Sediment sources in a small agricultural catchment: a composite fingerprinting approach based on the selection of potential sources

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Abstract: Fingerprinting techniques have been widely used as a reasonable and reliable means for investigating sediment sources, especially in relatively large catchments in which there are significant differences in surface materials. However, the discrimination power of fingerprint properties for small catchments, in which the surface materials are relatively homogeneous and human interference is marked, may be affected by fragmentary or confused source information. Using fingerprinting techniques can be difficult, and there is still a need for further studies to verify the effectiveness of such techniques in these small catchments. A composite fingerprinting approach was used in this study to investigate the main sources of sediment output, as well as their

relative contributions, from a small catchment (30 km²) with high levels of farming and mining activities. The impact of the selection of different potential sediment sources on the derivation of composite fingerprints and its discrimination power were also investigated by comparing the results from different combinations of potential source types. The initial source types and several samples that could cause confusion were adjusted. These adjustments improved the discrimination power of the composite fingerprints. The results showed that the composite fingerprinting approach used in this study had a discriminatory efficiency of 89.2% for different sediment sources and that the model had a mean goodness of fit of 0.90. Cultivated lands were the main sediment source. The sediment contribution of the studied cultivated lands ranged from 39.9% to 87.8%, with a mean of 76.6%, for multiple deposited sediment samples. The mean contribution of woodlands was 21.7%. Overall, the sediment contribution from mining and road areas was relatively low. The selection of potential sources is an important factor in the application of fingerprinting techniques and warrants more attention in future studies, as is the case with other uncertainty factors.

Keywords: Sediment fingerprinting; Source apportionment; Small catchment; China

1. Introduction

The dynamic change of river sediment transport can influence hydrologic regime in catchment. Increased suspended sediment concentrations can accelerate sedimentation and alter channel morphology. Sediment is also an important vector for the transport and transformation of nutrients, heavy metals and other organic or inorganic pollutants in a water body and thus has a substantial effect on the water quality and aquatic ecological environment in the lower reaches

46 (Owens and Walling, 2002; Bilotta and Brazier, 2008; Bird et al., 2010; Song et al., 2011).
47 Because non-point-source pollution in catchments has attracted worldwide attention in recent
48 decades, sediment and sediment-associated pollutants, as well as their resulting human health risks,
49 have also become foci of research on the control of water pollution in catchments (Yi et al., 2011;
50 Doody et al., 2012; Falbo et al., 2013;).

51 Implementation of appropriate and specific management solutions to soil erosion and water
52 pollution control require the information of the major sediment sources. Studies of sediment
53 sources facilitate a better understanding of soil erosion and the characteristics of sediment
54 transport and deposition in the catchment. Fingerprinting techniques, characterized as a “direct”
55 approach, have been shown to represent a valuable and effective alternative for apportioning
56 sediment sources. Sediment fingerprinting can be used to establish the relative importance of
57 multiple sediment sources and has been widely used in recent sediment source apportionment
58 studies (Collins et al., 1998, 2010a, 2012; Walling, 2005; D'Haen et al., 2013; Smith and Blake,
59 2014). The premise of the fingerprinting approach is that soils from different sources can be
60 distinguished based on their material composition. Two basic steps are involved in the application
61 of the fingerprinting approach. The first step involves the collection of soil samples from various
62 potential sediment sources and the selection of fingerprint properties that can discriminate among
63 different sources based on the comparison of the geochemical or geophysical properties of the soil
64 samples. The second step involves comparisons of the correlations and differences between the
65 fingerprint properties of the sediment samples and the soil samples from the potential sources;
66 additionally, this step includes quantitative analyses of the relative contribution of each potential
67 source to the sediment output.

68 Earlier works of sediment fingerprinting employed a single fingerprint property. However,
69 the discrimination power of a single fingerprint becomes inadequate when the spatial variability of
70 the potential sediment sources and the sediment mobilization process are relatively complex
71 (Collins et al., 1998). In contrast, a composite fingerprinting technique combines multiple
72 fingerprint properties that can effectively discriminate among different sediment sources to form
73 an optimum composite fingerprint. Such a composite technique serves as an integrated
74 discrimination tool and is based on the statistical examination of large soil-properties datasets.
75 Previous studies have shown that composite fingerprints markedly improve sediment source
76 discrimination (Collins et al., 1998; Walling et al., 1999). A study of five catchments in the UK
77 and Africa has shown that a composite fingerprint that consists of several properties from a
78 specific property type can improve the results over those achieved by with a single fingerprint.
79 However, the level of discrimination attained by such a composite fingerprint varied between
80 different catchments (Collins and Walling, 2002). That study also demonstrated that an optimum
81 composite fingerprint, comprising constituents selected from different groups of fingerprint
82 properties, could consistently provide a robust means of discriminating sediment sources. The key
83 aspect of the fingerprinting approach is to compare the contents of the fingerprint properties of the
84 sediment and of the source soils. Many studies have investigated the factors that affect such
85 comparisons. For example, several studies have considered the effects of particle size and organic
86 matter content on the fingerprint properties of sediment and the source soils, and have
87 incorporated correction factors into the mixing models (Collins et al., 1998; Russell et al., 2001).
88 Collins et al. (2010a) also simultaneously considered the within-source variability of the
89 fingerprint properties and the weighting of the discrimination power of each property in the

composite fingerprint. However, some researchers ([Walling et al., 1999](#); [Russell et al., 2001](#); [Smith and Blake, 2014](#)) believe that (1) particle size and organic matter affect the content of each fingerprint property to different extents, (2) unified corrections to all of the properties may generate new errors, and (3) simultaneous corrections to the particle size and organic matter contents of the fingerprint properties may result in "over-correction". With the continuous increase in applications of the fingerprinting approach, the optimization of the mixing models, the uncertainties of the sediment mobilization process and the analysis of the limitations of the fingerprinting approach have become foci of recent studies ([Rowan et al., 2000](#); [Koiter et al., 2013](#); [Nosrati et al., 2014](#)).

Previous studies have generally focused on relatively large catchments because (1) the spatial heterogeneities of geological units, soils and land use types are relatively high at a large scale, (2) different sources may have significantly different sediment properties, and (3) the application of fingerprinting technique can produce relatively good results ([Collins and Walling, 2002](#); [Cater et al., 2003](#); [Collins et al., 2010a](#)). In contrast, the surface materials in a small catchment tend to be relatively homogeneous. A successful application of a fingerprinting technique then requires greater numbers of discriminable fingerprint properties. However, properties meeting these requirements are rather difficult to identify and acquire. Moreover, relatively few studies have focused on small catchments. For example, [Russell et al. \(2001\)](#) attempted to discriminate the suspended sediment sources in two small catchments (areas of 1.5 and 3.6 km²) in the UK. [Smith et al. \(2011\)](#) investigated a forested upland catchment in Australia with an area of only 1.36 km². Most studies classify potential sediment sources based on the land use or special terrains or landscapes, which primarily include cultivated land, pastureland (grassland), woodland and

collapsed river banks. Several studies have focused on urban areas ([Carter et al., 2003](#); [Franz et al., 2014](#)) and damaged roads ([Collins et al., 2010b](#)). [Lin et al. \(2012\)](#) conducted a sediment source apportionment study in the collapsing gully erosion region in Fujian, China and quantified the relative contributions of different soil layers of the collapsing gully section to the sediment output.

Two assumptions of the fingerprinting approach are that (1) the potential sediment sources are known and the components of the sediment only originate from these sources, and (2) the contribution from each source is greater than zero and the sum of the proportions of the contributions is unity. However, when using the fingerprinting approach, the determination of potential sources is subjective, and it is uncertain whether the selected potential sources are all actual contributors to final sediment output. In particular, complex and interlaced sediment source types or improper sampling times and locations can lead to confusing source information, which may affect the selection of fingerprint properties and reduce the power of source discrimination ([Martínez-Carreras et al., 2010](#); [D'Haen et al., 2013](#)). Therefore, it is necessary to further analyze the reasonableness of the selection and classification of potential sediment sources.

Representative sediment source fingerprinting studies that have been carried out in China have mainly concentrated on the region in the upper reaches of the Yangtze River, the Three Gorges Reservoir region, the Loess Plateau, and the collapsing gully region in Fujian. Because these regions have relatively large sediment discharges and complex or varied geological conditions, the use of single-fingerprint ([Wen et al., 2000](#); [Wang, 2002](#); [Jia and Wei, 2009](#)) or composite-fingerprint methods ([Yang and Xu, 2010](#); [Lin et al., 2012](#); [Guo et al., 2014](#)) in studying sediment sources has several advantages. However, these studies have not thoroughly investigated improvements of the fingerprinting approach or discussed the uncertainty issues. No similar

studies have investigated the apportionment of sediment sources in small catchments in eastern China, which have relatively small sediment discharges and are disproportionately influenced by human activity. Therefore, it is necessary to further verify the feasibility of sediment source fingerprinting in such small catchments for clarity or strengthen the related issues. In addition, sediment source apportionment is conducive to studies of the control of non-point source pollution in this region. This study focused on a small catchment in the upper reaches of the Jiuxiang River in Nanjing, Jiangsu Province, eastern China. The main objectives of this study are (1) to explore the feasibility of the use of a composite fingerprinting technique to discriminate sediment sources in small agricultural catchments that are significantly affected by human factors, and (2) to discuss the selection of potential sediment sources and its impact on source discrimination.

2. Study area

Located in the eastern suburbs of Nanjing ($118^{\circ}52'-119^{\circ}1'E$, $32^{\circ}1'-32^{\circ}10'N$), the catchment of the Jiuxiang River is approximately 18 km long from south to north and 5.7 km wide from east to west, and has a total area of 106.2 km² (Fig. 1). The topography of the catchment is characterized by mounds and hills in the south and plains along the river in the north, where the maximum elevation is about 340 m and the elevations of plains are generally 10–25 m. A sub-catchment with an area of 30 km², which is located in the upper reaches of the Jiuxiang River, was selected as the study area (Fig. 1 and Fig. 2). The land use types in the study area include cultivated land, woodland, land that is used for mining, roads and rural residential areas (Fig. 3). It is likely that human effects, such as the development of mineral resources in Qinglong Mountain in the upper reaches and the agricultural activities in the middle and lower reaches, play a role in

sediment production in this area. In particular, long-term agricultural production has caused significant disturbances to the surface, and the non-point source pollution originating from this sub-catchment has also generated risks to the aquatic environment in the lower reaches (Hu et al., 2012). A main road that traverses the study area was the target of a road extension project in 2010. Since then, subgrade construction, with a substantial transport of large amounts of soil and rocks along the road, has resulted in significant sediment loss.

Fig. 1. The locations of Jiuxiang River catchment (left bottom) and the study area in Jiangsu Province, China.

Fig. 2. Elevations of the study area.

Fig. 3. Land use of the study area and location of sampling sites

3 Methods

3.1. Sample collection

A field survey of the study area showed that the woodlands, which had relatively steep slopes, the mining area in the upper reaches and the cultivated lands in the middle and lower reaches were areas where soil erosion could generally occur; these areas could thus be considered as potential sediment sources. The road might be an important sediment source during the construction period. In fact, the large amounts of soil and rocks that were piled along the road originated from the mining area in the upper reaches. That is, sediment from the road almost has the similar properties as the sediment from the mining activity. Therefore, the road construction and the mining were viewed as one source type for their same original source. Generally, the uncertainty of fingerprinting decreases as the numbers of sources in the composite fingerprint decrease. Therefore, the potential sources whose concentrations of the tracer properties are similar should be combined to minimize source numbers in order to improve confidence on estimated source

proportions (Zhang and Liu, 2016). Collapses and erosion also occurred on both banks of some sections of the river as well as on the sidewalls of the channels or gullies. These areas were also considered to be potential sources because this source type has been considered to be an important subsurface source in many previous studies. In order to derive composite fingerprints, representative samples should be collected from those four potential sources. From April to May 2012, sampling points were set at the locations where sediment likely to be mobilized by erosion and from which sediment might ultimately be transported to the lower reaches and likely to enter the river. A total of 76 surface soil samples (0–2 cm) were collected using the multi-point mixing method (Table 1). Stainless steel shovels were used to collect the samples. The collected soil samples were placed on a piece of plastic cloth to facilitate the removal of noticeable impurities, such as rocks and plants. The soil samples were then put into sample bags. Each sample weighed approximately 1 kg. Several previous studies have collected suspended sediment from rivers (Walling, 2005; Walling et al., 2008), whereas others used sediment that was deposited after a flood (Collins et al., 2010a; Franz et al., 2014) or used both suspended sediment and sediment that was deposited in riverbeds and reservoirs for comparison (Haddadchi et al., 2014). While in this study area, the flows of water are controlled by multiple sluice gates, it is difficult to continuously collect suspended sediment. That is, sediment derived from the sources may not reach the outlet and be collected with continuous sampling. In contrast, previously deposited sediment at the outlet of the catchment seems more representative than suspended sediment that could be collected only over a short period of time during rainfall or when the upper gates are open. The deposited sediment can reflect the average sediment output from the catchment for a relatively long period. A total of 17 deposited sediment samples were collected from the river section above the sluice

gate at the outlet of the catchment (Table 1). A piston-type columnar sediment sampler was used to collect sediment samples at multiple points at each site in the direction vertical to the direction of the water flow, and these samples were subsequently mixed to form a single sample. A lack of historical information on sediment load and deposition rate in this catchment makes it difficult to exactly judge which portion of the sediment column that could be selected as final samples. However, previous observations have shown that the catchment did not have a large sediment export. To better reflect the relationship between recent sediment output and sediment sources, the upper portion, varied from top 5 to 10 cm of the collected sediment column at each point was empirically selected to represent the sediment that had been recently deposited.

Table 1
Sampling information for source material and deposited sediment.

Sample type	Number of samples	Sample number	Description of the sampling locations
Woodland soil	20	W1–W20	Middle and lower locations of woodlands that are easily disturbed and relatively close to brooks
Cultivated land soil	21	C1–C21	Locations with relatively high farming intensities that are close to the drainage ditches
Mine and road soil	15	M1–M15	Locations on both sides of the drainage ditches and the road in the mining area in the upper reaches, and the roadbed construction sites that are close to the drainage ditches
Channel bank soil	20	B1–B20	Locations with significant scouring and erosion
Deposited sediment	17	#1–#17	River sections above the sluice gate where the water flow is relatively gentle (samples were collected at different locations along the water flows in the upper and lower reaches)

3.2. Laboratory analysis

All soil samples were air-dried for approximately 1 week in a shady and cool environment. Because some of the sediment samples had excessively high values of water content, they were transferred to a freeze dryer for further processing after being air-dried for a certain period of time. All samples were first sieved through a 2-mm sieve and then through a <63- μ m sieve prior to the analysis. A total of 23 geochemical properties of the soil and deposited sediment samples were examined. The Na, Mg, Al, Si, K and Ca contents were determined using inductively coupled

plasma mass spectrometry. The Mn, Zn, Cu, Cr, Pb, Co, As, Sb, Sn, Cd, Sr, Ni and Fe contents were determined using an X-ray fluorescence spectrometer. The results for Na, Mg, Al, Si, K, Ca and Fe content were expressed in terms of specified oxides of these elements. The ^{137}Cs content was determined using a low-background multichannel gamma spectrometer. Prior to the determination of the ^{137}Cs content, each sample was dried at 60°C for 6 h. The ^{137}Cs content was calculated based on the area of the 661.66 keV peak. The total phosphorus content was determined using the molybdenum blue extraction–ultraviolet spectrophotometric method, and the C and N contents were determined by pyrolysis using an automatic analyzer.

3.3. Selection of composite fingerprints

Prior to the fingerprinting procedure, all measured element contents were examined using the Dixon method, and the outliers in the samples were removed. The data on the deposited sediment samples were further subjected to a violation test, i.e., the content of each element in the sediment samples was observed to determine whether it was within the theoretical range of the content of that element in the source soil samples (Collins et al., 1997).

Two steps were involved in the selection of a composite fingerprint. The first step involved examining the data of the source soil properties using a Kruskal–Wallis H test and selecting fingerprint properties that could discriminate between different sediment sources. The null hypothesis of this Kruskal–Wallis H test was that all of the sediment originated from the same source. When the H value of the Kruskal–Wallis test was greater than the H_{critical} value of the chi-square test, the null hypothesis was rejected, which indicated that the property could discriminate between sediment sources. The second step involved searching for the optimum

composite fingerprint using a multivariate Discriminant Function Analysis (DFA) based on the results of the Kruskal–Wallis H test. Wilks' lambda was used as the main basis of discrimination in the stepwise discriminant analysis. In each step, the discriminant function was entered with the lowest Wilks' lambda.

The number of potential sediment sources and the magnitude of the differences between the samples from different sources are expected to have an impact on the selection of the fingerprint properties and the derivation of the optimum composite fingerprint. Errors in the pre-determination of potential source types or the unrepresentativeness of the samples will cause difficulties in source discrimination. It is important to determine whether the potential source types show significant differences from each other. This determination can be performed by applying a mean test of the properties of soil samples from the potential sources and by subsequently performing a comparison among the significant differences between the properties of the soil samples from different sources. If the difference between the properties of the soil samples from a potential source and those from other source types is insignificant, then it may be concluded that those properties are inadequate to effectively identify the source type. The more insignificant properties show in the comparison results, the less difference between the compared sources is determined. Therefore, it is necessary to reconsider whether this particular source can be used as an individual potential source or whether all samples from this source are representative. After the potential source types were determined by the method described above, a Kruskal–Wallis H test and a DFA were used to search for the optimum composite fingerprint. The re-examination of the preliminarily determined potential sources prior to the application of the sediment source discrimination process is expected to minimize the influence on the results that might occur if an

arbitrary determination of potential sources with insufficient prior information were adopted.

3.4. Apportionment of sediment sources

A mixing model was used to quantify the percentage of the contributions of the potential sediment sources to each sediment sample. The mixing model function is as follows (Walling, 2005):

$$R = \sum_{i=1}^n \{ (C_{di} - \sum_{s=1}^m C_{si} P_s) / C_{di} \}^2 \quad (1)$$

where R represents the sum of the squares of the residuals, C_{di} represents the concentration of the i -th fingerprint property in the deposited sediment sample (mg kg^{-1}), P_s represents the proportion of the contribution of the s -th sediment source s to the sediment sample (%), C_{si} represents the mean concentration of fingerprint property i in sediment source s (mg kg^{-1}), m represents the number of sediment sources, and n represents the number of fingerprint properties. The boundary conditions applied to the model are that the relative contributions, P_s , of all potential sediment sources are non-negative and that the sum of the P_s of all of the potential sediment sources is 1. The proportion of the contribution of each potential sediment source can be obtained when the sum of the squares of the relative errors from the algorithm is the minimum. The goodness of fit (GOF) between the results from the mixing model and the observed values of the samples can be assessed using the following model (Motha et al., 2003):

$$GOF = 1 - \{\sum_{i=1}^n (|C_{di} - \sum_{s=1}^m C_{si}P_s|/C_{di})\}/n \quad (2)$$

In general, results from a mixing model are acceptable if *GOF* is greater than 0.8.

4. Results and discussion

4.1. Selection of potential sources

The data validation step of the analysis showed that there were outliers in the data of eight soil samples: three from the cultivated lands, three from the woodlands and two from the mines and the road. These data were removed. Outliers were also present in the data of three depositional sediment samples, including the Na₂O content of sample #15, the Na₂O, Al₂O₃, SiO₂, As and C contents of sample #16 and the Zn and N contents of sample #17, which could not be used as effective fingerprint properties and were thus removed. Of the 23 properties that passed the test, the differences in the Na₂O, P, N and C contents between different potential source types were relatively large (Table 2). To illustrate the difference in the soil properties between different potential sources, two of the potential sources were paired, and each of the properties of the soil samples that were collected from the two sources was subjected to a test of significance of the means. If the concomitant probability, *P*, was less than 0.05, we assumed a significant difference in that property between the two source types. Table 3 lists the results of these significance tests for four pairs of potential sources. We found that the samples that were collected from the mines and the road had the fewest fingerprint properties that were significantly different from those that were collected from the other source types, followed by the samples that were collected from the channels and the subsurface soil samples. A further investigation of the environment surrounding the sampling points in the study area indicates that these results were caused by the following

factors: (1) There were large areas of woodlands near the mines and the road, and some of the woodlands were damaged by mining. The soil and rocks that were used to construct the road also came from some of the degraded woodlands and exposed mountain sites. Therefore, the soils from these sites might be similar to or might have originated from the same source as the soil from the woodlands. (2) The road was constructed on cultivated land, and several new ditches were created due to the filling or excavation process. As a result, the subgrade soil might have mixed with the soils from the cultivated lands and ditches. (3) The river and ditches were adjacent to the cultivated lands. There were no clear boundaries between many collapsed sites on the river banks and the adjacent cultivated lands. The ditches in the cultivated lands were significantly affected by the plowing of the soil in the cultivated lands. (4) The gullies that were formed by rainwater between the woodlands were originally relatively shallow. Thus, the exposed subsurface soil on the sides of these gullies might have mixed with the eroded soil in the adjacent woodlands.

Based on these possible reasons and the distribution of the sampling points, several sampling point types were adjusted. The following adjustments were made. Samples B1, B10–B13 and B18–B19, which were originally from the ditches and the subsurface, were adjusted to be in the group of samples from the cultivated lands, and samples B2, B4, B7, B9, B14–B15 and B17 were adjusted to be in the group of samples from the woodlands. Samples B3, B6 and B20 were adjusted to be in the group of samples from the mines and the road, and samples M4, M6–M8 and M10, which were originally from the mines and the road, were adjusted to be in the group of samples from the woodlands. After the adjustments, the potential sediment sources were classified into three types: cultivated land, woodland and land used for mining and the road. The differences in the soil properties between the different types then increased significantly (Table 3).

Table 2

Tracer properties in potential sediment source materials and the deposited sediments. The units are Bq kg⁻¹ for ¹³⁷Cs and mg kg⁻¹ for the other tracer properties.

Property	Cultivated land soil		Woodland soil		Mine & road soil		Channel bank soil		Deposited sediment	
	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev
Na ₂ O	9955.83	2046.80	7720.24	3249.33	4248.15	1717.59	8745.63	3101.13	7413.33	1043.25
MgO	7950.00	849.39	9982.35	3036.91	8261.54	4339.27	7625.00	1235.85	10458.82	3139.88
Al ₂ O ₃	102394.4 4	8226.39	127741.1 8	24648.5 1	127369.2 3	37951.2 5	108137.5 0	10253.0 6	128375.0 0	16768.8 4
SiO ₂	753905.5 6	21129.1 4	697611.7 6	43672.2 1	728307.6 9	85014.1 1	752962.5 0	24481.8 5	711266.6 7	25560.2 8
P	907.40	491.83	472.52	165.21	280.63	81.17	468.84	181.69	1301.59	770.25
K ₂ O	16344.44	1577.87	20176.47	4109.98	17284.62	8771.06	17306.25	3105.36	18341.47	2485.35
CaO	12566.67	8357.17	11370.59	7806.79	9384.62	7080.00	10043.75	7670.89	13766.67	6247.13
Cr	59.90	4.55	69.61	15.08	70.42	21.28	59.73	7.18	66.28	8.52
Mn	573.93	319.04	720.15	321.58	484.56	357.14	701.83	310.64	765.73	200.22
TFe ₂ O ₃	37400.00	4898.98	47152.94	11279.1 9	44615.38	20536.6 3	40762.50	6575.09	47664.71	6896.28
Co	13.00	1.90	16.02	3.85	14.62	6.27	13.88	2.65	15.91	2.42
Ni	22.10	2.17	27.69	7.67	26.68	13.54	23.06	4.42	27.68	3.85
Cu	25.84	2.69	26.77	4.91	23.72	9.12	23.88	4.16	30.94	4.45
Zn	66.40	13.65	75.11	11.13	58.01	25.37	56.95	12.55	81.71	16.31
Pb	28.28	2.87	31.81	6.62	25.57	4.69	26.29	3.63	28.48	3.02
Sr	90.31	7.77	84.46	19.70	84.25	23.97	88.58	19.93	94.93	8.35
Cd	0.18	0.06	0.23	0.14	0.09	0.03	0.14	0.05	0.18	0.05
As	7.78	2.08	10.54	1.89	8.89	4.19	9.35	1.93	11.19	5.08
Sb	0.87	0.26	0.83	0.22	0.83	0.29	0.69	0.12	0.96	0.29
Sn	4.48	1.70	3.23	0.58	3.68	0.73	3.77	1.53	4.18	0.47
N	1326.70	252.50	1704.22	1050.09	607.09	133.64	1025.72	371.57	1183.56	393.54
C	15616.67	3628.36	22435.29	17383.5 0	5161.54	2475.73	10850.00	5361.47	12039.63	3738.93
¹³⁷ Cs	1.23	1.07	1.74	2.54	0.47	0.79	1.00	0.78	1.04	0.22

Table 3

Mean test of the fingerprint property datasets for various source groups.

Tracer properties	Before adjustment						After adjustment		
	C&B	C&W	C&M	W&B	M&B	W&M	C&W	C&M	W&M
Na ₂ O	0.127	0.020	0.000	0.434	0.000	0.002	0.000	0.000	0.046
MgO	0.357	0.010	0.767	0.005	0.566	0.211	0.001	0.004	0.000
Al ₂ O ₃	0.081	0.000	0.011	0.004	0.052	0.974	0.000	0.574	0.048
SiO ₂	0.920	0.000	0.227	0.000	0.259	0.208	0.000	0.116	0.000
P	0.001	0.001	0.000	0.889	0.002	0.001	0.001	0.001	0.001
K ₂ O	0.299	0.001	0.658	0.022	0.971	0.239	0.002	0.401	0.035
CaO	0.371	0.665	0.275	0.640	0.782	0.479	0.675	0.043	0.016
Cr	0.962	0.013	0.050	0.021	0.063	0.904	0.000	0.704	0.010
Mn	0.120	0.186	0.470	0.599	0.064	0.068	0.078	0.094	0.010
TFe ₂ O ₃	0.067	0.002	0.160	0.062	0.505	0.669	0.000	0.478	0.002
Co	0.162	0.006	0.309	0.115	0.785	0.456	0.000	0.224	0.002

Ni	0.339	0.005	0.167	0.044	0.328	0.797	0.000	0.348	0.003
Cu	0.080	0.488	0.358	0.059	0.994	0.249	0.087	0.004	0.001
Zn	0.033	0.047	0.244	0.000	0.848	0.019	0.006	0.024	0.000
Pb	0.069	0.051	0.056	0.004	0.654	0.007	0.088	0.000	0.001
Sr	0.637	0.251	0.322	0.607	0.644	0.979	0.087	0.203	0.888
Cd	0.021	0.155	0.000	0.008	0.002	0.001	0.331	0.000	0.002
As	0.018	0.000	0.335	0.112	0.618	0.158	0.000	0.043	0.000
Sb	0.013	0.626	0.660	0.027	0.088	0.967	0.821	0.392	0.232
Sn	0.144	0.007	0.124	0.291	0.956	0.066	0.007	0.067	0.923
N	0.004	0.148	0.000	0.013	0.002	0.001	0.784	0.000	0.013
C	0.002	0.113	0.000	0.011	0.003	0.001	0.617	0.000	0.018
¹³⁷ Cs	0.358	0.445	0.038	0.223	0.122	0.094	0.957	0.043	0.244
Num.	7	13	8	12	5	7	13	12	19

C - Cultivated land soil, W - Woodland soil, M - Mine and road soil, B - Channel bank soil, Num. - Numbers of properties for statistically significant at $p < 0.05$

4.2. Discrimination of sediment sources

Based on the three post-adjustment potential source types, 23 soil properties were subjected to the Kruskal–Wallis H test, and 19 elements were selected as fingerprint properties (Table 4). Based on the DFA, a composite fingerprint comprising four properties (As, Na₂O, P and Cd) was selected. This composite fingerprint had a discriminatory efficiency of 89.2%.

To further explain the impact of the number of potential sediment sources and the size of the difference between different sources on the Kruskal–Wallis H test and the selection of the optimum composite fingerprint by DFA, optimum composite fingerprints were selected and compared based on different combinations of the samples from the four pre-adjustment potential sources and from the three pre-adjustment and post-adjustment potential sources (Table 5). The composite fingerprint selected using the original scheme involving four potential sources had a discriminatory efficiency of 64.6%, whereas the scheme involving three potential sources (prior to the sampling point adjustment) had a much higher discriminatory efficiency. The discriminatory efficiency was up to 87.5% with the composite fingerprint selected using the scheme involving the cultivated lands, the woodlands and the mines and the road.

Table 4
Results of the Kruskal–Wallis H test for datasets of source type fingerprint properties.

Property	H -value	p -value	Property	H -value	p -value
Na ₂ O	23.74	0.000	Cu	11.98	0.003
MgO	17.26	0.000	Zn	18.53	0.000
Al ₂ O ₃	13.99	0.001	Pb	14.36	0.001
SiO ₂	22.33	0.000	Sr	4.06	0.132*
P	27.07	0.000	Cd	22.09	0.000
K ₂ O	14.53	0.001	As	31.54	0.000
CaO	7.16	0.028	Sb	3.10	0.212*
Cr	16.01	0.000	Sn	4.51	0.105*
Mn	9.20	0.010	N	21.15	0.000
TFe ₂ O ₃	19.18	0.000	C	20.43	0.000
Co	16.26	0.000	¹³⁷ CS	5.50	0.064*
Ni	19.56	0.000			

*= not statistically significant at $P < 0.05$

Table 5
Optimum composite fingerprints and the discriminatory efficiency for different potential source combinations.

Potential sediment sources	Properties passed Kruskal–Wallis H test	Optimum composite fingerprint	% Discriminatory efficiency
C, W, M and B	Na ₂ O, Al ₂ O ₃ , SiO ₂ , P, K ₂ O, Zn, Pb, Cd, As, Sb, N and C	Na ₂ O, Al ₂ O ₃ , P and Cd	64.6
W, M and B	Na ₂ O, Al ₂ O ₃ , SiO ₂ , P, Zn, Pb, Cd, Sb, N and C	Na ₂ O, Al ₂ O ₃ and Cd	74.5
C, M and B	Na ₂ O, P, Cd, Sb, N and C	Na ₂ O and P	72.9
C, W and B	Al ₂ O ₃ , SiO ₂ , P, K ₂ O, TFe ₂ O ₃ , Co, Zn, Pb, As, Sb, N and C	SiO ₂ , P, As and N	82.7
C, W and M *	Na ₂ O, Al ₂ O ₃ , SiO ₂ , P, K ₂ O, Zn, Cd, As, Sn, N and C	Na ₂ O, Al ₂ O ₃ , P, Sn and N	87.5
C, W and M **	Na ₂ O, Mg, Al ₂ O ₃ , SiO ₂ , P, K ₂ O, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb, Cd, As, N and C	As, Na ₂ O, P and Cd	89.2

C - Cultivated land soil, W – Woodland soil, M - Mine and road soil, B - Channel bank soil, * Before adjustment, ** After adjustment

Table 5 shows that the optimum composite fingerprint, selected based on the sediment sources and classified using the adjusted sampling points, had the highest discriminatory efficiency (89.2%). However, for individual sediment samples, an optimum composite fingerprint could be used for discrimination only when there were no outliers in the fingerprint properties that were contained in this optimum composite fingerprint. Based on the results of the sediment data validation, outliers were present in the data of the Na₂O content of sample #15 and the Na₂O and As contents of sample #16; thus, these two properties could not be used as effective fingerprint properties. Therefore, after removing these outlier data, it was necessary to conduct another stepwise discriminant analysis to obtain another composite fingerprint. A suboptimum composite fingerprint could also be used in source discrimination, provided that it produces a sufficiently

high discriminatory efficiency. Table 6 lists the results of the Kruskal–Wallis H tests and the stepwise cumulative discriminatory efficiencies of the DFA of different sediment samples with and without the outliers, respectively. New composite fingerprints were obtained after the outliers in the data of samples #15 and #16 were removed. However, the cumulative discriminatory efficiency decreased by approximately 10% in both cases. There was no change in the composite fingerprint for sample #17 because the outliers Zn and N did not belong to the component of the original composite fingerprint.

Table 6
The optimum composite fingerprints for sediment samples those with or without outliers in tracer properties.

Sample	Outlier	Property passed Kruskal-Wallis H test	Step	Fingerprint Property	Wilks' lambda	Cumulative% source type samples classified correctly
#1-#14	–	Na ₂ O, MgO, Al ₂ O ₃ , SiO ₂ , P, K ₂ O, CaO, Cr, Mn, TFe ₂ O ₃ , Co, Ni, Cu, Zn, Pb, Cd, As, N and C	1	As	0.521	60.0
			2	Na ₂ O	0.337	80.0
			3	P	0.236	83.1
			4	Cd	0.207	89.2
#15	Na ₂ O	MgO, Al ₂ O ₃ , SiO ₂ , P, K ₂ O, CaO, Cr, Mn, TFe ₂ O ₃ , Co, Ni, Cu, Zn, Pb, Cd, As, N and C	1	MgO	0.521	66.2
			2	P	0.361	70.8
			3	As	0.304	70.8
			4	N	0.261	80.0
#16	Na ₂ O, Al ₂ O ₃ , SiO ₂ , As, C	MgO, P, K ₂ O, CaO, Cr, Mn, TFe ₂ O ₃ , Co, Ni, Cu, Zn, Pb, Cd and N	1	MgO	0.697	66.2
			2	P	0.495	70.8
			3	TFe ₂ O ₃	0.362	70.8
			4	Cd	0.313	81.5
#17	Zn, N	Na ₂ O, MgO, Al ₂ O ₃ , SiO ₂ , P, K ₂ O, CaO, Cr, Mn, TFe ₂ O ₃ , Co, Ni, Cu, Pb, Cd, As and C	1	As	0.521	60.0
			2	Na ₂ O	0.337	80.0
			3	P	0.236	83.1
			4	Cd	0.207	89.2

4.3. Apportionment of sediment sources

Fig. 4 shows the results of the sources apportionment of all 17 sediment samples using the multivariate mixing model that was based on different composite fingerprints (Table 6). The GOFs of samples #1–#4, #11 and #15–#17 were less than 0.8; thus, these samples were removed. The contributions of the cultivated lands to the sediment output ranged from 39.9% to 87.8%, with a mean of 76.6%, which indicates that the cultivated lands were the main sediment source; this finding could be explained by the relationship between the locations of the river and the cultivated

lands, as well as the management practices in the cultivated lands. The cultivated lands in the study area are generally located along the river. In particular, the lands near the river banks are low-lying; as a result, soil erosion can occur easily in these lands, which have been disturbed by long-term farming. However, the controls on sediment loss in this area are mainly focused on the mines in the upper reaches; there are few measures for managing the farming of the cultivated lands. The mean contribution from the woodlands was 21.7%, and the contribution of the woodlands to several samples was less than 0.1%. Although the woodlands cover a relatively large area and most of them are on slopes, the sediment loss in the woodlands is insignificant due to relatively good surface cover and less disturbance by human activity. In addition, most of the woodlands are located relatively far from the river, so a large amount of sediment in the runoff is intercepted during the mobilization process. However, the contribution of the woodlands to several individual samples exceeded 40%, which might be because some woodlands that were surrounded by residential areas were close to the river, and man-made cement roads and drainage ditches allowed the runoff on the slopes to flow directly into the nearby river. The overall contribution from the lands that were used for mining and the road under construction was relatively small. The reason for this relatively minor overall contribution might be that the mines were only located in the upper reaches and were far from the river channels in the lower reaches; the sediment that was generated in the mines had a relatively large particle size and thus was easily intercepted in the mountains and deposited in the small streams and creeks. As we explained before, soil erosion control in mine areas have been receiving more attentions in recent years. The road construction might have a pronounced impact on the sediment load. However, such impact existed only in a particular period, and the use of previously deposited sediment would not capture most part of the

sediment derived from the road in the short term. As the data also showed that the contribution of the mine and road to several samples reached approximately 25%, perhaps because these sediment samples were significantly affected by the recent road construction.

Fig. 4. Final results of the sediment source contribution for the individual deposited sediment sample and the whole catchment.

5. Conclusions

This study used a composite fingerprinting technique to apportion the sediment sources in a small catchment with intensive human activities. The sources were discriminated and major sediment contributions were apportioned to cultivated lands. The woodlands together with the mine and road contributed less than a quarter of the total sediment, and the role of mine and road was even almost insignificant. In the present study, the short-term impact from road construction was not emphasized, and the proportion of sediment from this source could be dependent on the timing and locations of sampling of source material and sediment, as stated by [Franz et al. \(2014\)](#). The proportions of sediment sources would be different if suspended but not relict sediment samples had been obtained, especially in the period of road construction. It implies that the choice of suspended or relict sediment sampling is crucial for source apportionment results and is dependent on the specific aims of fingerprinting studies.

Another objective of this study was to explore the impact of the selection of potential sources

on the results of source discrimination. By comparing the differences in the soil properties between potential sources, we found that a change in the selection of potential sources affected the selection of the fingerprint properties and the cumulative discriminatory efficiency of the composite fingerprints. The application of fingerprinting techniques assumes that the potential sediment sources are known, from which the direct corresponding relationship between the sediment output and the sources is determined. We believe that the real sources of the exporting sediment at the catchment outlet may be rationally determined if the soil erosion locations and the sediment mobilization process are fully understood. However, the sediment loss and mobilization within a catchment is often much more complex. Accurate information on soil erosion and management practices in a catchment cannot be fully obtained from field surveys. The lack of information regarding sediment mobilization processes may result in the inaccurate identification of potential sources because the sediment from some potential sources may rarely reach the outlet of the catchment. The landscape of the study area is highly fragmented, and some of the samples from one source type might include sediment information from different sources. However, the composite fingerprints that were selected before and after several samples were adjusted still had a discriminatory efficiency of 87.5–89.2%. Even so, further studies are necessary to investigate errors that may be caused by the selection of potential source types and the locations of the sampling points. In this study, optimum composite fingerprints were discussed both for different potential sources and for different sediment samples. It was found that re-obtained composite fingerprints for sediment samples with outliers in properties also could be used and produce acceptable source discrimination efficiency. The necessary and rationality of this procedure need to be discussed further. Future research on fingerprinting techniques should also address the

corrections to sediment sources and sediment material contents, errors caused by the possible transformation of matter during the sediment mobilization process, and other uncertainty factors.

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