCCA). A Bayesian un-mixing model was used to apportion sediment source contributions using the three composite fingerprints. Using the KW-H composite signature, the respective relative contributions (with uncertainty ranges) from channel banks, rangeland surface soils and quarrying were estimated as 28.4% (10.9-46.8), 15.1% (6.6-22.7), and 56.6% (38.3-74.2), compared to 35.4% (11.9-60.1), 13.4% (4.1-22.2) and 51.3% (26.5-74.3) using a composite signature selected using a combination of KW-H and DFA, or 20.7% (3.9-41.7), 17.2% (4.4-29.9) and 61.4% (44-78.8) using a fingerprint selected using KW-H and PCCA. The different composite signatures therefore all consistently suggested that quarrying is the dominant source of the fine-grained sediment samples. Potential mitigation measures targeting this land use include closure to permit re-vegetation to reduce exposure of bare surfaces to sediment mobilisation. Limitations and uncertainties associated with this preliminary investigation are briefly discussed.

Keywords: Fingerprinting, quarrying, bed sediment, mountainous catchment, multiple statistical techniques

1. Introduction

Anthropogenic geomorphology is defined as the discipline that embodies studying the influence of human activities on earth surface forms and processes and thereby the landforms shaped by weathering, erosion and particle transport (Li, Yang, Pu, & Liu, 2017). At least one-third of the Earth's continental surface is affected by human activities acting as a geomorphological agent that is equal in importance to other natural geomorphic factors in the shaping of landforms (Rózsa, 2010). Such impacts have resulted in the use of the term Anthropocene to refer to the current geological Epoch (Lewis & Maslin, 2015). The geomorphic impact of humans is increasing and the identification and assessment of unintended consequences will therefore be important.

One of the most important human impacts on some landscapes concerns quarrying. Quarrying for the excavation of raw materials for construction in mountain settlements generates a range of anthropogenic landforms including excavated, accumulated and planation (anthropogenic features further modified by natural erosive processes) forms (Dávid, 2010). Thus, land disturbance associated with quarrying generally increases erosion and sediment yields and impacts on landscape sediment source patterns. In particular, surface mining areas can accelerate natural soil erosion, which increases sediment loads in rivers (Chalov, 2014; Chalov et al., 2015; Jaramillo, Baccard, Narinesingh, Gaskin, & Cooper, 2016; Pietroń, Chalov, Chalova, Alekseenko, & Jarsjö, 2017). Average accelerated soil erosion rates in Iran have been estimated at 23 to 25 t ha^{-1} $year^{-1}$ (Afshar, Ayoubi, & Jalalian, 2010; Karchegani, Ayoubi, Lu, & Honarju, 2011; Rahimi, Ayoubi, & Abdi, 2013), but, importantly, the contribution of quarrying has not been determined.

Identifying the relative contributions of fine-grained (<63 μm) sediment from quarrying can be used to help inform erosion mitigation strategies. Historically, different techniques have been used to identify and apportion fine-grained sediment sources (Collins & Walling, 2004). Sediment fingerprinting is a field based technique that apportions or un-mixes, sampled target sediment into distinguishable sources through the use of different natural and artificial tracers combined in a so-called composite fingerprint or signature. Comprehensive recent literature reviews (e. g. Collins et al., 2017; Owens et al., 2017) reveal that the fingerprinting approach has not been used to investigate fine-grained sediment contributions from quarrying in mountainous environments. Accordingly, the main objective of this study was to use a composite fingerprinting procedure combining geochemical tracers and different statistical tests for source discrimination with a Bayesian un-mixing model for source apportionment, to determine the relative importance of quarrying in a small sub-catchment of the Farahzad drainage basin, northern Tehran, Iran. It was hypothesized that quarrying is the primary fine-grained sediment source in the study catchment. Different statistical tests provide a basis for exploring uncertainties in source apportionment provided by alternative composite signatures.

2. Materials and methods

2.1. Study catchment

The study area is a sub-catchment (77.4 ha) of the Farahzad (Younjeh-Zar) drainage basin and is located to the north of the capital city of Iran, Tehran city, located between 51^{0} 19′ 32″E to 51^{0} 20′ 15″E longitude and 35^{0} 47′ 50″N to 35^{0} 48′ 30″N latitude in the Southern Alborz Mountains (Figure 1; S1). Land cover comprises 72% grazing land (55.8 ha), 12% orchard (9.5 ha), and 15% quarrying (11.8 ha). The catchment lithology comprises middle Eocene massive green tuff and shale with basic lava flows (E^{tsv}). Mean annual discharge at the outlet of the Farahzad drainage basin, based on regional analysis, is 0.37 m^3 s^{-1}. The annual average suspended and bed sediment loads, based on regional analysis of data collected at eight gauges, are 10646 t yr^{-1} and 2661 t yr^{-1}, respectively.

Figure 1

Mining in the study area comprises stone (green tuff stone) quarrying for excavating raw materials for buildings, recreational complexes (parks), and ornamental stones. The quarrying in the study area has been active for ca. 25 years. At least 10,000 ton yr^{-1} are extracted from the main mine. Quarry walls and floors, talus slopes, rainwater grooves and debris aprons are visible at the main mine.

2.2. Catchment sampling and laboratory measurements

Sediment source sampling: Prior to sampling, field surveys were undertaken to identify potential sediment sources across the study area and these were classified on the basis of soil erosion types: quarrying, rangeland surface soil erosion and subsurface erosion of stream channel banks. A total of 24 source samples were collected to represent these key potential sediment sources, comprising eight samples from each of the three source types. In order to increase the representativeness of the individual source samples, each surface sample for quarrying (i.e. the excavated bed or disposal surface) or the rangeland, comprised a composite of five sub-samples collected within ca. 40 m^2 at a specific site, whereas each subsoil sample from eroding channel banks or quarry walls comprised a composite of 10 sub-samples collected within a ~20 m long reach (interval 2 m) at each sampling site. Surface erosion source samples were collected from the upper 5 cm of the soil layer (Nosrati, 2017). Channel bank samples were collected by scraping material from the full vertical extent of actively eroding profiles (Nosrati, Govers, Semmens, & Ward, 2014).

Fine-grained sediment sampling: Samples of fine-grained sediment deposited on the river bed were collected at the overall outlet of the study catchment (Figure 1). The focus here was on samples of the 'drape' material that appeared to have been recently deposited (i.e. no vegetation/macrophyte cover; (e. g. Collins & Walling, 2007). Successful use of such deposits has previously been reported in Iran to fingerprint sediment in a region with poor site access (Nosrati, 2017; Nosrati, Collins, & Madankan, 2018). In order to ensure that the sediment samples were as representative as labour and financial resources permitted, 10 sub-samples were collected at each of four channel sampling sites along a ~20 m reach (interval 2 m) and combined into four individual composite samples. All source and sediment samples were retrieved from the field between April 4th and April 10th 2017 after a continuous rainfall period.

Laboratory analyses: Any sediment source tracing study needs to make careful decisions about the particle size fraction used, since this decision can impact heavily on the comparability of source and sediment samples and the reliability of the apportionment results generated (Collins et al., 2017; Laceby et al., 2017). Dry sieving (using sieve apertures of 500 µm, 300 µm, 250 µm, 212 µm, 125 µm, 75 µm and 63 µm) revealed that the <63 µm fraction was the dominant fraction of the 'drape' sediment samples. Consequently, only the <63 µm fraction of the target sediment and source samples was used for the analysis and comparison of fingerprint properties. In order to measure the geochemistry (elements selected *a priori* on the basis of previous experience) of samples (S2), one gram (<63 µm) of the sediment and source samples was digested for two hours at 95 °C in aqua regia (HCl–HNO3; 3:1) using a Velp Thermo-reactor. Extracts were filtered through S&S ME24 (0.2 µm) filter papers and the solutions analysed by a Varian SpectrAA-20 Plus calibrated using an element standard solution (Merck KGaA, Frankfurter, Germany) for Ca, Fe, K, Mg, Mn, Na, and Ni concentrations. Analytical errors were <5%. Total organic carbon (TOC) content was measured by the Walkley-Black method (Skjemstad & Baldock, 2008).

2.3. Selection of composite signatures for discriminating the potential fine-grained sediment sources

A three-part procedure was used to assess tracer conservation. Firstly, a standard bracket or range test (Foster & Lees, 2000) was used to identify non-conservative tracers. Secondly, the tracers were screened using a stricter test whereby the sediment sample means should fall within the corresponding source means rather than their full ranges (Wilkinson, Hancock, Bartley, Hawdon, & Keen, 2013). Thirdly, biplots of tracers included in the final statistically-verified composite fingerprints were also used to compare source and sediment samples (Collins et al., 2017).

Statistical analysis (STATISTICA V.8.0; (StatSoft, 2008) for identifying three different composite fingerprints for discriminating between the potential sediment sources used three approaches (Nosrati et al., 2018): the Kruskal-Wallis H-test (KW-H); KW-H combined with discriminant function analysis (DFA); and KW-H combined with principal component and classification analysis (PCCA).

2.4. Source apportionment

The Modified MixSIR model (Nosrati et al., 2018; Nosrati et al., 2014) provides a Bayesian (e. g. Cooper, Krueger, Hiscock, & Rawlins, 2014; Massoudieh, Gellis, Banks, & Wieczorek, 2013) rather than frequentist approach (Collins, Walling, & Leeks, 1997) to apportionment modelling.

Modified MixSIR (S3) estimates source apportionment as probability distributions for the relative contribution of each source to target sediment samples using: 1) determination of the prior probability distributions, 2) generation of a likelihood function, and 3) generation of posterior probability distributions to adjust the priors.

10^6 samples were drawn from the posterior distribution of the estimated target sediment mixtures in MATLAB. The model predictions of source proportions were evaluated using a small set of virtual sediment mixtures (Collins et al., 2017; Leticia Palazón et al., 2015) for each composite signature. Here, three virtual sediment mixtures were constructed using a range of source proportions: equal proportions from all sources; 90% quarrying, 5% rangeland surface soils, 5% channel banks, and; 5% quarrying, 75% rangeland surface soils and 20% channel banks. Since the virtual sediment mixtures were constructed using the measured tracer data for the source samples, the tracer concentrations in the virtual mixtures satisfied the bracket test for tracer conservation. The accuracy of the modelling in solving the virtual sediment mixtures was assessed using the averaged root mean square error (RMSE) and mean absolute error between the predicted ($Y_{\text{Predicted}}$) and known (Y_{Known}) source proportions using each final composite signature (Eqs. 1 and 2):

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(Y_{\text{Known}} - Y_{\text{Predicted}})^2}{n}} \qquad \text{Eq. 1}$$

$$MAE = \frac{\sum_{i=1}^{n}\left|Y_{Known} - Y_{\Pr edicted}\right|}{n} \qquad \text{Eq. 2}$$

3. Results and discussion

3.1. Composite fingerprints for discriminating the potential sediment sources

Table 1 presents the tracer concentrations in the samples. In addition, Table 1 presents the results of normality tests showing that all tracers exhibited normal distributions ($p > 0.05$) (a prerequisite for using the tracers in a Bayesian un-mixing model). The results of the standard bracket test suggested that all tracers were generally conservative in terms of their concentrations, despite the potential risk of change during sediment mobilisation, transport and delivery. In addition, the results of comparing the sediment means with the corresponding source means likewise suggested that all tracers were conservative following mobilisation and delivery to, and through, the channel system (Table 1). Here, it is important to remember that the range tests provide a simple mathematical means of assessing whether processes such as dissolution, adsorption and precipitation have substantially altered the concentrations of the sediment tracers in comparison with those of the sources. These mathematical tests do not provide definitive evidence that non-conservative behaviour is totally absent. Table 1 also presents the results of applying the KW-H test which indicated that six tracers (Ca, Fe, Mg, Mn, Ni and TOC) exhibited a statistically significant difference ($p \leq 0.05$) between the three potential sediment sources. Those tracers (K and Na) unable to discriminate the potential sources using KW-H were discarded from further analysis.

Table 1

The six tracers selected by the KW-H test were used in stepwise DFA (Table 2). The largest eigenvalue of the first function (12.6) corresponds to the eigenvector in the direction of the maximum spread of the groups' means. The Wilk's lambda value of the first function (0.019) suggested that 98.1% of the total variance among the potential sediment sources was explained by these tracers. The canonical correlation value was 0.96, revealing a strong correlation between the discriminant scores and individual sources.

The squared Mahalanobis distance showed that the sediment sources were distinguished by the shortlisted tracers (Table 2), with the greatest differences being between channel banks and rangeland surface soils (57.6) and rangeland surface soils and quarrying (49.6). For channel banks and quarrying, the squared Mahalanobis distance was the least (14.4). The forward stepwise DFA yielded classification matrices assigning 95.8% of the cases (i.e., source samples) to the correct groups (Table 2). Stepwise selection using Wilks' lambda generated a composite signature comprising four tracers (Ca, Fe, Mn and Ni) which provided significant discriminatory power on the basis of the DFA model (Table 3). The results of different tests within DFA indicated that the discriminatory power of Mn is perfect (Table 3). Here, Partial Wilks' lambda is the Wilks' lambda for the unique contribution of the respective tracer to the discrimination between individual sediment source groups. The smaller the Partial Wilks' lambda, the greater the contribution to the overall discrimination provided by the composite fingerprint. In this case, the Partial Wilks' lambda values suggested that Mn contributed the most, Ni second most, Ca third most and Fe the least to the overall discrimination (Table 3). A scatterplot using the first and second discriminant functions calculated using backward DFA confirmed that the samples collected to characterise the different potential sediment sources were well separated (Figure 2).

Table 2

Table 3

Figure 2

Tracers selected by the KW-H test (Ca, Fe, Mg, Mn, Ni and TOC) were also entered into PCCA to help reduce the number of tracers and multicollinearity. The results of a scree plot (Figure 3a) showed that the first three principal components (PCs) yielded the most interpretable factor pattern (Table 4). These three PCs accounted for >88% of the variability among the tracer values for the three source groups (Table 4). The highly-weighted tracers under PC1 with absolute values within 10% of the highest tracer (0.90 value for TOC) loading (the loading of selected tracers should be larger than 0.81) were Fe, Mn and Ni. Only TOC was retained for the final composite signature because these four tracers were strongly correlated ($r > 0.60$). Under PC2, the Mg was the highest tracer with a loading value of 0.79. In this case, the loading of selected tracers should exceed 0.71, but all loading values were less than this threshold and therefore only Mg was retained for the final composite signature. Under PC3, the highly-weighted tracer (0.66 value for Ca) with an absolute value within 10% of the highest tracer loading (the loading of selected tracers should be larger than 0.59) was Ca (Table 4). Accordingly, these results selected three tracers (TOC, Mg and Ca) as an alternative composite fingerprint on the basis of the PCCA model. Projection of the cases on the PC-plane using PCCA (Figure 3b) confirmed that the set of selected tracers (i.e. composite fingerprint) clearly provided good discrimination between the three potential sediment sources.

Figure 3

Table 4

PCs scores were also calculated using the resulting component score coefficient matrix and tested for significant differences between the potential sediment sources using one-way ANOVA (F-test) and Tukey HSD post-hoc tests ($p \leq 0.05$) (Table 4). PC scores for all three PCs varied significantly with sediment sources (Table 4). Thus, the tracers related to these PCs provided a basis for selection of a third alternative composite signature (TOC, Mg and Ca).

For the tracers selected in the three final composite signatures, the biplots of all tracer pairings for source and sediment samples were compared as part three of the screening for conservative behaviour. The results confirmed that there was no major tracer transformation during sediment mobilisation and delivery (Figure 4). Of the final tracers selected, TOC has the potential to be influenced by instream productivity. The dataset assembled for this study, however, was subjected to three tests for tracer non-conservative behaviour (basic and stricter range tests, biplots). Since TOC passed all three tests, significant transformation was not deemed to be present on the basis of the sediment sampling location used.

Figure 4

3.2. Sediment source contributions

Model runs converged on the posterior contributions from the sources using each of the three different composite signatures selected using the statistical tests (Figure 5). Using the composite fingerprint selected by KW-H, relative contributions (with corresponding uncertainty ranges) from channel banks, rangeland surface soils and quarrying were estimated as 28.4% (10.9-46.8), 15.1% (6.6-22.7), and 56.6% (38.3-74.2), respectively. Using the KW-H and DFA signature, the corresponding respective contributions and associated uncertainty ranges were predicted as 35.4% (11.9-60.1), 13.4% (4.1-22.2) and 51.3% (26.5-74.3). Finally, on the basis of the KW-H and PCCA signature, the relative contributions from channel banks, rangeland surface soils and quarrying were computed as 20.7% (3.9-41.7), 17.2% (4.4-29.9) and 61.4% (44-78.8), respectively. Root mean square differences between the estimated sediment contributions from channel banks, rangeland surface soils and quarrying using the three different composite signatures were estimated as 10.4%, 2.7% and 7.1%, respectively. Source contributions were therefore sensitive to the signature used, underscoring the need to use multiple fingerprints when investigating sediment source contributions (cf. Collins et al., 2017; Nosrati et al., 2018; Owens et al., 2017; L. Palazón & Navas, 2017). Here, it is more informative to use a combination of different statistical tests rather than selecting alternative composite signatures using the same test, since application of more than one test ensures additional dimensionality in the tracer assessment.

Figure 5

Comparison of the predicted and known relative contributions from channel banks, rangeland surface soils and quarrying using the three different composite signatures and the virtual sediment mixtures showed that the RMSE and MAE ranged between 0.3% to 20.9% and 0.3% to 18.9%, respectively (Table 5). The overall average RMSE and MAE for the modelled source predictions using the virtual mixtures were 12.1% and 8.3%, respectively (Table 5). These error levels were judged to be acceptable.

Table 5

The different composite signatures all suggested that quarrying was the dominant source of the fine-grained sediment samples. Using the areas of rangeland surface soils, quarrying and channel banks (52, 11.8 and 3.8 ha, respectively) the respective specific importance (based on the overall mean relative contributions from the three composite fingerprints) of these sources was estimated as 0.3, 4.8 and 7.4. Here, the quarrying and channel bank areas are small and so the high specific contributions indicate much higher erosion and sediment delivery rates for these sources. Recent studies in other areas of the world have also revealed the impact of mining and quarrying on sediment dynamics. Pietroń et al. (2017), for example, concluded that patterns of increased sediment load along the Tuul River that runs through the Zaamar Goldfield in Mongolia is consistent with soil loss being two to three orders of magnitude higher in mining areas than in the surrounding natural areas dominated by grasslands. The same authors also reported that the sediment load contribution from mining areas was insensitive to changes in hydrometeorological conditions. Likewise, Jaramillo et al. (2016) reported that a limestone quarry in the Don Juan River sub-catchment of the Maracas-Saint Joseph River catchment (MSJRC) located in Trinidad, is the largest producer of suspended and bed sediment in terms of soil loss per unit area. Chalov (2014) estimated the total sediment delivery from opencast placer mining located in the north of Russia's Kamchatka Peninsula is 60 t yr^{-1} which is three orders of magnitude higher than from non-mined streams. Chalov et al. (2015) highlighted mining areas as important contributors to sediment fluxes in the Selenga River basin, draining areas of Russia and Mongolia. Our findings are therefore consistent with other studies; quarrying can be a major fine-grained sediment source.

3.3 Limitations

The sediment source fingerprinting study reported here inevitably has some inherent limitations and uncertainties. Some of these are associated with either available resources or the challenges of working in a mountainous environment, but others remain common to source tracing work more generally. Limited numbers of source and sediment samples were collected and although the sampling strategy was not probability based, nor are those strategies reported by most studies in the existing international literature (Collins et al., 2017). Since the target bed sediment samples were collected from the study catchment outlet only, rather than at a number of locations along the channel network, the estimated source proportions should be interpreted as scale dependent. Clearly, in steep mountainous terrain, it is very challenging to sample multiple channel locations, but it is also noteworthy that many existing published studies suffer from this limitation regardless of the study environment and any potential fieldwork challenges (Collins et al., 2017). Specifically, in the case of this study, it would be useful to sample sediment upstream and downstream of the quarrying to explore the evolution of the sediment signatures and the corresponding source proportions. Target sediment sampling focused on surface drape bed sediment rather than suspended sediment samples and it is useful to bear in mind that source ascription can differ for different sediment types (e. g. channel bed versus suspended sediment) as a result of erosion process dynamics (Nicholls, 2000). Clearly, the sediment sampling needs to be extended to improve the temporal representativeness of the dataset and here the findings presented in this paper should be interpreted as preliminary and providing confirmation that the fingerprinting approach works in the study area. Differing transport characteristics of mobilised minerogenic and organic fractions of source material require more explicit consideration in the context of the tracers combined in final composite signatures. The preliminary source estimates underscore the importance of quarrying, but these results need to be confirmed by extending the sampling both spatially (i.e. more channel locations) and temporally (i.e. more storms). The Modified MixSIR model uses Bayesian as opposed to frequentist distribution-based principles and predicted source proportions can be biased by the choice of sediment un-mixing model structure (Laceby & Olley, 2015; Smith & Blake, 2014). Previous work has explored a range of weightings including those for tracer analytical precision (Collins et al., 1997) or discriminatory power (e. g. Collins et al., 2014) and spatial variations in tracers by source category (e. g. Gellis & Noe, 2013; Wilkinson et al., 2013) as well as corrections for particle size (Collins et al., 1997) or organic matter (e. g. Gellis & Noe, 2013) selectivity. Here, given the inherent uncertainties associated with these numerical model parameters

(Koiter, Owens, Petticrew, & Lobb, 2018; Laceby et al., 2017), such additions to un-mixing model structure were avoided. The predictions for source apportionment generated by Modified MixSIR were not evaluated using artificial mixtures (Brosinsky, Foerster, Segl, & Kaufmann, 2014) of known source material proportions. Instead, virtual mixtures were constructed from the measured data on the sediment samples. Where possible, it is preferable to use artificial mixtures by mixing real source samples to better represent any potential effects of grain size contrasts between the individual source groups in the study catchment. The source discrimination and apportionment relied on statistically-verified solutions, but it remains important to consider the physico-chemical basis for tracer utility in fingerprinting studies. Where access to facilities and resources permit, it is meaningful to explore the corresponding estimates provided by alternative tracer property types as a means of testing consistency in predictions.

4. Conclusion

Further research is needed to corroborate the preliminary findings here using extended (spatially along the channel network and temporally) sediment sampling and testing additional types of tracers with the potential to discriminate between different surface and subsurface sediment sources. Future management activities to reduce suspended and bed sediment loads, not only from the study catchment but also from others with similar land use issues, should focus on improving the regulation and management of quarrying operations. Here, it remains important to compile evidence on the efficacy of sediment control options as such information will in itself, assist uptake by stakeholders.

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Table 1
Tracer concentration data for the source and fine-grained sediment samples, results of the Kolmogorov-Smirnov test for normality, and Kruskal-Wallis H-test results for sediment source discrimination.

Sediment sources		Ca ($mg\ kg^{-1}$)	Fe ($mg\ kg^{-1}$)	K ($mg\ kg^{-1}$)	Mg ($mg\ kg^{-1}$)	Mn ($mg\ kg^{-1}$)	Na ($mg\ kg^{-1}$)	Ni ($mg\ kg^{-1}$)	TOC ($g\ kg^{-1}$)
Channel banks	Mean	23125.0	15625.0	13433.5	26713.6	669.1	1873.4	112.2	4.8
	SD	10870.9	2754.4	2354.0	10585.7	133.1	492.5	25.9	2.8
Rangeland surface soils	Mean	14687.5	29050.5	14652.1	23489.0	1383.3	1606.2	52.4	13.4
	SD	5560.6	2881.5	3493.2	3071.5	135.7	218.1	17.3	2.3
Quarrying	Mean	45044.6	19116.2	15807.6	31816.7	887.2	1706.3	147.9	5.9
	SD	13993.8	4699.4	1836.5	4240.8	157.8	651.5	29.2	2.3
Kolmogorov-Smirnov test for normality	K-S d	0.18	0.15	0.10	0.11	0.12	0.19	0.16	0.13
	p-value	0.45	0.64	1.00	0.95	0.91	0.38	0.57	0.81
Kruskal-Wallis H-test	Chi-Square	15.4	15.6	3.4	6.2	18	1.1	17	15.7
	p-value	<0.001*	<0.001*	0.18	0.04*	<0.001*	0.6	<0.001*	<0.001*
Sediment sample 1		31428.5	17131.3	15157.2	31730.0	827.8	1666.0	99.5	8.2
Sediment sample 2		36785.5	21121.2	14654.5	28985.0	733.4	1745.5	104.2	7.0
Sediment sample 3		36785.5	19484.8	14883.8	26925.0	750.0	1785.3	118.0	5.9
Sediment sample 4		43928.5	16646.5	15617.8	28985.0	1175.0	1685.8	104.2	5.5
Mean		37232.0	18596.0	15078.3	29156.3	871.5	1720.7	106.5	6.7

* Statistically significant at critical p-value ≤0.05.

Table 2

Summary results of the forward DFA.

DFA parameters	Result
Function 1	
Eigenvalue	12.8
Wilks' lambda	0.019
Canonical correlation	0.96
Function 2	
Eigen value	2.6
Wilks' lambda	0.27
Canonical correlation	0.85
Sediment source samples classified correctly (%)	
Channel banks	100.0
Rangeland surface soils	100.0
Quarrying	87.5
Total	95.8
Sampling sites for the sediment sources assigned by the DFA	
Channel banks	8.0
Rangeland surface soils	8.0
Quarrying	7.0
Squared Mahalanobis distance	
Channel banks × Rangeland surface soils	57.6
Channel banks × Quarrying	14.4
Rangeland surface soils × Quarrying	49.6
Squared Mahalanobis F-value	
Channel banks × Rangeland surface soils	49.3*
Channel banks × Quarrying	12.4*
Rangeland surface soils × Quarrying	42.4*

* Statistically significant at critical $p \leq 0.01$.

Table 3

Final results of the stepwise forward DFA.

Tracer	Wilks' lambda	Partial Wilks' lambda	F-remove	p-level	Tolerance
Mn	0.06	0.35	17.0	<0.001	0.90
Ni	0.04	0.52	8.2	0.003	0.84
Ca	0.04	0.53	8.0	0.003	0.82
Fe	0.04	0.56	7.0	0.006	0.74

Table 4
PCCA factor coordinates of the variables and the eigenvalues of the correlation matrix.

Tracer	PC 1	PC 2	PC 3	Communalities
Ca	-0.68	-0.18	**0.66**	0.93
Fe	0.87	-0.31	0.04	0.86
Mg	-0.47	**-0.79**	-0.37	0.98
Mn	0.82	-0.29	0.36	0.88
Ni	-0.86	-0.20	0.17	0.81
TOC	**0.90**	-0.18	0.10	0.85
Eigenvalue	3.66	0.92	0.74	
% Total variance	61.0	15.3	12.4	
Cumulative % variance	61.0	76.3	88.7	
Mean scores of the three sediment sources				
Channel banks	-0.56 a[1]	0.81 a	-0.75 a	
Rangeland surface soils	1.30 b	-0.16 ab	-0.12 ab	
Quarrying	-0.75 a	-0.65 b	0.63 b	
ANOVA results				
F-value	90.8	6.5	5.4	
p-value	<0.0001	0.006	0.01	

[1]Different lower case letters indicate that the scores are significantly different at critical p ≤0.05 level, based on the Tukey HSD Post Hoc test.

Table 5
Comparison of the predicted and known relative contributions from the sediment sources to the virtual sediment mixtures using the composite signatures selected by different statistical approaches and the corresponding root mean squared error (RMSE) and mean absolute error (MAE).

Statistical approaches for selecting final composite fingerprints	Source proportions	Sediment source			RMSE	MAE
		Channel banks (%)	Rangeland surface soils (%)	Quarrying (%)		
KW-H (Tracers: Ca, Fe, Mg, Mn, Ni, TOC)	Known	33.3	33.3	33.3	0.3	0.3
	Predicted	33.2	33.8	33		
	Known	5.0	5.0	90.0	19.2	17.4
	Predicted	24.3	11.8	63.8		
	Known	20.0	75.0	5.0	5.5	5.1
	Predicted	15.0	72.3	12.7		
Combination of KW-H and DFA (Tracers: Ca, Fe, Mn, Ni)	Known	33.3	33.3	33.3	2.5	2.2
	Predicted	36.6	32.9	30.5		
	Known	5.0	5.0	90.0	20.9	18.9
	Predicted	26.3	12.1	61.6		
	Known	20.0	75.0	5.0	5.1	4.8
	Predicted	16.2	71.7	12.2		
Combination of KW-H and PCCA (Tracers: Ca, Mg, TOC)	Known	33.3	33.3	33.3	2.5	2.3
	Predicted	29.9	34.4	35.7		
	Known	5.0	5.0	90.0	20.2	18.6
	Predicted	24.2	13.7	62.1		
	Known	20.0	75.0	5.0	6.8	6.1
	Predicted	17.85	67.96	14.17		

Figure captions

Figure 1. Map of the study catchment and sampling sites.

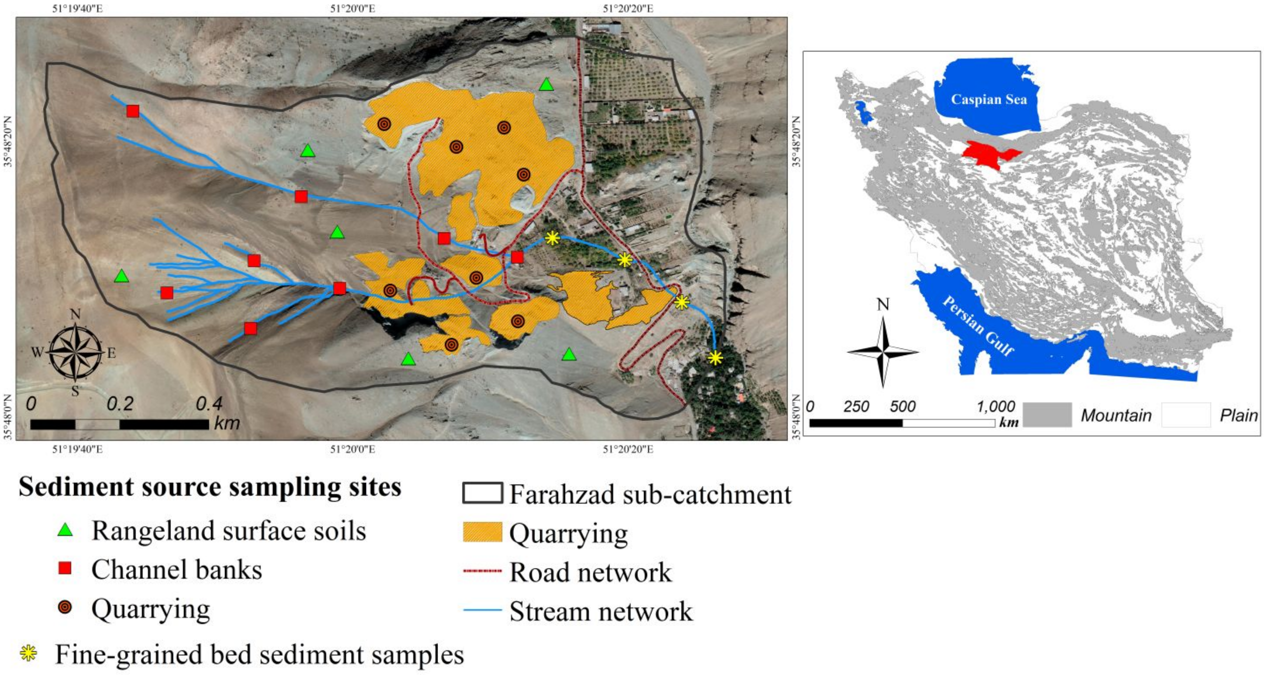
Figure 2. Scatterplot of the first and second discriminant functions calculated using backward DFA associated with selection of the final composite signature comprising Ca, Fe, Mn, and Ni.

Figure 3. (a) Scree plot output from the PCCA analysis for sediment source discrimination, (b) Projection of the cases on the PC-plane using PCCA.

Figure 4. Biplots of all pairings for the tracers selected in the three final composite signatures for discriminating and apportioning source contributions to the target sediment samples.

Figure 5. Probability density functions for the estimated mean sediment source contributions using the final composite signatures selected by (a) KW-H, (b) a combination of KW-H as step one and discriminant function analysis (DFA) as step two, and (c) a combination of KW-H as step one and principal components & classification analysis (PCCA) as step two.

Fig. 1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51°20'20"E
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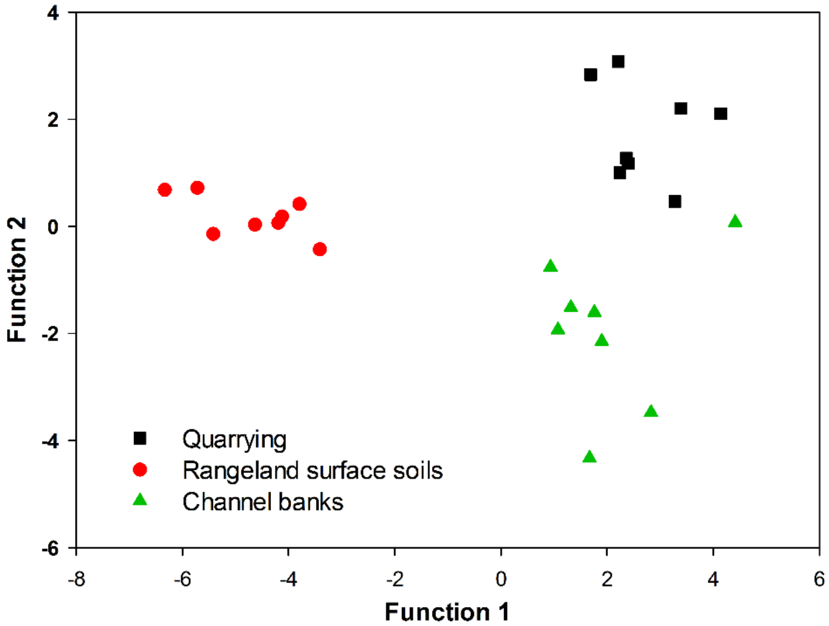
35°48'0"N
N
W
E
S
0 0.2 0.4 km
Caspian Sea
Persian Gulf
N
0 250 500 1,000 km
Mountain
Plain
Sediment source sampling sites
Rangeland surface soils
Channel banks
Quarrying
Fine-grained bed sediment samples
Farahzad sub-catchment
Quarrying
Road network
Stream network

Fig. 2


4
2
0
-2
-4
-6
Function 2
-8
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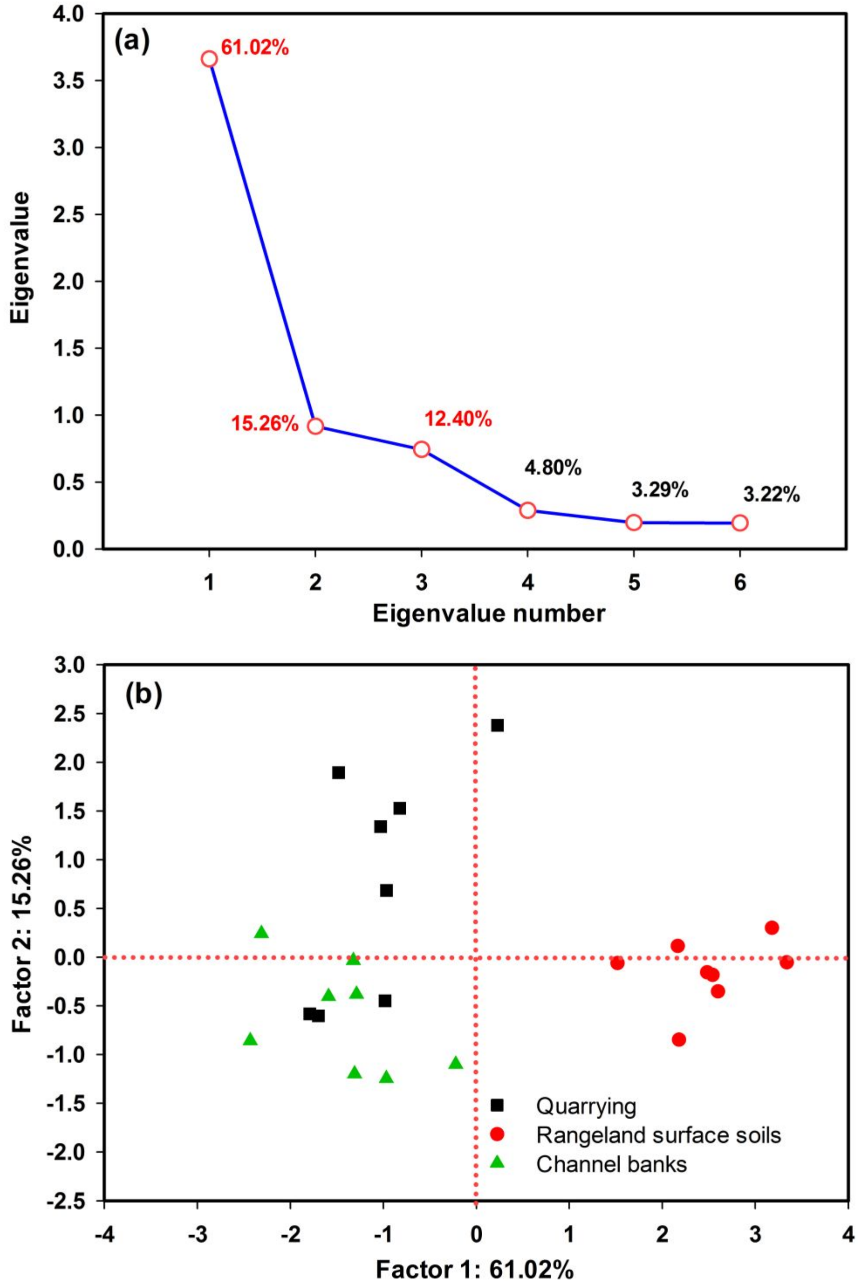
0
2
4
6
Function 1
Quarrying
Rangeland surface soils
Channel banks

Fig. 3



(a)
61.02%
15.26%
12.40%
4.80%
3.29%
3.22%
Eigenvalue
Eigenvalue number
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1
2
3
4
5
6
(b)
Factor 2: 15.26%
Factor 1: 61.02%
Quarrying
Rangeland surface soils
Channel banks
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-4
-3
-2
-1
0
1
2
3
4

Fig. 4

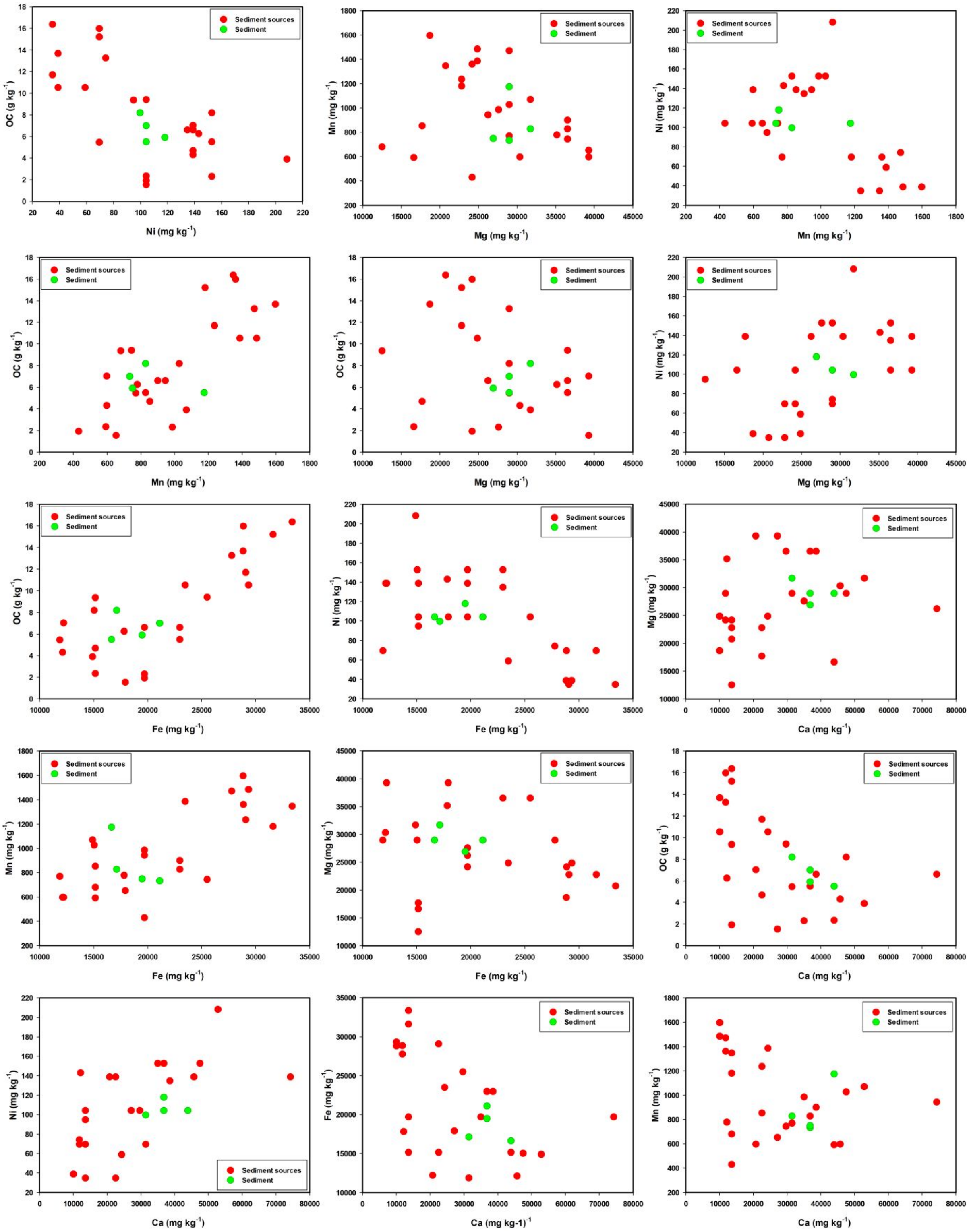
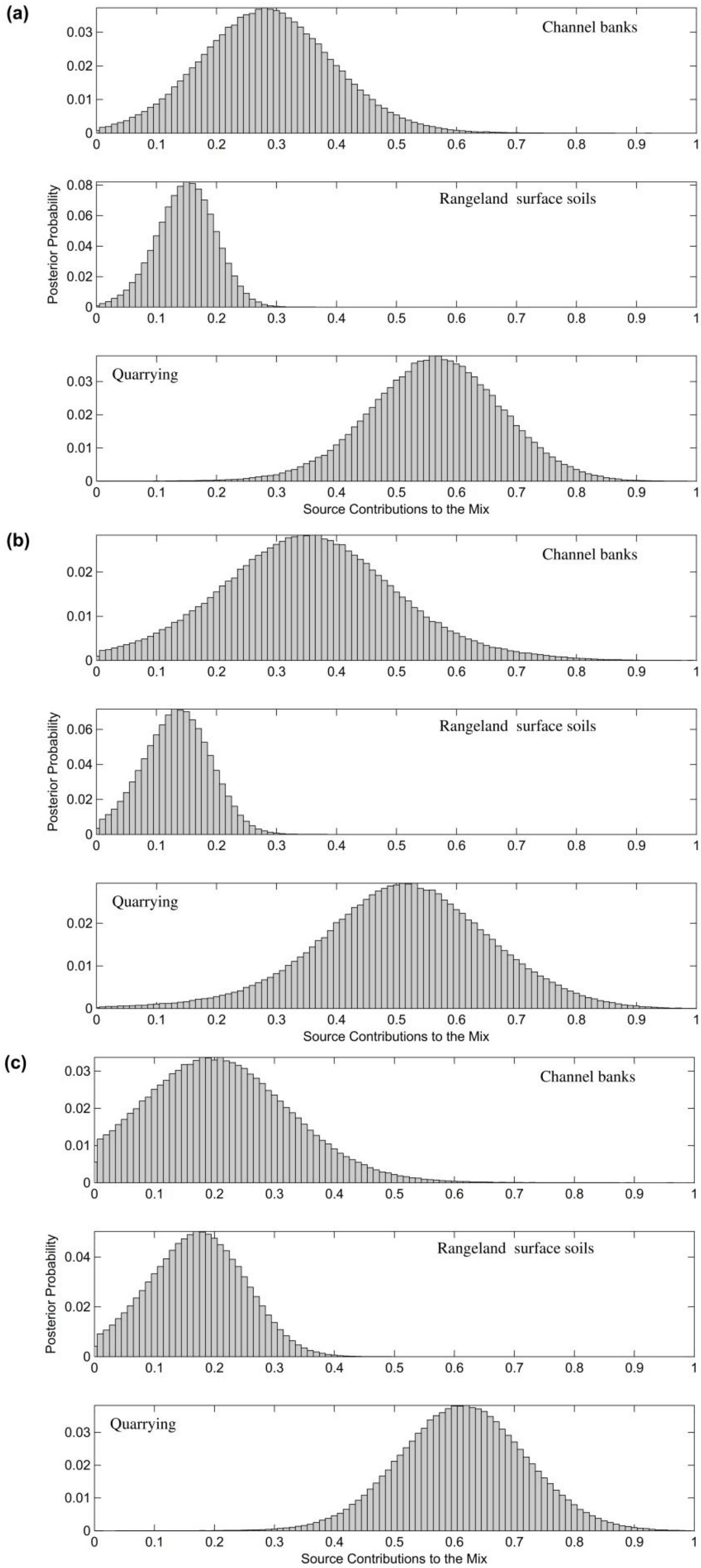

Sediment sources
Sediment
OC (g kg-1)
Ni (mg kg-1)
Mn (mg kg-1)
Mg (mg kg-1)
Fe (mg kg-1)
Ca (mg kg-1)
Ca (mg kg-1)-1

Fig. 5


(a)
Channel banks
Rangeland surface soils
Quarrying
Posterior Probability
Source Contributions to the Mix
(b)
Channel banks
Rangeland surface soils
Quarrying
Posterior Probability
Source Contributions to the Mix
(c)
Channel banks
Rangeland surface soils
Quarrying
Posterior Probability
Source Contributions to the Mix