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Determining Suitable Fingerprinting Properties for Discrimination of Sediment Sources (Case study: Amrovan and Atary Catchments)

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Abstract

This contribution determines suitable fingerprinting properties for sediment source discrimination within the Amrovan and Atary catchments in Semnan Province, Iran. These catchments are representative of a range of geology formations and should therefore provide a meaningful basis for a general assessment of the degree of sediment source discrimination afforded by a range of fingerprint properties. By field investigation, 10 representative samples were collected from each sediment sources per catchments. Geological formation map was selected as the base of grouping samples. For the case of Amrovan catchment Hezar Dareh, Upper Red and Quaterrnary formations as well as gully walls were selected as the origin of sediments whereas in Atary Catchment karaj, Qum, Upper Red, Hezar Dareh and Quaternary formations were selected as the origin of sediments. The 15 properties selected as a tracer, comprised five groups of fingerprinting properties, including Organic constituents (C, N, P), base cations (Na, K, Ca, Mg), acid extractable metals (Cr, Co), clay minerals (Smectite, Colorite, Illite, Kaolinite) and magnetic properties consisting of Low Frequency Magnetic Susceptibility (X_{LF}) and Frequency Dependent Magnetic Susceptibility (X_{FD}). Several statistical methods were applied to the data including the Kruskal-Wallis, discrimination function analysis (DFA) and multivariate stepwise selection algorithm. Results indicate that the most powerful individual fingerprint property is organic constituent C, which successfully classifies 70% and 66% of samples in Amrovan and Atary catchments respectively. Composite fingerprints incorporating constituents selected from several groups of properties using a stepwise statistical selection procedure consistently provide the most robust discrimination of potential sediment sources. Results show also that organic constituents group of properties is extremely useful for sediment source discrimination in this catchments.

Keywords: Composite fingerprinting; Sediment source discrimination; Catchment; Iran

1. Introduction

The provision of reliable information on sediment production is important. For example, to establish catchment sediment budgets (Walling et al., 2001, 2002), and to validate physically based distributed soil erosion and sediment yield models (Taken et al., 1999). An understanding of the nature and relative importance of the principle sediment sources within a catchment is needed to support the design and implementation of sediment control

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strategies in catchments (Collins et al., 2001). Because of the problems associated with conventional procedure for establishing the primary sediment sources within a catchment, the fingerprinting approach has attracted increasing attention as an alternative indirect means of assembling such information (Collins et al, 2008). One of the principal assumptions of Sediment fingerprinting is that potential catchment sediment sources can be distinguished on the basis of their physical, geochemical and biological properties or fingerprints. Existing research has provided valuable information on the range of properties that can be successfully employed to discriminate potential sediment sources in drainage basin. These have included mineralogy, and colour (Grimshaw and Lewin, 1980), mineral magnetism (Caitcheon, 1993), environmental radionuclides (Wallbrink and Murray, 1996), geogimical composition (Foster and Walling, 1994), Organic constiuence (Collins and walling, 2002), acid extractable metals (Collins and Walling, 2002) and particle size (Stone and Saunderson, 1992). Although in some cases, such studies have been based upon the exclusive use of a particular finger printing property, the reliability of this approach is likely to be compromised by spurious source sediment linkages (Yu and Oldfield, 1993) and the quest for a single diagnostic property is increasingly seen as being unrealistic (Walling et al., 1993). The value of an individual fingerprinting property measured for a given sediment sample could, for example, match that of a specific sediment source, but might actually represent a mixture of sediment originating from a number of potential sources. Using a several properties reduces the potential for spurious source sediment linkages by being more representative of the source material mixtures comprising sediment samples.

In response to these concerns, source fingerprinting investigations now commonly employ several diagnostic sediment properties in combination. The use of such "composite fingerprinting" affords a more reliable and consistent means of establishing sediment provenance and frequently allow a greater number of sources to be distinguished. Composite fingerprints can comprise a selection of parameters drawn either from a particular group of properties, for example several mineral- magnetic or radiometric properties, or from several groups of properties, including, for example, several mineral- magnetic, radiometric and organic parameters. These composite fingerprints are frequently used in association with multivariate mixing models to provide quantitative source ascription and such procedures have been successfully applied in a variety of contexts. These can include individual source types, for example, surface soils from areas of different land use and channel banks (Russell et al., 2001); spatially-defined sediment sources representing contrasting geological zones (Collins et al, 1998; Bottrill et al., 2000); and a combination of the both (Walling and Woodward, 1995; Collins et al 1997b).

Although the use of sediment fingerprinting procedure has now been shown to offer considerable potential for addressing a range of geomorphological and catchment management issues, less attention has been directed to the methodological uncertainties associated with the approach. In terms of source discrimination, one major uncertainty is the lack of generic guidelines fore selecting the most appropriate suite of fingerprinting properties for discriminating sediment sources in different catchments (Collins et al.,1997a) and of the degree of uncertainty associated with the resulting numerical solutions (Rowan et al., 2000).

The adoption of sediment fingerprinting as a standard methodology will be heavily dependent upon the rigorous testing of its principal assumptions and the resolutions of these methodological uncertainties (Foster and Lees, 2000). Because the use of composite fingerprints is founded on the assumption that the use of several properties, and particularly different types of property affords more robust sediment source discrimination, this contribution addresses this assumption and use a combination of statistical procedure to investigate the degree of discrimination of potential sediment sources afforded by: Individual fingerprinting properties, Composite fingerprints comprising constituents drawn from a single group of properties, Composite fingerprints comprising constituents drawn from several different groups of properties. The results should provide a basis for formulating general guidelines for pre-selecting properties for use in source fingerprinting investigations.

2. The study catchments

The study catchments for which fingerprinting property are two Amrovan and Attary catchments in Semnan province, Iran (Figure 1). These catchments are representative of a range of geology formations, physiographic conditions and should therefore provide a meaningful basis for a general assessment of the degree of sediment source discrimination afforded by a range of fingerprint properties. Land use in two catchments is homogenous, comprising rangeland.

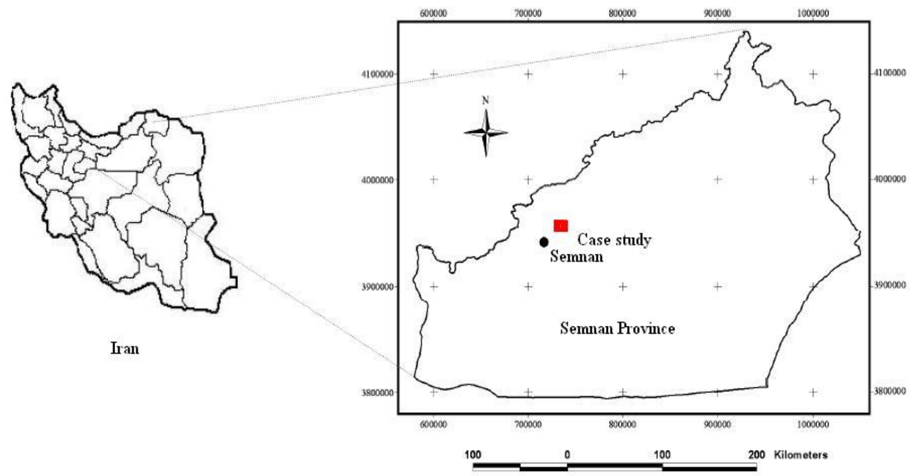

Fig. 1. Location map of study area

2. 1. The Amrovan catchment

Total area of the Amrovan catchment is 102.35 ha. The Altitudes range from 1795 meter at the catchment outlet to 1925 m in the upstream areas and the catchment slope average is commonly 11.4%. The mean annual precipitation is 174 mm and occurs in winter and spring months generally. In this catchment Quaternary, Hezar-Dareh and Upper Red formations as well as gully walls selected as the origin of sediment. All of the catchment area is covered by bush ranges (Figure 2).

2. 2. The Atary catchment

The Atary catchment drains an area of 627.96 ha, with its moderate relief (maximum and minimum altitude 2220 and 1750 m, respectively), relatively low annual precipitation (180 mm) and the catchment slope average is commonly 11.4%. Most of the rainfall occurs in winter and spring. The land use of the catchment is dominated by rangeland (100%). All of the catchment area is covered by bush ranges. Quaternary, Hezar-Dareh, Upper Red, Qum and Karag Formations selected as the origin of sediment (Figure 2).

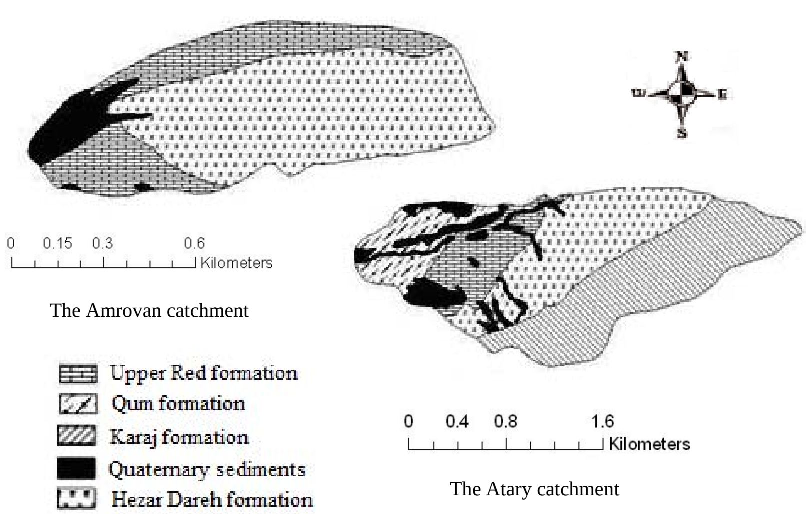

Fig. 2. Geological formation of Amrovan and Atary catchments

3. Materials and Methods

Field sampling involved the collection of representative samples of the main potential sediment sources identified within each study catchment. Potential sediment sources were categorized surface soils from different geological formations and eroding gullies. 10 representative samples were collected from each of primary sediment sources in each of catchments. Due to the negligible amount of some area as well as their same, some of units combined.

All samples were collected using stainless steel spade, which was regularly cleaned to avoid inter-sample contamination. Care was taken to ensure that only materials likely to be mobilized by erosion (dept of high 2 cm) were collected. Upon return to the libratory, the samples were air-dried, gently disaggregated using a pestle and mortar and dry sieved through a 63 mesh to ensure sample consistency.

Laboratory analysis of the source material samples involved the use of analytical procedures to assemble values for five groups of fingerprinting properties, including Organic constituents (C, N, P), base cations (Na, K, Ca, Mg), acid extractable metals (Cr, Co), clay minerals (Smectite, chlorite, Illite, Kaolinite) and mineral magnetism (X_{Lf}, X_{FD}) because this property has proved useful in several fingerprinting studies. These groups of fingerprinting properties were selected on the basis of available analytical equipment and their successful use in previous studies to discriminate sediment sources (Collins et al, 2008; Collins and Walling, 2002). Both C and N were determined directly using a Carlo Erba Elemental Analyzer, and P was determined calorimetrically using UV Visible Spectrophotometry, after extraction with perchloric acid (Olsen and Dean, 1965). Ammonium acetate was used to extract Na, Mg, Ca and K (Qui and Zhu, 1993). Acid extractable metals were extracted using direct acid digestion (Allen, 1989). Clay minerals were determined using X-ray diffraction (Garrad, and Hey 1989) and Mineral magnetisms were determined using a Bartington meter and MS2B dual frequency sensor (Caitcheon, 1998).

The discrimination of potential sediment sources afforded by the range of individual fingerprint properties and the groups of properties was tested statistically. First the Kruskal-Wallis test has been used for eliminating redundant fingerprint properties as a whole, then discrimination function analysis (DFA) was used to test the ability of the parameters passing the Kruskal-Wallis test to classify all the source samples from a given catchment into the correct categories. DFA calculates discriminant functions coefficients reflecting the explanatory power of the included variables and this procedure were employed in a number of ways. Firstly, it was used to assess the discriminatory power of individual fingerprint properties. Secondly, DFA was employed to assess the discrimination of potential catchment sediment sources afforded by composite fingerprints comprising constituents passing the Kruskal-Wallis test drawn from the individual groups of fingerprint properties. In combination, these two procedures, which involved forcing a particular property or groups of properties into the analysis, provided a rigorous means of testing the assumption that composite fingerprints afford more powerful source discrimination than individual fingerprint properties. Finally, a multivariate stepwise selection algorithm, based on the minimization wilks' lambda, was used to identify the smallest combination of properties (the optimum composite fingerprint), drawn from any group that provided the maximum discrimination of the source categories within each study catchment.

The minimization of wilks' lambda represents one of the five stepwise selection algorithms available within SPSS under the METHOD sub command (Nie et al., 1975). A lambda of one occurs when all source category means are equal, whilst values close to zero occur when inter-category variability exceeds within- category variability. This approach afforded a rigorous basis for testing the assumption that composite fingerprinting comprising constituents drawn from different groups of fingerprint properties offer greater discriminatory power than those based on single group of properties.

4. Results

4. 1. Sediment source discrimination afforded by individual fingerprinting properties in the Amrovan catchment

Table 1 summarises the descriptive statistics for the Amrovan catchment and the corresponding Kruskal-Wallis Statistics. According to this table, except N, Cr and Co all fingerprinting properties are below of the critical value (0.05) and so survive the elimination process. These successful properties generate test statistics ranged from 0.00 to 0.35

(See the column of 6 in table 1). Table 1 also includes the results of employing DFA to assess the percentage of source material samples classified correctly by each individual property passing the Kruskal-Wallis test. These results indicate that the most powerful individual fingerprint property is organic constituent C, which successfully classifies 70% of source material samples into the correct categories. Ca, Illite and X_{FD} are the weakest individual fingerprint property, correctly distinguishing only 45% of the source samples. No individual property classifies 100% of the source samples correctly.

4. 2. Sediment source discrimination afforded by individual fingerprinting properties in the Atary catchment

A summary of the descriptive statistics of the fingerprinting property data sets from the Atary catchment and the associated Kruskal-Wallis statistics are presented in Table 2. In total 14 properties were below the critical value and were therefore used in DFA. No single fingerprint property correctly classifies the entire set of source samples. However, C correctly classifies 66% of the samples, whilst Cr classifies 41.7 of the samples correctly (Table 2).

Table 1. The ability of individual fingerprint properties to distinguish sediment source types in the Amrovan catchment, assessed using the Kruskal-Wallis test and DFA

Fingerprinting properties	Minimum	Maximum	Mean	Std. Deviation	P-value[a]	%source type samples classified correctly
N[b] (%)	0.03	0.11	0.07	0.024	0.35	-
P[b] (ppm)	9.31	27.2	15.54	4.99	0.00	65
C[b] (%)	0.48	1.86	1.09	0.38	0.00	70
Cr[c] (ppm)	40.00	138	100.11	31.31	0.19	-
Co[c] (ppm)	7.20	13	10.12	1.92	0.06	-
Ca[d] (%)	16.05	26	21.67	3.20	0.00	45
Mg[d] (%)	0.55	1.52	1.03	0.30	0.00	55
K[d] (%)	0.51	1.03	0.72	0.17	0.00	65
Na[d] (%)	0.03	0.4	0.21	0.12	0.00	60
Smektite[e] (%)	13.00	65	48.74	13.35	0.00	57.5
Cholorite[e] (%)	0.00	44	25.45	12.49	0.00	52.5
Illite[e] (%)	16.65	34	21.61	6.18	0.00	45
Kaolinite[e] (%)	0.00	15	4.14	5.05	0.01	55
X_{LF}[f] (%)	3.20	24	13.32	7.53	0.02	45
X_{FD}[f] (%)	2.16	5	3.87	0.88	0.00	52.5

[a] Critical P-value = 0.05 [b] Organic constituents [c] acid extractable metals [d] base cations [e] Clay minerals [f] mineral magnetism

Table 2. The ability of individual fingerprint properties to distinguish sediment source types in the Atary catchment, assessed using the Kruskal-Wallis test and DFA

Fingerprinting properties	Minimum	Maximum	Mean	Std. Deviation	P-value[a]	%source type samples classified correctly
N[b] (%)	0.04	0.10	0.0605	0.01553	0.26	-
P[b] (ppm)	7.68	21.35	15.8548	4.34576	0.00	64
C[b] (%)	0.07	0.61	0.3568	0.16724	0.00	66
Cr[c] (ppm)	70.00	188.00	132.8889	36.89157	0.04	41.7
Co[c] (ppm)	7.80	16.90	12.2667	2.98254	0.01	42
Ca[d] (%)	11.70	21.80	16.4167	3.14387	0.00	52
Mg[d] (%)	0.84	1.95	1.4356	0.38062	0.00	54
K[d] (%)	0.34	1.19	.9067	0.25621	0.00	48
Na[d] (%)	0.17	0.51	0.3589	0.11387	0.00	54
Smektite[e] (%)	0.00	58.00	38.6811	15.26026	0.00	62
Cholorite[e] (%)	5.00	40.00	22.2833	12.84294	0.00	44
Ilite[e] (%)	13.95	35.00	25.6189	8.20958	0.00	54
Kaolinite[e] (%)	8.31	25.00	13.3767	4.87728	0.00	46
X_{LF}[f] (%)	10.88	43.84	27.4011	10.90750	0.00	44
X_{FD}[f] (%)	0.48	3.37	1.3829	0.90506	0.00	50

[a] Critical P-value = 0.05 [b] Organic constituents [c] acid extractable metals [d] base cations [e] Clay minerals [f] mineral magnetism

4. 3. Sediment source discrimination afforded by composite fingerprinting in the Amrovan catchment

The results of using DFA to test the discriminatory power of individual groups of fingerprint properties are represented in Fig. 3. These scatterplots are a useful means of examining the relationship between the source categories and of identifying misclassification resulting from using set of properties passing the Kruskal-Wallis elimination procedure drawn from the different property groups. A set of acid extractable metals fingerprint property provides the weakest source type discrimination, correctly distinguishing only 47.5 of the source samples (Figure 3c). This scatterplot indicates that the discrimination functions calculated using the acid extractable metals data is characterized by considerable overlap between the samples representing surface soils beneath different geological formation and those under eroding gully walls. Similarly, although a composite fingerprint based on organic constituents provides more robust discrimination of the sources (90%), the corresponding scaterplot presented in Fig. 3a also shows considerable overlap between the source categories. Fig. 3f demonstrates the discrimination of the four potential source types identified for the Amrovan catchment provided by the composite fingerprint selected using stepwise analysis of all retained properties. This final composite fingerprint comprising the following constituents from the different groups of properties: three base cations, one organic constituent, one mineral magnetism and one clay mineral and correctly distinguishes 100% of the source material samples (Table 3). In this case the source categories are tightly clustered and no overlap is observed.

Table 3. The optimum composite fingerprint for discriminating sediment source types in the Amrovan catchment derived using stepwise DFA of all properties accepted by the Kruskal-walis test

Step	Fingerprint property	Wilks' Lambda	%source type samples classified correctly
1	Mg	.170	55
2	C	.053	92.5
3	Ca	.014	95
4	$X_{F D}$	.003	92.5
5	Esmectite	.001	100

4. 4. Sediment source discrimination afforded by composite fingerprinting in the Atary catchment

Figure 4 examines the discrimination of the potential sediment sources within the Atary catchment afforded by a number of composite fingerprints. The composite fingerprint comprising a set of acid extractable metals provides the weakest source type discrimination (43.8%), followed in ascending order by the fingerprints comprising sets of organic constituents (84%), base cations (68%), clay minerals (76%) and mineral magnetism (48%). However, the optimum composite fingerprint selected by using stepwise DFA (Table 4) is capable of correctly classifying 100% of the source material samples. Accordingly, the scaterplot presented in Figure 4f shows no overlap between the source categories. As shown in Table 4, this signature comprises two clay minerals, one mineral- magnetism, one organic constituent and one base cation.

Table 4. The optimum composite fingerprint for discriminating sediment source types in the Atary catchment derived using stepwise DFA of all properties accepted by the Kruskal-walis test

Step	Fingerprint property	Wilks' Lambda	%source type samples classified correctly
1	C	.131	66
2	Esmectite	.035	88
3	K	.016	90
4	X_{LF}	.004	98
5	Kaolinite	.002	100

5. Discussion

Determining and discriminating the origin of sediment represents a key requirement from the management perspective, since identification of sediment sources is a key precursor to the design of effective sediment management and control strategies. However by investigation of field observation geological formation and gully walls were selected as the origin of sediment (Collins et al., 1997b). The results of the statistical analysis clearly demonstrate that no single property is capable of classifying 100% of the source material samples into the correct source categories for any of the study catchments. Levels of sediment source discrimination afforded by individual properties can, however, be used as a potential indication of the likelihood of correctly classifying all source samples using composite signatures. It is more valuable to attempt to identify the most useful groups of fingerprint properties. Such an approach recognizes the fact that a single extraction procedure can frequently be used to provide several potential properties for inclusion in a composite fingerprint.

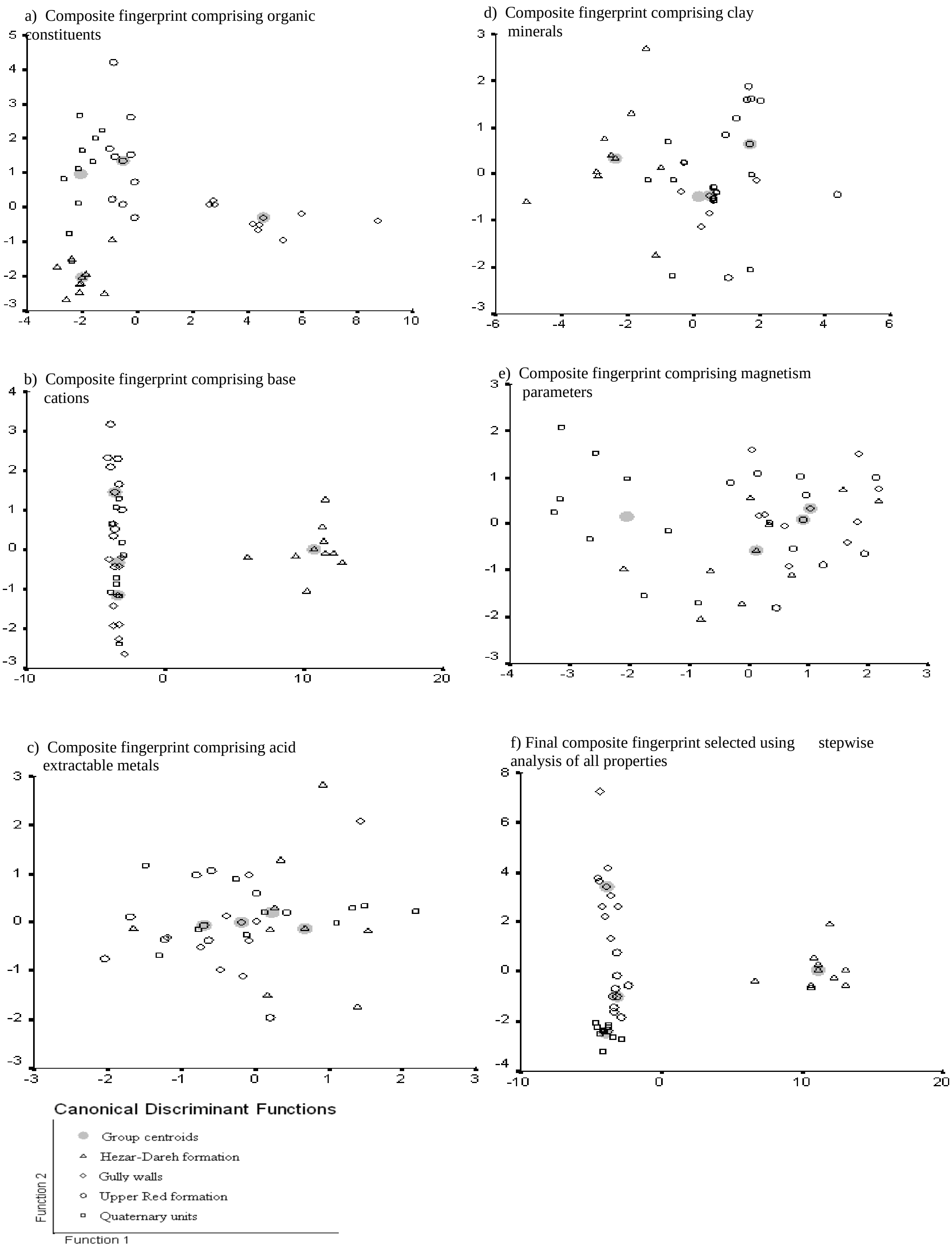

Fig. 3. Scaterplots constructed from the first and second discrimination functions calculated using DFA to test the power of different groups of fingerprint properties for distinguish potential sediment sources in the Amrovan catchment

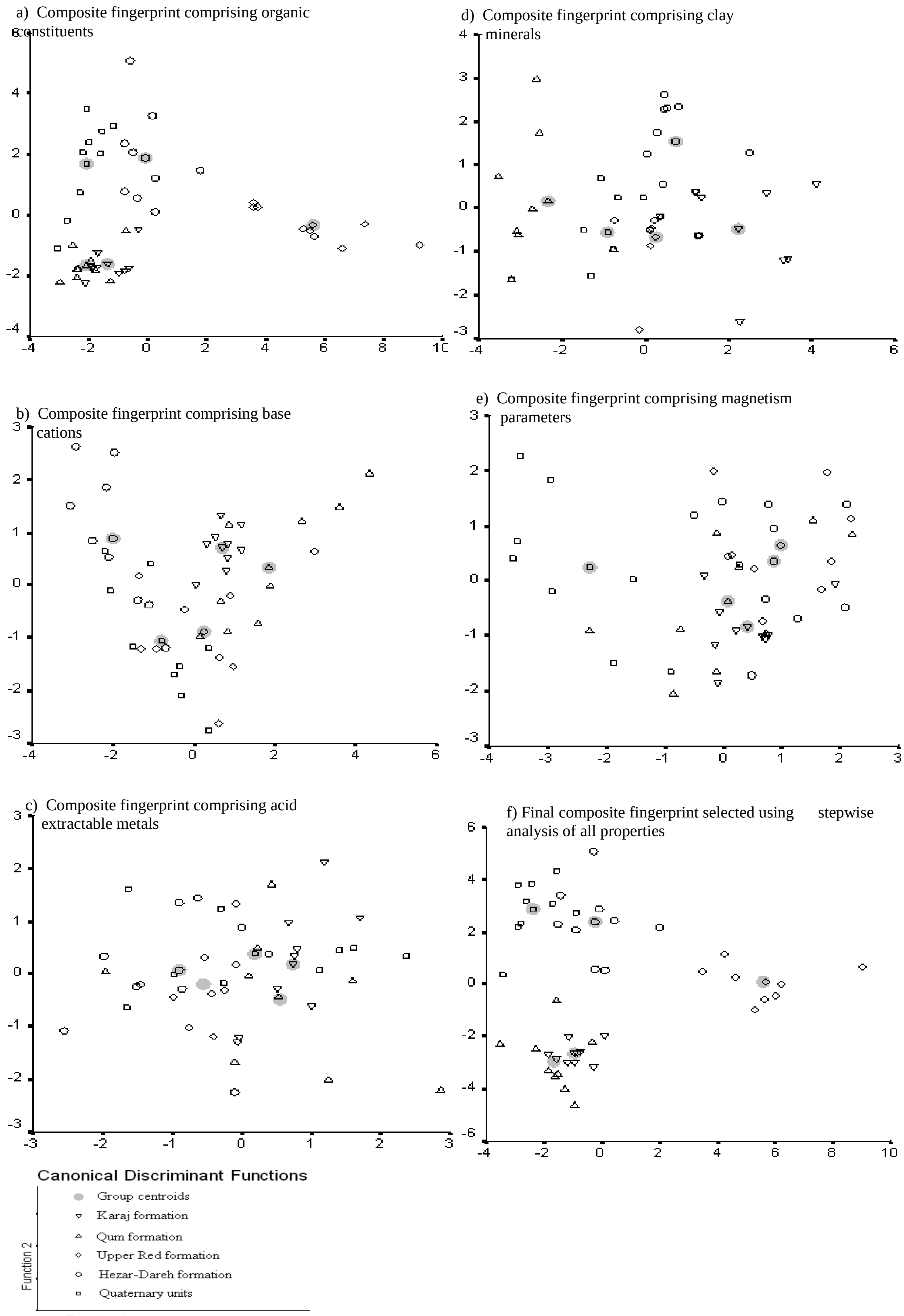

Fig. 4. Scaterplots constructed from the first and second discrimination functions calculated using DFA to test the power of different groups of fingerprint properties for distinguish potential sediment sources in the Atary catchment

In considering individual groups of properties, the results presented earlier clearly indicate that the use of a composite signature based on a specific property group consistently enhances the level of sediment source discrimination over that afforded by any one of its constituents. For example the highest proportion of source samples from the Amrovan catchment correctly classified by an individual property from the group of organic constituents is 70% (C), whilst the combined use of a number of properties in the group correctly classifies 90% of the source material samples. Similarly, for the Atary Catchment, the best single property (C) from the group of group of organic constituents correctly classifies 66% of the source samples, whilst this increases to 84% for a set of properties from the group.

The proportion of source samples correctly discriminated using the set of properties drawn from the group of organic constituents have the highest classified correctly in all catchments. This is an important finding in terms of the cost-effectiveness of composite fingerprinting procedures, spatially for situations where laboratory resources limit analysis to a restricted range of properties. The results from the stepwise DFA clearly indicate that the optimum composite fingerprint comprising constituents selected from a number of the different groups of properties generally affords the most robust discrimination of the sediment sources within the study catchment. For example, the final composite fingerprint identified for the Amrovan catchment, correctly classifies 100% of the source material samples, whereas the maximum discrimination afforded by an individual group of properties is 90%. Likewise, for the Atary catchment, the optimum fingerprint provided by stepwise DFA correctly classifies 100% of the source material samples; whereas the best performance for fingerprints based on single group of properties is 84%. This result reflect the likelihood that the different groups of properties tested are influenced by contrasting environmental controls and therefore characterized by a substantial degree of independence. Consequently, when used in combination (for example to construct a composite finerprint) the different types of property afford a more robust means of discriminating catchment sediment sources (Walling et al., 1999; Collins et al., 1997a, 1998, 2001).

The ability to pre-select potentially successfully groups of fingerprint properties would clearly be an important advantage in sediment source investigation. Although composite fingerprints based on several properties from a single group consistently improve the level discrimination over that afforded by their individual constitutes, some entire groups offer less robust discrimination than individual properties associated with alternative groups. The results of this study, for example, demonstrate that the group of acid extractable metals consistently provides poorer source discrimination than many individual properties from the alternative groups. It can therefore be suggested that the acid extractable metals represent the least potentially useful group of properties tested by this study and no member of this group is included in the final composite signature as well as. In contrast, organic constituents are selected in two final composite fingerprints, suggesting that this group of properties is extremely useful for sediment source discrimination in similar catchments.

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