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Determining the Ability of Acid Extractable Metals as a Fingerprint in Sediment Source Discrimination

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Abstract Sediment-related environmental problems pose a serious threat to sustainable land management in many developing countries, including Iran. Information regarding sediment sources represents a key requirement from the management perspective since identification of sediment sources is a precursor to the design of effective sediment management and control strategies. The fingerprinting approach has increasingly been adopted as an alternative to assembling such information. A wide range of fingerprint properties has been used as a means of discriminating potential sediment sources. However, determining the ability of these properties is very important in the design of cost-effective catchment management strategies before each study. This contribution addresses the ability of two acid extractable metals (Co and Cr) that were used extensively in previous studies to be used to differentiate sediment sources. The results of the statistical analysis demonstrate that no single property is capable of classifying the source material samples into the correct source categories at the Amrovan drainage basins. In the case of the Atary drainage basin, Cr and Co were found in only 47.5 and 43.8% of the source material samples respectively. According to the result obtained, it is recommended that acid extractable metals for sediment sources differentiation in conjunction with the composite of other properties to improve sediment source discrimination.

Key words: *Acid extractable metal, Iran, Sediment sources discrimination*

1 INTRODUCTION

Information regarding sediment sources represents a key requirement from the management perspective, since identification of sediment sources is a precursor to the design of effective sediment management and control strategies. Sediment control programs are primarily concerned with downstream problems and must consider a wider range of potential sources (Walling, 2005). Information regarding sediment source is also of fundamental importance to understand the sediment dynamics and the sediment budget of a catchment (Walling *et al.*, 2001 and 2002). Although the need for information regarding sediment source is clear, it has been difficult to assemble such data (Collins and Walling, 2004). However, the fingerprinting approach has increasingly been adopted as an

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alternative and more direct and reliable means of assembling such information (Walling *et al*., 2008). In particular, source fingerprinting techniques provide a relatively simple and cost-effective basis for assembling spatially- and temporally-integrated data for catchments of different scales (Collins and Walling, 2004; Walling, 2005). Sediment source fingerprinting is founded on the link between the physical and geochemical properties of the sediment and those of its sources. If potential source materials can be distinguished based on their properties, the likely provenance of the sediment can be established using a comparison of the properties of the sediment with those of the individual potential sources. A wide range of fingerprint properties has been used as a means of discriminating potential sediment sources, and these include mineral magnetism (Caitcheon, 1993; Feiznia and Kouhpeima, 2010; Kouhpeima *et al*., 2010a,b), clay minerals (Feiznia and Kouhpeima, 2010; Kouhpeima *et al*., 2010a,b), environmental radionuclides (Wallbrink and Murray, 1996), base cations (Feiznia and Kouhpeima, 2010; Kouhpeima *et al*., 2010a,b), acid extractable metals (Collins and Walling, 2002; Kouhpeima *et al*., 2010a,b), particle size (Walling *et al*., 2008), and organic constituents (Collins and Walling, 2002; Walling *et al*., 2008; Feiznia and Kouhpeima, 2010; Kouhpeima *et al*., 2010a,b). However determining the ability of these properties to discrimination of sediment sources is very important in the design of cost-effective catchment management strategies before each study. This contribution addresses the ability of two acid extractable metals (Co and Cr) that were used extensively in previous studies to be used to differentiate sediment sources in two small drainage basins in Semnan, Iran.

2 MATERIALS AND METHODS STUDY AREA

The study area consisted of two small catchments (the Amrovan and Atary catchments) in the Semnan Province of Iran, (Fig. 1). The areas are homogenous with respect to different aspects such as land use, climate and hydrological conditions, but differ with respect to the geological formations. This study area is including the two catchments: 1. The Amrovan Catchment has a total area of 102.35 ha, altitudes ranging from 1795m 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, most of which occurs in winter and spring. The geology is dominated by Quaternary, Hezar-Dareh and Upper Red Formations (see Table 1). The entire catchment area is covered by bush ranges. The Atary catchment has a total area of 538.83 ha. The area has an annual rainfall of 184 mm, most of which occurs in winter and spring. The altitude of the catchment ranges from 1855 m at the catchment outlet to 2070 m in the upstream areas and the average slope is 23.95%. The geology is dominated by Quaternary, Hezar-Dareh, Shemshak, Lar and Upper Red Formations (see Table 1). All of the catchment area is covered by bush ranges. The reservoirs were created by constructing earth embankments to harvest seasonal runoff.

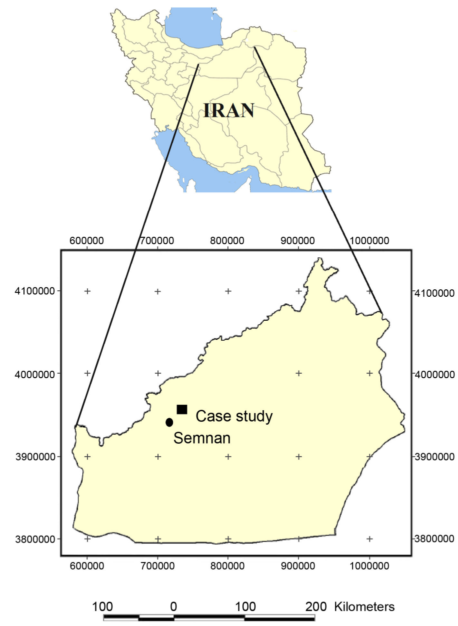

Fig. 1 Map of the study areas.

Table 1 Description of the geological nature of the source catchments.

Catchment	Sediment sources	Description of lithology
Amrovan	Quaternary Units	Young alluvial of river bed, alluvial traces of river bed
	Hezar-Dareh Formation	Conglomerate with sandstone and clay
	Upper Red Formation	Conglomerate and gypsiferous marn
Atary	Quaternary Units	Young alluvial river bed, alluvial traces of river bed old alluvial deposits
	Hezar-Dareh Formation	Conglomerate with sandstone and clay
	Upper Red Formation	Conglomerate and gypsiferous marn
	Qum Formation	Limestone and gypsiferous marn
	Karaj Formation	Shale and igneous rocks

3 METHODOLOGY

Representative source material samples were collected between April and May 2008. Sampling was stratified to encompass the primary potential source types identified within the study drainage basins. These comprised surface soils within areas under different geological formations, as well as subsurface sources, which included eroding gully walls. Samples collected from potential surface sediment sources comprised topsoil (0–2 cm) susceptible to mobilization by water erosion and subsequent routing to the river channel network (Russell *et al*., 2001). Sampling of subsurface sources focused on actively eroding gully systems. Ten representative samples were collected from each primary sediment source in each drainage basin. All source material samples were collected using a stainless steel spade, which was regularly cleaned to avoid inter-sample contamination. Laboratory analysis of source material samples was undertaken at the University of Tehran, Faculty of Natural resources. The samples were air-dried at 40ºC, gently disaggregated using a mortar and pestle, dry sieved through a 63 mesh and used in analytical procedures to assemble values for two acid extractable metals (Co and Cr). Co and Cr concentrations were determined by atomic adsorption spectrophotometry (AAS) following direct acid digestion (Allen, 1989).

Discrimination of potential sediment sources was tested statistically using a two-stage procedure (Collins *et al*., 2001). In stage one, the Kruskal–Wallis test was used to test the ability of individual constituents to distinguish potential sediment sources in an unequivocal manner. In stage two, discriminated function analysis (DFA) was used to test the ability of the properties passing the Kruskal–Wallis H-test to classify all source material samples from a given drainage basin into the correct categories. DFA was conducted in two ways. First, it was used to assess the discriminatory power of individual fingerprint properties. Second, DFA was employed to assess the discrimination of potential drainage basin sediment sources afforded by composite fingerprints drawn from the individual fingerprint properties.

4 RESULTS

Table 2 summarizes the descriptive statistics for the Amrovan and Atary Drainage Basins and the corresponding Kruskal-Wallis Statistics. According to this table, all fingerprinting properties yield test statistics below the critical value (0.05) in the Atary drainage basin. In the case of the Amrovan drainage basin, two fingerprinting properties were higher than the critical value (0.19 and 0.06 for Cr and Co, respectively) and therefore not capable of use in sediment source discrimination. Table 2 also includes the results obtained from DFA analysis of the percentage of source material samples classified correctly by each individual property.

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These results indicate that the best individual fingerprint properties were provided by Co, which enabled successful classification of only 42% of the source material samples into the correct categories. Cr enabled classification of only 41.7% of the source material samples into the correct categories. The results of DFA of the discriminatory power of composite of Co and Cr for the Amrovan and Atary catchments are presented in Figs. 1 and 2, respectively. These scatter plots are useful for examining the relationship between the source categories and identifying misclassifications resulting from the use of two properties passing the Kruskal-Wallis elimination procedure. A composite fingerprint based on these two acid extractable metals identified 47.5 and 43.8% of source type samples classified correctly in the Amrovan and Atary drainage basins, respectively (See Figs. 1 and 2).

Table 2 Descriptive statistics and the corresponding Kruskal-Wallis and DFA statistics.

Drainage basins	Fingerprinting properties	Minimum (ppm)	Maximum (ppm)	Mean (ppm)	Std. Deviation	P-value[a]	% source type samples classified correctly
Amrovan	Cr	40.00	138	100.11	31.31	0.19	-
	Co	7.20	13	10.12	1.92	0.06	-
Atary	Cr	70.00	188.00	132.89	36.89	0.04	41.7
	Co	7.80	16.90	12.27	2.98	0.01	42

a: Critical P-value = 0.05.

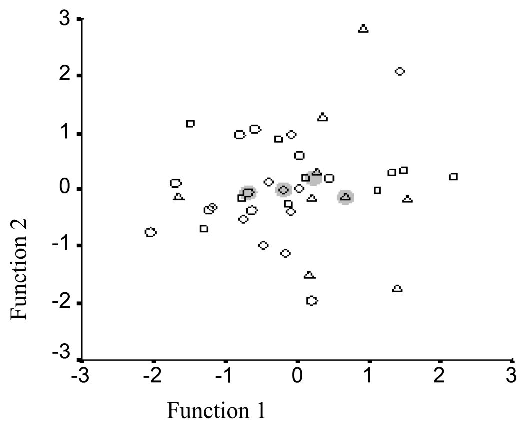

Fig. 2 Scatterplots constructed from the first and second discrimination functions calculated using DFA to test the power of different groups of fingerprint properties to distinguish potential sediment sources in the Amrovan drainage basin (each symbol group is representative of each sediment source).

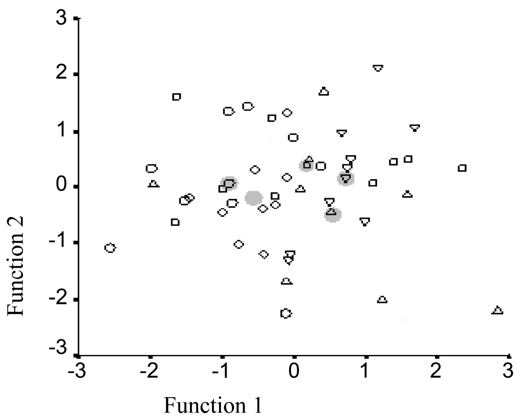

Fig. 3 Scatterplots constructed from the first and second discrimination functions calculated using DFA to test the power of different groups of fingerprint properties to distinguish potential sediment sources in the Atary drainage basin (each symbol group is representative of each sediment source).

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5 DISCUSSION

The results of the statistical analysis demonstrate that no single property is capable of classifying the source material samples into the correct source categories in the Amrovan drainage basin; therefore, no individual properties are suitable for discrimination of sediment sources in this drainage basin. In the case of the Atary drainage basin, Cr and Co were only classified 41.7 and 42% of the source material samples, respectively. Although the results demonstrated that the discrimination of sediment sources by Cr and Co is meaningless, the results presented by Collins *et al*. (2002) indicate the more discrimination power of these properties. Therefore, the discrimination power of fingerprinting properties varies in different areas. This difference can be attributed to variations in lithology, soil and climate condition. The results presented herein indicate that the use of a composite signature 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 Atary drainage basin correctly classified by an individual property is 42% (Co), while the combined use of Co and Cr correctly classified 43.8% of the source material samples. Similarly, for the Amrovan drainage basin, no single property correctly classified source samples, while a combination of these two properties could classify 48.5% of the samples. These results are similar to those of a study conducted by Collins *et al*. Although a composite fingerprint based on acid extractable metals provides more discrimination of the sources, the corresponding scatterplot presented in Figs. 1 and 2 still shows considerable overlap between the source categories, which indicates that the discrimination functions calculated, are characterized by considerable overlap between samples representing surface soils beneath different geological formations and those under eroding gully walls. The discriminatory power of composite fingerprinting properties was higher in the Amrovan drainage basin than the Atary drainage basin. In the Atary drainage basin, there is a greater slope and rainfall; therefore, the sediments are well mixed, making discrimination of their source more difficult than that in the Amrovan drainage basin, which has a lower slope and less rainfall. The existence of four sediment sources in the Amrovan drainage basin and five sediment sources in the Atary drainage basin also facilitates the discrimination of sediment sources in the Amrovan drainage. According to the results of the present study, it is recommended that acid extractable metals for sediment sources differentiation in conjunction with the composite of other properties to improve sediment source discrimination. Collins *et al*. (2002) suggested that measurements of a combination of base cations, acid and pyrophosphate-dithionite extractable metals and organic constituents should provide an effective basis for establishment of composite fingerprints for the discrimination of individual sediment source types. However, the use of composite fingerprinting properties has been shown to afford more robust sediment source discrimination than individual fingerprinting properties in many previous studies (Collins *et al*., 2002; Collins and Walling, 2004; Walling *et al*., 2008).

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بررسی قابلیت فلزات اسیدی به عنوان منشأیاب در تفکیک منابع رسوب

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چکیده مشکلات زیست محیطی مربوط به رسوب در بسیاری از کشورهای در حال توسعه از جمله ایران تهدید جدی برای توسعه پایدار اراضی ایجاد می‌کند. از نظر مدیریتی کسب اطلاعات در مورد منابع رسوب نیازی اساسی است چون تعیین منابع رسوب نقش کلیدی در طراحی استراتژی‌های کنترل و مدیریت رسوب دارد. تکنیک‌های منشأیابی به طور فزاینده‌ای به عنوان روشی در کسب این اطلاعات استفاده می‌شوند. ردیاب‌های متعددی به منظور تعیین پتانسیل آنها در تفکیک منابع رسوب استفاده شده‌اند. به هر حال قبل از هر مطالعه‌ای تعیین قدرت هر یک از این خصوصیات در طراحی استراتژی‌های مدیریت حوزه از نظر اقتصادی بسیار مهم می‌باشد. این مقاله توانایی دو فلز اسیدی (کروم و کبالت) که به طور گسترده‌ای در مطالعات گذشته در تفکیک منابع رسوب استفاده شده است را مورد بررسی قرار می‌دهد. نتایج بررسی‌های آماری نشان می‌دهد که در حوزه آبخیز عمروان هیچ کدام از خصوصیات منشأیاب به تنهایی نتوانسته نمونه‌های مواد منشأ را به درستی تفکیک کند. در حوزه آبخیز عطاری کروم و کبالت به ترتیب ۴۷/۵ و ۴۳/۸ درصد نمونه‌های منابع رسوب را تفکیک کرده است. با توجه به نتایج به دست آمده، استفاده از فلزات اسیدی به عنوان منشأیاب برای تفکیک منابع رسوبی همراه با ترکیبی از سایر منشأیاب‌ها به منظور افزایش تفکیک منابع رسوب توصیه می‌شود.

کلمات کلیدی: ایران، تفکیک منابع رسوب، فلزات اسیدی