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Research article

Use of sediment source fingerprinting to assess the role of subsurface erosion in the supply of fine sediment in a degraded catchment in the Eastern Cape, South Africa

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ABSTRACT

Sediment source fingerprinting has been successfully deployed to provide information on the surface and subsurface sources of sediment in many catchments around the world. However, there is still scope to re-examine some of the major assumptions of the technique with reference to the number of fingerprint properties used in the model, the number of model iterations and the potential uncertainties of using more than one sediment core collected from the same floodplain sink. We investigated the role of subsurface erosion in the supply of fine sediment to two sediment cores collected from a floodplain in a small degraded catchment in the Eastern Cape, South Africa. The results showed that increasing the number of individual fingerprint properties in the composite signature did not improve the model goodness-of-fit. This is still a much debated issue in sediment source fingerprinting. To test the goodness-of-fit further, the number of model repeat iterations was increased from 5000 to 30,000. However, this did not reduce uncertainty ranges in modelled source proportions nor improve the model goodness-of-fit. The estimated sediment source contributions were not consistent with the available published data on erosion processes in the study catchment. The temporal pattern of sediment source contributions predicted for the two sediment cores was very different despite the cores being collected in close proximity from the same floodplain. This highlights some of the potential limitations associated with using floodplain cores to reconstruct catchment erosion processes and associated sediment source contributions. For the source tracing approach in general, the findings here suggest the need for further investigations into uncertainties related to the number of fingerprint properties included in un-mixing models. The findings support the current widespread use of ≤5000 model repeat iterations for estimating the key sources of sediment samples.

1. Introduction

Although some research in a range of environments globally suggests that gully erosion represents an important sediment source (Wallbrink et al., 1996; Wasson et al., 1998; Wilkinson et al., 2013), it is still a much debated issue (Govers and Poesen, 1988). For example, Wallbrink et al. (1996) found that 90% of the suspended sediment load in the lower Murrumbidgee River, Australia, was derived from subsurface sources and gullies in particular. Wasson et al. (1998) noted that much of the sediment in Australian rivers is derived from gully sources and estimated that the presence of gullies increased sediment emissions by a factor of 10. Poesen et al. (2002) reported that gully erosion represents an important sediment source in dryland environments contributing, on average, 50%–80% of overall sediment production. The effect of gully erosion on sediment generation and catchment scale sediment delivery is,

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however, dependent on the ability of the gullies to route sediment efficiently into fluvial systems (Foster et al., 2012; Fuller and Marden, 2010). This is best described by looking at the degree of coupling (Harvey, 2001) or connectivity (Fryirs et al., 2007), between sediment producing areas and channel systems. Clearly, the role of gully erosion as a catchment sediment source may not be generalized and needs a case by case analysis.

Gully erosion is a major feature of Eastern Cape landscapes in South Africa (Boardman et al., 2015; Kakembo et al., 2009; Keay-Bright and Boardman, 2009; Le Roux and Sumner, 2011). Where the problem is most serious, large expanses of land are heavily dissected forming extensive so-called 'badlands'. Most of these are deeply incised into colluvial hill slopes and weathered shale bedrock (Boardman and Foster, 2008; Boardman et al., 2015; Kakembo et al., 2009). Studies have found that gullies differ in size in response to different factors. For example, Dollar and Rowntree (1995) measured gullies up to 22 m wide and 13 m deep in cultivated fields in the Bell River catchment. Hanvey et al. (1991) described gullies 20 m wide and 16 m deep on a fossil dune complex in the east coast of South Africa. Gullies eroding on bedrock in the arid landscapes of the Karoo region of the Eastern Cape in South Africa, have been known to reach depths of 5 m and widths of over 20 m and even deeper in valley bottoms (Boardman and Foster, 2008). Both short and medium term rates of gully erosion have been estimated in the Eastern Cape province. For example, Boardman et al. (2010; 2015) reported gully erosion rates of between 32.3 t ha^{-1} y^{-1} and 136 t ha^{-1} y^{-1} in the Karoo. Other studies have estimated gully erosion rates in terms of changes in spatial extent on the basis of aerial photographs. Dollar and Rowntree (1995) noted an increase in the total gully length of 69% between 1952 and 1975 in the Bell River catchment, Eastern Cape and by a further 169% up to 1991. Vetter (2007) noted a substantial increase in erosion from 1950 to 1995 in the Sterkspruit District with more than 50% of the surface area affected by sheet, rill or gully erosion by 1995.

Investigations have reached varied conclusions in relation to the linkages between gully erosion and high sediment yields in catchments of the Eastern Cape province. Foster et al. (2007, 2012) reported that rather than being a major source of contemporary sediment, gullies only provide connectivity between the eroding upper section and the river systems in some of the catchments in the Karoo region. This was consistent with Keay-Bright and Boardman (2006) who reported that gully and badland expansion in the same region has slowed down, stabilized and even decreased. However, Rowntree and Foster (2012) reported that regardless of the above observation, some gullies continue to erode at high rates and continue acting as 'partial areas' for sediment contribution to river systems even when the badland area is relatively reduced in size.

It is known that sheet and rill (i.e. top soil source) and gully and bank erosion (i.e. subsoil sources) are the major sources of the fine-grained bed and suspended load in many river systems (Wethered et al., 2015). However, the contributions of topsoil and subsoil vary from catchment to catchment undermining generalisations. Knowledge of the relative importance of surface and subsurface sources of sediment helps identify the main erosion process mobilizing sediment and thus provides assistance in the design and targeting of rehabilitation measures to reduce downstream sediment loads and associated off-site impacts. This information may also be important to understand catchment sediment delivery processes and the degree of lateral and longitudinal (dis)connectivity of the catchment sediment cascade (Fryirs et al., 2007; Koiter et al., 2013a,b; Wethered et al., 2015). Given the uncertainty surrounding the role of gullies as a sediment source in South African catchments, this study explores the issue further by focussing on a catchment located in the Ngqushwa Local Municipality, Eastern Cape, South Africa, where severe soil erosion resulting from land use change has led to landscape dysfunction (Kakembo et al., 2009) and excessive sedimentation in the local stream channels (Kakembo and Rowntree, 2003).

Quantitative sediment source fingerprinting has demonstrated potential to help reconstruct historical sediment source dynamics in terms of surface and subsurface contributions on the basis of the sediment signatures preserved in floodplain sediment cores (Collins et al., 1997b, 2010a; Owens et al., 1999). Different types of mixing models or algorithms have been used to estimate the relative contributions of potential sediment sources (see Collins et al., 1997b; Fox and Papanicolaou, 2008; Nosrati et al., 2014). The type and structure of statistical mixing models can significantly affect the estimates of source contributions (Haddadchi et al., 2014; Smith et al., 2015; Cooper et al., 2014), hence they constitute a significant research issue for sediment fingerprinting studies. Besides the type of models, recent research has shown that there are many other factors that may influence the consistency or accuracy of the estimates of source contributions obtained from sediment source fingerprinting models and thus needing further research. These include the use of correction factors and weightings (Smith and Blake, 2014; Laceby and Olley, 2015; Laceby et al., 2015; Collins et al., 2010b), the issue of conservativeness of the fingerprints used (Laceby and Olley, 2015; Pulley et al., 2015), source group classification (Pulley et al., 2016), the number and type of tracers included in the mixing model (Martinez-Carreras et al., 2008; Koiter et al., 2013a,b; Sherriff et al., 2015; Smith and Blake, 2014; Pulley et al., 2015) and the use of either local and global optimization methods (Haddadchi et al., 2013; Collins et al., 2010c; Collins *et al.*, 2012). However other issues that have the potential to influence the outputs from mixing models require examination, including the number of repeat iterations and the use of different sectioned sediment cores in the case of floodplains.

In the context of the above background, this paper specifically aimed to: 1) examine the potential impact of numbers of properties in optimised signatures, number of model iterations and the use of replicate depositional sink sampling on the modelled sediment source estimates generated, and; 2) use sediment source fingerprinting to assess the extent to which the supply of fine-grained sediment in the study catchment is dominated by gully and stream bank erosion.

2. The study area

The study catchment (90 km^2) is located south of the town of Peddie, Eastern Cape province, South Africa (Fig. 1). Topography is generally undulating, rising from sea level on the coast to about 365 m above sea level in the north. Slopes rise steeply (>10°) alongside major stream channels. The catchment is dominated by shale and arenite of the Ecca Group and Karoo Supergroup (Permian-Triassic). The Ecca Group shale weathers to form highly erodible soils (Mills and Cowling, 2006). Greyish brown shallow litholic soils of the Mispah and Glenrosa Form (Entisols and Inceptisols in Soil Taxonomy) which are dominant in the catchment, are typically low in organic matter content and sometimes with high sodium content (Kakembo and Rowntree, 2003). Severe soil erosion which ranges from sheet and inter-rill erosion in grazing lands to gully erosion in abandoned cultivated lands has been well documented in the study catchment (see Kakembo, 2009; Kakembo and Rowntree, 2003; Kakembo et al., 2009; Manjoro et al., 2012a). Gully erosion is mostly predominant in lower slope positions.

The average annual rainfall is 491 mm and is bi-modally distributed, with peaks in October or November and March or

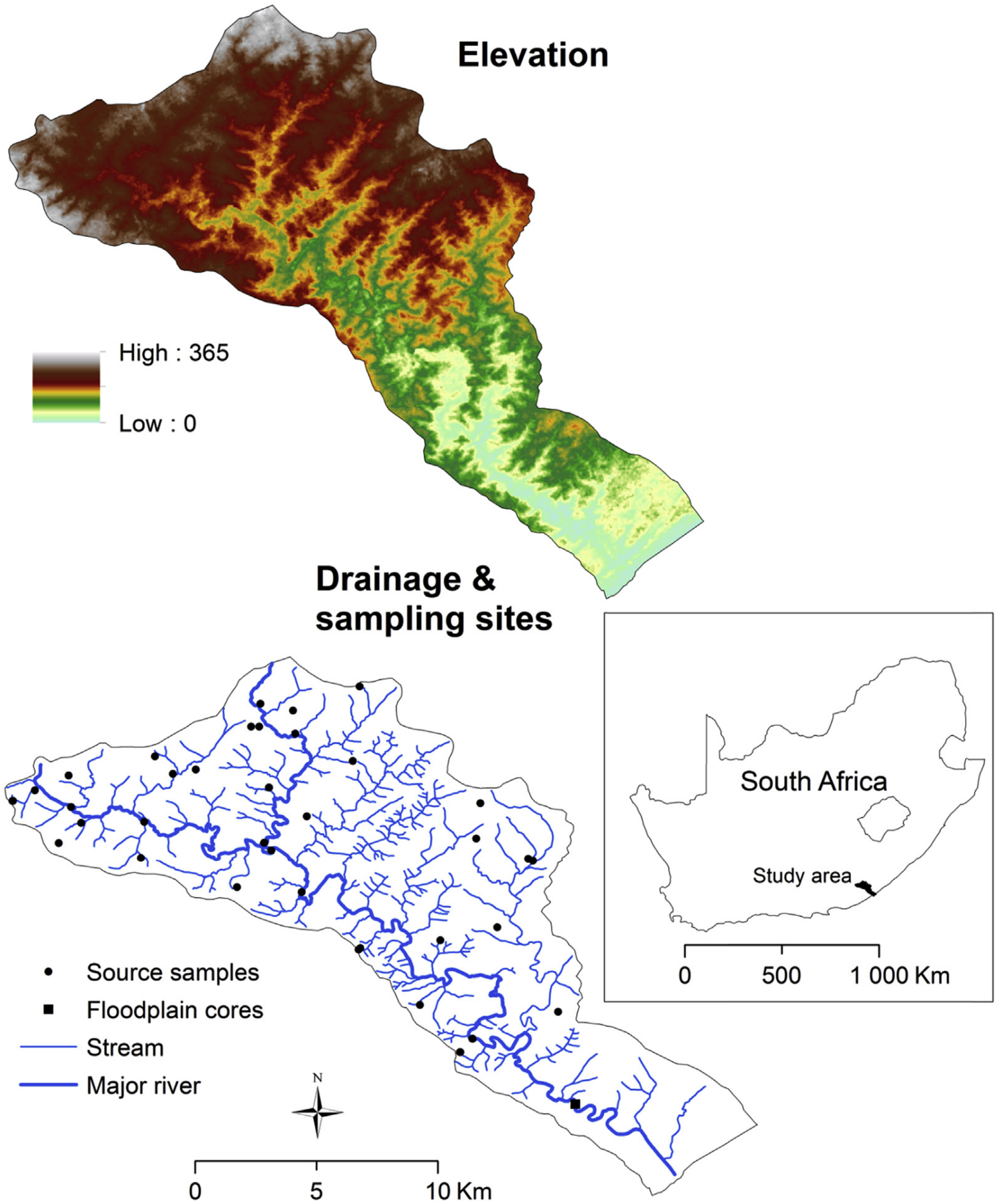

Fig. 1. Study area.

April. Vegetation is heavily modified by human activity and only a mosaic of the degraded thicket vegetation exists in patches within the study catchment and along some riparian and coastal corridors. The main land cover categories are grassland, mostly used for extensive grazing and, areas of woody shrub vegetation cover, most of which is *Pteronia Incana* found mainly in abandoned cultivated lands and some grazing lands. Some cultivation (mainly pine apples and maize) takes place in the north-east and north-west of the study catchment.

3. Methodology

Sediment source fingerprinting is increasingly being used to quantify the contribution of different sediment sources (different land uses, topsoil/subsoil, geological sub-areas, sub-catchments), evaluate catchment soil erosion dynamics and develop management plans to tackle sediment-related problems including reservoir siltation and sediment-bound pollutant transfers (Rowan et al., 2012; Walling et al., 2008). The technique relies upon the link between sediment properties and those of its principal sources (Foster and Lees, 2000; Walling, 2005). Sediment source fingerprinting has been used successfully to identify and apportion the relative importance of topsoil and subsoil in different environmental settings (Evrard et al., 2011; Wallbrink and Olley, 2004; Wethered et al., 2015; Wilkinson et al., 2013). On the basis of the previous reported success in using sediment fingerprinting to apportion topsoil and subsoil sediment sources, this study investigated the extent to which subsoil is the main sediment source in the study catchment. Sediment source fingerprinting was used to discriminate and apportion the surface and subsurface sources of fine sediment deposited in a major floodplain in the study catchment and to help infer the main erosion processes mobilizing sediment in the catchment for the purpose of informing targeted management.

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3.1. Sampling of potential sediment sources and the floodplain sink

Sampling of the potential sediment sources was stratified to generate information on the major observed processes mobilizing fine sediment in the study catchment; that is, whether the processes are surface (sheet and inter-rill erosion) or subsurface (rill or gully or river bank erosion). Topsoil samples were collected regardless of land use or geology on the basis of visual evidence of erosion. For sediment source fingerprinting purposes, researchers have used various representative depths for surface soil samples ranging from the top 0.5 cm (Minella et al., 2008) or 2–3 cm (Laceby and Olley, 2015; Wethered et al., 2015) and up to 5 cm (Devereux et al., 2010). In this study, all topsoil samples ($n = 17$) were collected from the upper 3 cm of the soils. This sampling depth ensured that only surface material likely to be mobilized by surface processes was sampled (cf. Collins et al., 1997; Walling, 2005). Roddy (2010) reported about various sediment source material sampling strategies ranging from randomised to targeted approaches. Targeted sampling of actively eroding sites was the main strategy used. This sampling strategy was adopted to ensure that only those eroding areas with clear connectivity to river channel systems were sampled. Manjoro et al. (2012b) noted cases of slope-channel disconnectivity in the upper parts of the study catchment. This is important since previous research has shown that assumptions about source-channel connectivity can have considerable impact on uncertainties associated with sediment source fingerprinting (Koiter et al., 2013a,b; Martínez-Carreras et al., 2008). Four to five topsoil samples (individual sample size typically $\geq$ 500 g) were collected in the vicinity of each sampling point covering a radius of about 30 m and put in separate sample bags. After oven drying (40 °C) back in the laboratory, an equal mass (250 g) from each of the individual samples was combined and homogenized to make one composite sample for each catchment sampling point ($n = 33$). Compositing samples for subsequent laboratory analyses helps make the source material samples representative of the potential spatial variability within the individual sources (Minella et al., 2008; Wethered et al., 2015), while reducing laboratory analysis costs. Subsoil samples ($n = 16$) were obtained directly from actively eroding gully sidewalls, head cuts and exposed river channel banks and comprised material from the full vertical extent of the exposures by scraping soil/regolith from erosion scars (Collins et al., 2010a). Global positioning system (GPS) coordinates of all sampling points were recorded and plotted on a map (Fig. 1).

To provide sediment for the source tracing exercise, two sediment cores were collected 35 m apart in a floodplain of the Mgwalana River, the main stream of the study catchment (Fig. 1). The selected sampling sites were located in the mid-section of the inside of a meander loop and were informed by visual observations and reports on inundation patterns during overbank events. The first site was located 5 m from the river bank and Site 2 was located 35 m away. The floodplain cores were retrieved using a manually operated Eijkelkamp corer with a plastic lined chamber of 5 cm diameter and 30 cm depth. At Site 1, it was only possible to collect the sediment core up to 103 cm depth, whereas at Site 2, the core was collected up to a depth of 213 cm. The botton part of this core was not used as it consisted mostly of coarse sediment. The collection of two floodplain cores provided an opportunity to examine uncertainties in sediment source estimates associated with using two sediment profiles collected from the same floodplain sink.

3.2. Laboratory methods

All source and floodplain core (sectioned at 4 cm depth intervals) sediment samples were manually disaggregated using a mortar and pestle and dry sieved to isolate the fine-grained fraction (<63 μm). It was assumed that this size fraction was representative of fluvial suspended sediment (Walling et al., 2000) transported through most river systems. Sediment source fingerprinting involves measuring sediment properties that are capable of distinguishing different catchment sediment sources (Collins et al., 1996; Olley and Caitcheon, 2000). Mineral-magnetic and geochemical analyses were undertaken on all soil and sediment samples and caesium-137 (^{137}Cs) activity was measured on selected sediment samples for the purpose of dating one of the floodplain sediment cores. Standard mineral-magnetic measurements (Dearing, 1999; Walden, 1999) were undertaken on all samples. These included low (χlf) and high (χhf) frequency magnetic susceptibility, anhesteric remanent magnetisation (ARM), soft isothermal remanent magnetisation (IRM_{-100mT}) and saturation isothermal remanent magnetisation (IRM_{1000mT}) (SIRM). Various other mineral-magnetic parameters were derived from the measurements (e.g. frequency dependent susceptibility (χfd), susceptibility of ARM (χARM and hard isothermal remanent magnetisation (HIRM)). Organic matter content was estimated by loss-on-ignition (LOI) at low temperature (550 °C, 3 h) (Heiri et al., 2001). Inductively coupled plasma mass spectrometry (ICP-MS) was undertaken on all samples following microwave oven-assisted digestion using aqua regia ($HCl:HNO_3$,3:1, v/v) (US EPA, 2007). This yielded concentrations of various rare earth (La, Ce, Eu, Sm, Lu, Tb, Yb), trace (As, Co, Ba, Cr, Cs, Th, Zn, Cd, Mn, Cu, Ni, Pb, Tl, V, Li, B, Sc, Ga, Rb, Sr, Y, Ru, Rh, Pd, Pr, Nd, Gd, Dy, Ho, Er, Tm, Re, Os, Ir, Pt, Au, U) and major (Fe, K, Na, Al, Ca, Mg) elements which were assessed for sediment source tracing purposes.

Mineral-magnetic, geochemical and radionuclide signatures are often controlled by the particle size distribution (He and Walling, 1996; Owens et al., 2000). To enable correction for the potential effects of particle size differences between source and sediment samples on the corresponding signatures, the absolute grain size composition of all samples was determined using a sedigraph (Micromeritics SediGraph III 5120, USA) following sample pretreatment with hydrogen peroxide (H_2O_2) (30% v/v) and boiling at 100 °C on a hotplate to eliminate organic matter (Walling et al., 2000). This was followed by chemical dispersion with sodium hexametaphosphate and 5 min in an ultrasonic bath before analysis. Estimates of specific surface area (SSA; $m^2\ g^{-1}$) for each individual sample were obtained from the particle size measurement software, based on cumulative particle size distributions of the sample and assuming spherical particles (Collins et al., 1998). ^{137}Cs activity was measured by a high-resolution, high purity germanium (HPGe) 'well' detector. Foster et al. (2005) provide details of energy and efficiency calibration methods, and of quality control used for such analysis. Count times were typically 172 000 to 216 000 s, with the counting errors reported to 2σ (i.e. 95% confidence limits).

3.3. Statistical selection of composite fingerprints to discriminate surface and subsurface catchment sediment sources

As a first step, it was necessary to test normality of the fingerprint datasets for each sediment source category (Collins et al., 2012a). This was used as a means of selecting appropriate statistics for estimating the location and scale of the probability density functions (pdfs) used to represent the fingerprint properties of each potential source end member and the target sediment. Lilliefor's Test (Henderson, 2006; Lilliefors, 1969) was used with a null hypothesis that all properties are random and come from a normal distribution. The Lilliefor's test represents an adaptation of the Kolmogorov–Smirnov test and provides a two sided goodness-of-fit procedure in situations where the fully specified null population for each fingerprint property is unknown, thereby requiring the estimation of its parameters using the significance of comparison at p = ≤0.05. During the application of the Lilliefors test, the sample mean and standard deviation were used to represent the corresponding values for the benchmark population against which the measured fingerprint property data were compared. Table 1 shows that the null hypothesis, that the samples came from a normal distribution, was not satisfied in all cases, suggesting some tracers were not normally distributed.

The next step was the tracer mass conservation test (Collins et al., 2013). In situ post-depositional change in sediment properties can be a serious problem for applying sediment source fingerprinting using historical sediment (Collins et al., 1997b; D'Haen et al., 2012; Koiter et al., 2013a,b; Macklin et al., 1994; Pulley et al., 2015a). Thus, it was necessary to assess whether the ranges of values for individual tracers associated with the sediment comprising each floodplain core were within the corresponding range of values measured for the study catchment potential sources. This range test was undertaken using the tracer parameter source end member and sediment medians and a robust scaling

Table 1
The results of the Lilliefors test.

Site 1				Site 2			
Surface		Subsurface		Surface		Subsurface	
Property	p-Value	Property	p-Value	Property	p-Value	Property	p-Value
Li	0.50	Li	0.03[a]	Li	0.50	Li	0.02[a]
B	0.27	B	0.50	B	0.41	B	0.50
Na	0.00[a]	Na	0.00[a]	Na	0.00[a]	Na	0.00[a]
Mg	0.04[a]	Mg	0.25	Mg	0.02[a]	Mg	0.12
Al	0.17	Al	0.14	Al	0.26	Al	0.31
K	0.10	K	0.50	K	0.04[a]	K	0.50
Ca	0.12	Ca	0.50	Ca	0.10	Ca	0.50
Sc	0.50	Sc	0.34	Sc	0.50	Sc	0.40
V	0.50	V	0.20	V	0.50	V	0.16
Cr	0.00[a]	Cr	0.41	Cr	0.00[a]	Cr	0.23
Mn	0.01	Mn	0.47	Mn	0.03	Mn	0.27
Fe	0.29	Fe	0.41	Fe	0.50	Fe	0.23
Co	0.09	Co	0.15	Co	0.04[a]	Co	0.28
Ni	0.00[a]	Ni	0.01[a]	Ni	0.00[a]	Ni	0.00[a]
Cu	0.19	Cu	0.23	Cu	0.20	Cu	0.46
Zn	0.50	Zn	0.27	Zn	0.50	Zn	0.13
Ga	0.20	Ga	0.50	Ga	0.20	Ga	0.50
As	0.00[a]	As	0.34	As	0.00[a]	As	0.18
Rb	0.50	Rb	0.34	Rb	0.37	Rb	0.40
Sr	0.03[a]	Sr	0.19	Sr	0.01[a]	Sr	0.25
Y	0.05	Y	0.50	Y	0.02[a]	Y	0.50
Pd	0.46	Pd	0.25	Ru	0.32	Ru	0.20
Cd	0.14	Cd	0.26	Rh	0.00[a]	Rh	0.00[a]
Cs	0.50	Cs	0.01[a]	Pd	0.42	Pd	0.37
Ba	0.01[a]	Ba	0.12	Cd	0.06	Cd	0.34
La	0.49	La	0.50	Cs	0.50	Cs	0.02[a]
Ce	0.06	Ce	0.50	Ba	0.03[a]	Ba	0.07
Pr	0.50	Pr	0.50	La	0.50	La	0.50
Nd	0.50	Nd	0.50	Ce	0.15	Ce	0.50
Sm	0.19	Sm	0.50	Pr	0.50	Pr	0.50
Eu	0.27	Eu	0.50	Nd	0.50	Nd	0.50
Gd	0.08	Gd	0.31	Sm	0.11	Sm	0.50
Tb	0.00[a]	Tb	0.30	Eu	0.13	Eu	0.41
Dy	0.05	Dy	0.17	Gd	0.03	Gd	0.30
Ho	0.10	Ho	0.16	Tb	0.02[a]	Tb	0.21
Er	0.05	Er	0.35	Dy	0.02[a]	Dy	0.40
Tm	0.07	Tm	0.08	Ho	0.04[a]	Ho	0.20
Yb	0.12	Yb	0.07	Er	0.11	Er	0.25
Lu	0.50	Lu	0.18	Tm	0.03[a]	Tm	0.06
Os	0.00[a]	Os	0.01	Yb	0.20	Yb	0.05
Tl	0.27	Tl	0.00	Lu	0.50	Lu	0.14
Pb	0.28	Pb	0.31	Re	0.04[a]	Re	0.00[a]
Th	0.14	Th	0.29	Os	0.00[a]	Os	0.03[a]
U	0.35	U	0.13	Ir	0.01[a]	Ir	0.15
χ_{lf}	0.12	χ_{lf}	0.16	Pt	0.03	Pt	0.08
χ_{fd}	0.50	χ_{fd}	0.14	Au	0.22	Au	0.40
ARM	0.50	ARM	0.04[a]	Tl	0.34	Tl	0.00[a]
χ_{ARM}	0.50	χ_{ARM}	0.04[a]	Pb	0.20	Pb	0.30
SIRM	0.30	SIRM	0.29	Th	0.32	Th	0.17
				U	0.31	U	0.30
				χ_{lf}	0.22	χ_{lf}	0.23
				χ_{fd}	0.50	χ_{fd}	0.26
				ARM	0.50	ARM	0.09
				χ_{ARM}	0.50	χ_{ARM}	0.09
				SIRM	0.50	SIRM	0.49

[a] Statistically significant at $p < 0.05$ and suggesting a non-normal distribution.

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estimator Qn (Collins et al., 2012a; Rousseeuw and Croux, 1993) with a correction factor for absolute particle size differences between the floodplain sediment core and the source samples. The median and Qn are considered more appropriate where a small number of samples have been collected to characterize potential sources (Stone et al., 2014) and are more robust in estimating tracer property parameter location and scale rather than the conventional parameters (mean and standard deviation) in situations where some properties are not uniformly distributed. The latter are more prone to be influenced by outliers (Collins et al., 2012a, 2010; Tabachnick and Fidell, 1996). Because the Lilliefors test results (Table 1) clearly indicated that not all tracers are normally distributed, robust as opposed to parametric statistics were used in further analyses. The range test was applied separately to each floodplain core section. It is important to note that the range test does not signify the absence of any tracer transformation during mobilisation and delivery to the sediment sink, or as a result of being sequestered within the sink (Collins et al., 2013, 2014). Instead, the range test indicates that tracers are sufficiently conservative to satisfy the basic rules of the sediment apportionment modelling. The potential for tracer non-conservatism was also taken into account explicitly on the basis of the apportionment modelling (see detail below) by including distributions of sediment values for each core section rather than a single value. In doing so, the modelling includes a population of sediment tracer values, which can be assumed to include a mix of concentrations some of which will be more and some less transformed or corrupted from the original concentrations in material delivered to the sediment sink.

Consistent with an existing procedure for selecting statistically robust composite signatures for discriminating potential sediment sources (Collins et al., 2012a), all the conservative fingerprint properties were tested for discriminatory efficiency using three different statistical tests: Kruskal-Wallis H-Test (KW−H), Principal Component Analysis (PCA) and genetic algorithm discriminant function analysis (GA-DFA), to select the composite signature consisting n+1 fingerprints (where n is the number of sources) offering the best discrimination of the potential catchment sediment sources. N+1 represents the minimum number of fingerprints that are needed to satisfy dimensionality. Many previous fingerprinting studies have taken a similar approach in minimising the number of tracers in composite signatures, although not necessarily being driven by n+1 (e.g. Owens et al., 1999; Evrard et al., 2011; Stone et al., 2014). Such reductionist approaches have been driven by a desire to minimise goodness-of-fit errors between source-weighted predicted and measured sediment tracer values. It is important to note, however, that such reductionist approaches can increase the risk of erroneous predictions of source apportionment by increasing susceptibility to corruption of any individual tracer included in the composite signature (Sherriff et al., 2015). Equally, it is important to note that whilst reductionist approaches help improve performance using some goodness-of-fit metrics, tests using artificial and virtual sediment mixtures underscore that larger composite fingerprints typically return more accurate source apportionment (e.g. Martinez-Carreras et al., 2008; Palazón et al., 2015).

The rationale of using three independent statistical procedures to select different sets of composite fingerprints was that it will increase the robustness of the source discrimination and the corresponding mass balance modelling. The KW-H test is a nonparametric version of the classic one-way ANOVA (Gibbons and Chakraborti, 2011; Hollander et al., 2013). It was applied to examine the ability of individual fingerprints to distinguish the catchment source samples. The PCA provides a useful means to analyse variance in tracer datasets and reduces dimensionality by using an orthogonal transformation to convert observations of potentially correlated variables into uncorrelated principal components (Jolliffe, 2002). The Chi-square and p-values associated with each individual property passing the Kruskal−Wallis H-test or the PCA were ranked and the top 3 selected as the optimum composite fingerprints. Each optimum composite fingerprint was run through a step-wise DFA to calculate the percentage of correct source category sample classification accorded by each individual fingerprint property within, and the overall, composite fingerprint. The DFA also accorded the opportunity to calculate a tracer discriminatory weighting (TDW) (Collins et al., 2012a) for the mass balance modelling. The use of this weighting has been shown to help constrain the uncertainty ranges associated with source proportions (Collins et al., 2010b; Wilkinson et al., 2013).

A third set of alternative composite fingerprints was obtained by applying the GA-DFA. This is a discriminant function analysis based fitness function for optimum composite signature selection using genetic algorithm optimization (Jarvis and Goodacre, 2005). The GA-DFA was iterated for each sample group using minimisation of Wilks' lambda, a stepwise selection algorithm (cf. Collins et al., 1997a) and a probability value for parameter entry of 0.05. The GA-DFA was run three times to obtain composite fingerprints consisting of three, four and five individual properties for investigating the potential sensitivity of the source apportionment estimates to the number of tracers constituting each composite signature. Similar to the KW-H and PCA, the percentage correct classification and tracer discriminatory weightings of each composite signature were calculated.

3.4. Sediment source apportionment using a mass balance un-mixing model

Sediment sources apportionment was completed using a numerical mass balance un-mixing model first described by Collins et al. (1997a). The model represents an example of a frequentist approach to the fingerprinting problem. Alternatively, end users can decide to adopt a Bayesian approach (Fox and Papanicolaou, 2008; Massoudieh et al., 2012; Nosrati et al., 2014). This model has been used in many studies (Bottrill et al., 2000; Collins and Walling, 2007; Minella et al., 2008; Walling et al., 2008) and was recently revised by Collins et al. (2010a, 2012a,b). An alternative approach would be to use linear programming (e.g. Yu and Oldfield, 1989). The model operates through minimising the sum of squares of the weighted relative errors in the objective function (f) by changing the relative source proportions:

$$f = \sum_{i=1}^{n} \left\{ \left(Ci - \left(\sum_{s=1}^{m} P_s S_{si} Z_s \right) \right) \Big/ C_i \right\}^2 W_i \tag{1}$$

where: C_i = deviate median concentration of fingerprint property (i) in each floodplain sediment core sample; P_s = the optimised percentage contribution from each sediment source category (s); S_{si} = deviate median concentration of fingerprint property (i) in source category (s); Z = particle size correction factor for source category (s); W_i = tracer discriminatory weighting; n = number of fingerprint properties comprising the optimum composite fingerprint; m = number of sediment source categories. The model solutions were subject to two boundary constraints:

$$0 \le P_s \le 1 \tag{2}$$

$$\sum_{s=1}^{n} P_s = 1 \tag{3}$$

Many mass balance model formulations include particle size content correction factors (Collins et al., 2013; Walling et al., 2008) to take account of the effects of contrasts in grain-size composition between sediment and source material samples on fingerprint property values. Consistent with other related studies (Fox and Papanicolaou, 2008; Walling et al., 1999), the particle size correction factor was calculated using a ratio of the mean specific surface area ($m^2\ g^{-1}$) of the floodplain sediment samples to the corresponding mean values for each potential source. The tracer discriminatory power weighting was based on the relative outputs of each individual fingerprint property comprising the specific composite signature identified using the statistical tests following Collins et al. (2010a). Thus the discriminatory power of the property providing the lowest discrimination (%) of the sediment source samples was assigned a value of 1.0 and the corresponding weightings for the rest of the properties were calculated using the ratio of their discriminatory power to that of the weakest property in any specific composite signature. Given the similarity between the estimated values of the tracer discriminatory weighting, no standardisation of these values was required.

The mass balance model was operated using a Monte Carlo framework. The input values to the model were obtained from fingerprint property distributions generated for both the source and floodplain sediment samples using the median as a robust estimator of location and the scaler Qn (Collins et al., 2012a). The mixing model was repeatedly solved either 5000 or 30 000 times for each composite fingerprint and each individual sediment sample comprising the floodplain cores, to assess whether the number of model iterations affects the source apportionment results and associated goodness-of-fit (GOF). The model iterations were undertaken on the basis of a stratified approach based on Latin Hypercube Sampling (McKay et al., 1979; Collins et al., 2012a). Results generated by each model repeat iteration were retained or discarded on the basis of needing to satisfy an absolute relative mean error of ≤20% (cf. Collins et al., 1997a; Walling and Collins, 2000; Martinez-Carreras et al., 2008). Where this was not satisfied, the criterion was weakened to ensure an output pdf could be generated. Relaxation of the error threshold clearly impacts on the final errors reported. A local, as opposed to global optimization algorithm, was used to identify solutions to the mass balance model. Research has suggested that local optimization algorithms can be less efficient as they fail to identify globally representative solutions. But in a case like the one presented here where there are only two potential sediment sources and each specific composite signature consists of only a few individual fingerprint properties ($n = 3$, 4 or 5), the local optimization search tool performs better than the GA-driven equivalent. Outputs from the Monte Carlo analysis were summarized as output pdfs. The pdfs were used to estimate relative frequency-weighted average median contributions from the individual sediment sources (cf. Collins et al., 2012a) and to estimate uncertainty ranges in the predicted source proportions. Two GOF estimators were compared to assess the robustness of the optimised mixing model solutions:

$$\mathrm{GOF} = 1 - \left[\frac{1}{n} * \sum_{i=1}^{n} \left\{ \left(Ci - \left(\sum_{s=1}^{m} P_s S_{si} \right) \right) / C_i \right\}^2 W_i \right] \quad (4)$$

$$\mathrm{GOF} = \left(1 - \left[\sqrt{\sum_{i=1}^{n} \left\{ \left(Ci - \left(\sum_{s=1}^{m} P_s S_{si} \right) \right) / C_i \right\}^2 W_i} \right] \right) / n \quad (5)$$

Many sediment source fingerprinting studies compare unmixing model performance on the basis of estimates of the model GOF. These GOF estimators are based on reducing errors between the source-weighted modelled and measured sediment properties. A commonly used objective function (Eq. (4)) includes multiplication by the inverse of the number of properties in the composite signature in question. The implication of this is that improved GOF with measured sediment tracer concentrations is achieved as the number of fingerprint properties entered into the model is increased. However, some recent work (e.g. Laceby and Olley, 2015) has underscored the risk of divergence between the widely-used GOF estimator represented by Eq. (4) and the more traditional estimator based on the absolute error (cf. Collins et al., 1997a; Walling and Collins, 2000). This divergence reflects the performance of Eq. (4) in that a composite signature with more constituent tracers will typically return an improved GOF, whereas in the case of using the absolute error, the inclusion of additional

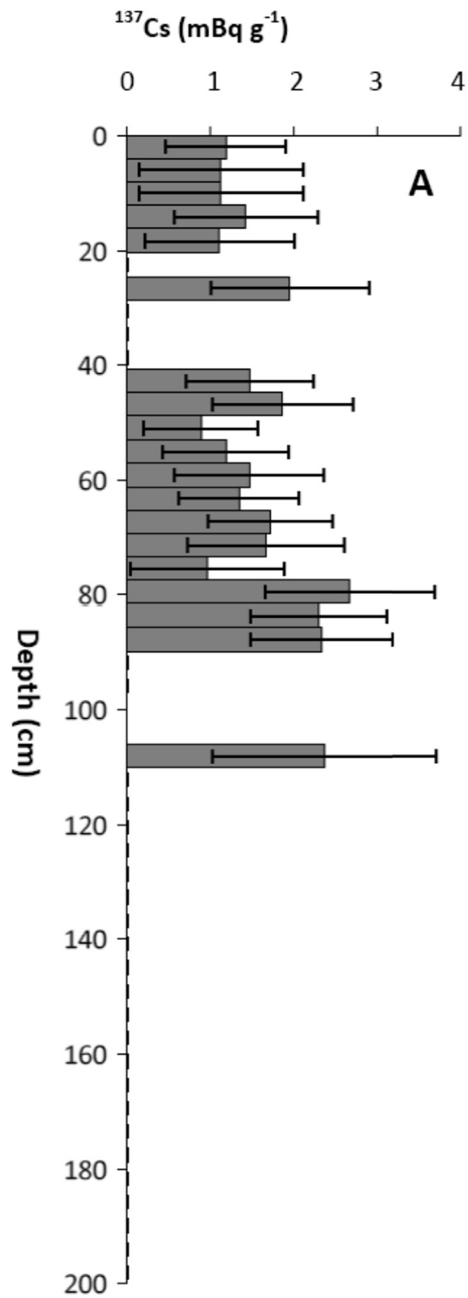

Fig. 2. ^{137}Cs depth profile for the floodplain core collected at site 2. The error bars represent measurement precision (95% confidence limits).

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Table 2
The sediment tracer properties which failed the mass conservativeness test. The results for the uppermost sediment were used to screen properties for the two lower sections.

Site 1		Site 2		
2000–2010	1958–2000	2000–2010	1958–2000	Pre-1958
Li	Mg	Li	B	B
Mg	Ca	B	Mg	Na
Al	Sc	Mg	Al	Mg
K	Fe	Al	K	Ca
Ca	Cd	K	Ca	Ru
Sc	La	Ca	Ru	Rh
V	Pr	V	Rh	Pd
Cr	Nd	Cr	Pd	Nd
Fe	Sm	Fe	Cd	Sm
Zn	Eu	Ni	Eu	Yb
As	Gd	Cu	Gd	Lu
Y	Tb	Zn	Tb	Re
Pd	Dy	Ga	Dy	Os
Cs	Ho	As	Ho	Ir
La	Er	Rb	Er	Pt
Pr	Tm	Ru	Tm	χ_{lf}
Nd	Yb	Rh	Lu	χ_{fd}
Sm	Lu	Pd	Re	ARM
Eu	Th	Cs	Os	χ_{ARM}
Gd		Sm	Ir	SIRM
Tb		Eu	Pt	
Dy		Gd	Au	
Ho		Tb	Pb	
Er		Dy	χ_{lf}	
Tm		Ho	SIRM	
Yb		Er		
Lu		Tm		
Os		Yb		
Pb		Lu		
Th		Re		
U		Os		
χ_{lf}		Ir		
χ_{fd}		Pt		
ARM		Tl		
χ_{ARM}		Pb		
SIRM		Th		
		χ_{lf}		
		SIRM		

tracers will likely degrade the GOF. In recognition of these potential issues, we used a GOF estimator (Eq. (5)) based on the square root of the objective function – i.e. based on the absolute mixing model error, normalised by the number of tracers in any given composite signature. Here, it is timely to bear in mind that acceptable performance on the basis of GOF simply confirms the capacity of the model to generate an acceptable agreement between source-weighted and measured target sediment geochemistry. Artificial or virtual sediment mixture tests are required to assess confidence on the predictions more robustly.

4. Results and discussion

4.1. Establishing the floodplain sediment chronology

Fig. 2 presents the ^{137}Cs depth profile of the sediment core extracted at Site 2. It can be observed that there is no clearly defined peak in the profile and some of the depth incremental samples in the upper half have ^{137}Cs activity below detection limits. This normally reflects input of sediment derived from areas with low or no ^{137}Cs activity such as stream bank and gully erosion sites (Amos et al., 2009; Wallbrink et al., 1996). As such, the accuracy of the ^{137}Cs date of first detection (Leslie and Hancock, 2008) or peak fallout, both of which are used as chronological markers for dating purposes is reduced (Amos et al., 2009). Thus, without a reliable detailed chronology an attempt to investigate specific temporal variations in sediment source was considered unfeasible. The ^{137}Cs activity profile was, however, used to obtain a general temporal framework for the reconstruction of both contemporary and historical surface and subsurface sediment source contributions in the study area, by dividing the sediment core into three time frames. The first 8 cm represented contemporary sediment (2000–2010). The rest of the older deposited sediment was divided into two: the mid-section (8–110 cm; 1958–2000) where most of the sediment had detectable ^{137}Cs and the bottom section (110–200 cm) with no detectable ^{137}Cs content. The bottom-most layer with the detectable ^{137}Cs is normally allocated to 1955 in the southern hemisphere (Leslie and Hancock, 2008). However, studies have demonstrated that ^{137}Cs is not likely to be measurable in South African environments before 1958 (Rowntree and Foster, 2012). Thus, the first occurrence of ^{137}Cs in the sediment core was ascribed to 1958. Assuming no substantial post-depositional down-profile mobility of the ^{137}Cs, we ascribed 1958 to the depth of 110 cm. Sediment below a depth of 110 cm was therefore taken to pre-date 1958.

Table 3
Kruskal–Wallis H-test results for selecting fingerprint properties for distinguishing catchment surface and subsurface sediment sources.

Site 1						Site 1								
2000–2010			1958–2000			2000–2010			1958–2000			Pre-1958		
Property	H-value	p-value	Property	H-value	p-value	Property	H-value	p-value	Property	H-value	p-value	Property	H-value	p-value
Mn	9.375	0.002*	Mn	9.375	0.002*	Mn	10.249	0.001*	Mn	10.249	0.001*	Mn	10.249	0.001*
Ni	9.375	0.002*	Ni	9.375	0.002*	Pr	9.880	0.373	Sc	9.422	0.002*	Sc	9.422	0.002*
Na	8.513	0.004*	Na	8.513	0.004*	Sc	9.422	0.002*	Y	6.127	0.013*	Y	6.127	0.013*
B	8.513	0.004*	B	8.513	0.004*	Ce	7.593	0.817	Co	3.664	0.056	Co	3.664	0.056
Co	8.098	0.004*	Co	8.098	0.004*	Cd	6.127	0.013*	Xfd	2.109	0.146	Pr	2.109	0.146
Cu	8.098	0.004*	Cu	8.098	0.004*	Y	5.808	0.016*	Nd	2.109	0.146	Sr	1.657	0.198
Ba	5.825	0.016*	Ba	5.825	0.016*	Nd	4.746	0.029*	Sr	1.657	0.198	Ba	1.259	0.262
Ce	5.825	0.016*	Ce	5.825	0.016*	Co	3.664	0.056	Ba	1.259	0.262	U	0.794	0.373
Cd	5.315	0.021*	Sr	5.315	0.021*	Au	2.109	0.146	Ce	0.794	0.373	Ce	0.794	0.373
Sr	4.991	0.025*	Ga	4.365	0.037*	Sr	1.657	0.198	Na	0.736	0.391	La	0.053	0.817
Ga	4.365	0.037*	Rb	3.115	0.078	Ba	1.259	0.262	U	0.480	0.488			
Rb	3.115	0.078	Tl	0.047	0.829	Na	0.736	0.391	Pr	0.070	0.792			
Tl	0.047	0.829				U	0.480	0.488	La	0.053	0.817			
						La	0.053	0.817						
						χ_{fd}	0.053	0.817						
						ARM	0.053	0.817						
						χ_{ARM}	0.053	0.817						

* = statistically significant at $p < 0.05$.

Table 4
Ranked fingerprint property loadings generated using PCA for floodplain Site 1 and Site 2.

Site 1				Site 2			
2000–2010				2000–2010			
Property	PC1[a]	Property	PC2[b]	Property	PC1[a]	Property	PC2[b]
Na	0.992	Mn	0.982	Na	0.991	Mn	0.956
Mn	0.126	Ba	0.132	Mn	0.130	X_{fd}	0.231
Ba	0.028	Na	0.129	Ba	0.029	Ba	0.134
Sr	0.009	Rb	0.017	X_{fd}	0.026	Na	0.123
B	0.004	Co	0.017	Sr	0.009	Co	0.016
Rb	0.002	Ni	0.011	Co	0.002	Ce	0.008
Co	0.002	Cu	0.011	La	0.002	Sr	0.005
Cu	0.001	Ce	0.008	Ce	0.001	Y	0.004
Ce	0.001	Ga	0.007	Nd	0.001	Nd	0.004
Ga	0.001	Sr	0.006	Y	0.000	Sc	0.002
Ni	0.000	B	0.002	Pr	0.000	χ_{ARM}	0.001
VE%	81.26	VE%	16.67	Au	0.000	U	0.001
				χ_{ARM}	0.000	La	0.000
				VE%	78.22	VE%	16.82
1958–2000				**1958–2000**			
Na	0.992	Mn	0.982	Na	0.991	Mn	0.956
Mn	0.126	Ba	0.132	Mn	0.130	X_{fd}	0.231
Ba	0.028	Na	0.129	Ba	0.029	Ba	0.134
Sr	0.009	Rb	0.017	X_{fd}	0.026	Na	0.123
B	0.004	Co	0.017	Sr	0.009	Co	0.016
Rb	0.002	Ni	0.011	Co	0.002	Ce	0.008
Co	0.002	Cu	0.011	La	0.002	Sr	0.005
Cu	0.001	Ce	0.008	Ce	0.001	Y	0.004
Ce	0.001	Ga	0.007	Nd	0.001	Nd	0.004
Ga	0.001	Sr	0.006	Y	0.000	Sc	0.002
Ni	0.000	B	0.002	Pr	0.000	U	0.001
VE%	81.26	VE%	16.67	VE%	78.22	VE%	16.82
				Pre-1958			
				Mn	0.990	Ba	0.988
				Ba	0.142	Mn	0.142
				Co	0.017	Ce	0.041
				Sr	0.011	Sr	0.039
				Ce	0.007	La	0.028
				Y	0.004	Y	0.011
				Sc	0.002	Pr	0.007
				La	0.001	Co	0.006
				U	0.000	U	0.001
				Pr	0.000	Sc	0.001
				VE%	90.29	VE%	9.09

VE% variance explained.
[a] Principal component 1.
[b] Principal component 2.

4.2. Tracer conservation and statistical source discrimination

The tracer range test (Table 2) shows that both geochemical and mineral-magnetic properties failed the test in each period. There were more non-conservative properties in the recent sediment than in the older sediment. The opposite was expected as post-depositional tracer transformation normally affects historical sediment more than the recent sediment (Belmont et al., 2014; D'Haen et al., 2012). Additionally, a situation whereby most of the topsoil was completely removed by severe erosion, it can be expected that the sampled contemporary surface source material may not be representative of the former topsoil material eroded and deposited on the floodplain various decades ago. This might complicate the expected source-sediment linkages. Thus, to accommodate these conservation results any properties failing the range test in the upper part of the core (recent sediment) were not considered for the rest of the core since the anomaly of more properties being non-conservative in the upper sections could be an indication of post-depositional fingerprint property transformation over time. Proceeding with sediment source modelling using fingerprint properties that potentially violate the mass conservation assumption would increase the modelling output uncertainty (Belmont et al., 2014; Collins et al., 2010a; D'Haen et al., 2012; Koiter et al., 2013a,b; Pulley et al., 2015b; Sherriff et al., 2015; Smith and Blake, 2014). It is important to bear in mind that the range test confirms the absence of major property transformation rather than of any transformation.

All the conservative fingerprint properties were used to select fingerprint properties for distinguishing catchment surface and subsurface sediment sources based on KW-H, PCA and GA-DFA. For the KW-H it can be seen in Table 3 that the majority of the individual fingerprints showed statistically significant differences between surface and subsurface sources. For the PCA the loadings and variance explained by the first two principal components for each sediment sample are shown in Table 4. Table 5 and Table 6 show the optimum composite fingerprints selected by KW-H and PCA for discriminating between surface and subsurface sediment sources.

It can be observed that similar individual sediment properties (Mn, Ni, and Na, and Mn and Sc) were consistently selected in the first two and all the three sections of the sediment core in Site 1 and Site 2, respectively. Also Na and Mn were selected by KW-H and PCA for the first two sediment sections in both sites. There was consistency in most of the individual fingerprints selected by the

Table 5
Optimum composite fingerprints selected by the KW-H test for discriminating between surface and subsurface sediment sources.

Site 1					Site 2				
2000–2010					2000–2010				
Property	Chi-square	p-Value	%[a]	TDW[b]	Property	Chi-square	p-Value	%[a]	TDW[b]
Mn	9.375	0.002	72.6	1.00	Mn	10.249	0.001	74.2	1.30
Ni	9.375	0.002	59.7	1.10	Cd	6.127	0.013	71.4	1.25
Na	8.513	0.004	65.8	1.06	Sc	9.422	0.002	57.2	1.00
Total[c]			72.6		Total[c]			74.2	
1958–2000					**1958–2000**				
Mn	9.375	0.002	72.6	1.22	Mn	10.249	0.001	74.2	1.30
Ni	9.375	0.002	59.7	1.00	Sc	9.422	0.002	57.2	1.00
Na	8.513	0.004	65.8	1.10	Y	6.127	0.013	62.6	1.09
Total[c]			72.6		Total[c]			74.2	
					Pre-1958				
					Mn	10.249	0.001	74.2	1.30
					Sc	9.422	0.002	57.2	1.00
					Y	6.127	0.013	62.6	1.09
					Total[c]			74.2	

[a] % source samples classified correctly by individual tracers.
[b] Tracer discriminatory weighting used in the un-mixing modelling.
[c] % source samples classified correctly by composite signature.

Table 6
Optimum composite fingerprints selected by PCA for discriminating between surface and subsurface sediment sources.

Site 1			Site 2		
2000–2010			2000–2010		
Property	%[a]	TDW[b]	Property	%[a]	TDW[b]
Na	65.8	1.00	Na	67.8	1.32
Mn	72.6	1.10	Mn	74.2	1.45
Ba	69.5	1.06	χ_{fd}	51.3	1.00
Total[c]	78.9		Total[c]	74.2	
1958–2000			**1958–2000**		
Na	65.8	1.00	Na	67.8	1.32
Mn	72.6	1.10	Mn	74.2	1.45
Ba	65.8	1.06	Xfd	51.3	1.00
Total[c]	78.9		Total[c]	74.2	
			Pre-1958		
			Mn	74.2	1.04
			Ba	71.2	1.00
			Co	74.2	1.04
			Total[c]	79.9	

[a] % source samples classified correctly by individual tracers.
[b] Tracer discriminatory weighting used in the un-mixing modelling.
[c] % source samples classified correctly by composite signature.

Table 7
Optimum composite fingerprints selected by the GA-DFA for discriminating between surface and subsurface sediment sources.

Site 1								
2000–2010								
Run 1[a]			Run 2[b]			Run 3[c]		
Property	%[d]	TDW[e]	Property	%[d]	TDW[e]	Property	%[d]	TDW[e]
Tl	73	1.05	Cd	69.7	1	Cd	69.7	1.11
Cu	75.9	1.09	Co	72.6	1.04	Cu	75.9	1.11
Ba	69.5	1	Ba	69.5	1.09	Na	65.8	1.15
Total[f]	84.9		B	66.5	1.05	Tl	73	1.06
			Total[f]	84.7		G[a]	72.8	1
						Total[f]	84.9	
1958–2000								
Tl	73	1.05	Sr	66.2	1	Cu	75.9	1.15
Cu	75.9	1.09	Co	72.6	1.1	Rb	69.7	1.05
Ba	65.8	1	B	66.5	1.01	Sr	66.2	1
Total[f]	84.9		Ba	65.8	1.05	Ga	72.8	1.1
			Total[f]	78.9		Co	72.6.0	1.1
						Total[f]	81.8	
Site 2								
2000–2010								
Mn	74.2	1.19	Co	74.2	1.52	Ba	71.2	1.46
Y	62.6	1	Na	67.8	1.39	Pr	54.4	1
Sr	68.1	1.09	Ce	48.7	1	Ce	48.7	1.12
Total[f]	74.2		Nd	54.4	1.12	U	62.9	1.29
			Total[f]	77		Na	67.81	1.39
						Total[f]	82.7	
1958–2000								
Ce	48.7	1	Ba	71.2	1.46	Ba	71.2	1.46
Ba	71.2	1.46	Pr	54.4	1.12	Pr	54.4	1.12
Co	74.2	1.52	Ce	48.7	1	Ce	48.7	1
Total[f]	79.9		U	62.9	1.29	U	62.9	1.29
			Total[f]	82.7		Na	67.8	1.39
						Total[f]	82.7	
Pre-1958								
Pr	54.4	1	Pr	54.4	1.12	Ce	48.7	1
Mn	74.2	1.36	U	62.9	1.29	Pr	54.4	1.12
Ba	71.2	1.31	Ce	48.7	1	Sr	68.1	1.4
Total[f]	82.8		Ba	71.2	1.46	Ba	71.2	1.46
			Total[f]	82.7		U	62.9	1.29
						Total[f]	82.7	

[a] GA-DFA run with for composite fingerprint with a maximum of 3 properties.
[b] GA-DFA run with for composite fingerprint with a maximum of 4 properties.
[c] GA-DFA run with for composite fingerprint with a maximum of 5 properties.
[d] % source samples classified correctly by individual tracers.
[e] Tracer discriminatory weighting used in the un-mixing modelling.
[f] % source samples classified correctly by composite signature.

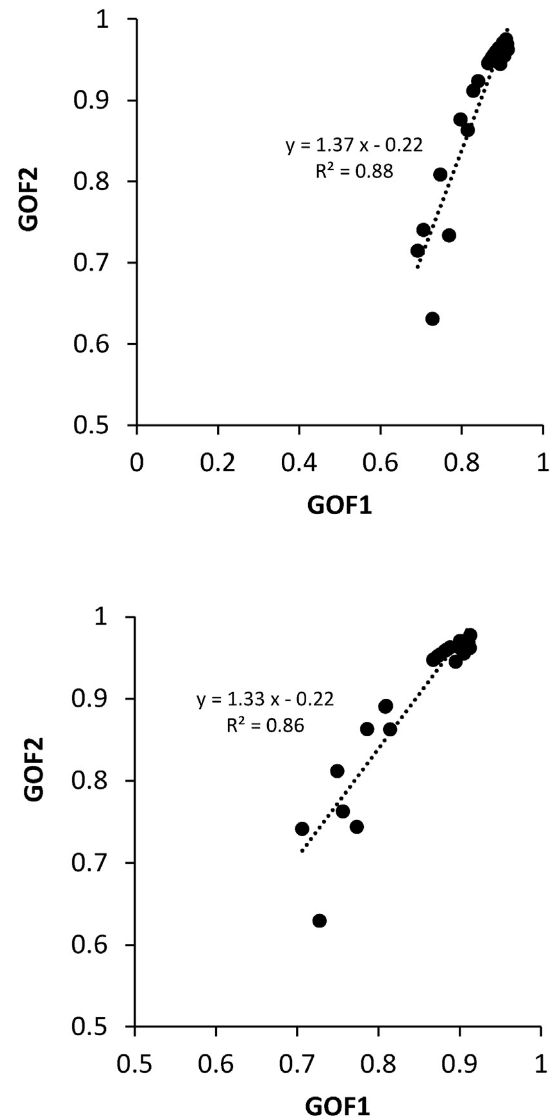

Fig. 3. Plots showing the relationships between the two model GOF estimators used.

KW-H and PCA statistical procedures for the two floodplain sites. The GA-DFA results are presented in Table 7. As opposed to KW-H and PCA whereby there was consistency in the individual properties selected in the composite signatures for the two sites, each composite signature selected by GA-DFA generally consisted of a different set of properties reflecting the basis of the GA approach driving this specific test.

The optimum signatures selected using KW-H classified correctly 72.6% – 74.2% of the most recent sediment samples in both sites, 72.6%–74.2% of the 1958–2000 sediment and 74.2% of the pre-1958 sediment. The percentage correct discrimination of the sediment sources accorded by the composite signatures were constant for both sediment sections at Site 1 and for the three sections at Site 2. The optimum composite fingerprint selected by PCA classified correctly 74.2% – 78.9% of the most recent sediment samples, 74.2% – 78.9% of the 1958–2000 sediment and 79.9% of the pre-1958 sediment. The GA-DFA results presented an opportunity to assess whether an increase in the number of individual fingerprints in each composite signature (from 3 up to 4 or 5) affects the percentage correct classification of the catchment source samples or the un-mixing model GOF. For illustrative purposes and

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Table 8
The goodness-of-fit associated with each composite fingerprint for the model iterations in each period.

Period	Optimum composite signature	Number of properties	GOF[a]	GOF[b]
	KW-H	3	0.87	0.83
	PCA	3	0.81	0.84
	GA-DFA 1	3	0.75	0.75
2000–2010	GA-DFA 2	4	0.81	0.82
	GA-DFA 3	5	0.73	0.73
	Average		**0.79**	**0.79**
	KW-H	3	0.87	0.84
	PCA	3	0.87	0.87
	GA-DFA 1	3	0.90	0.87
1958–2000	GA-DFA 2	4	0.91	0.90
	GA-DFA 3	5	0.91	0.91
	Average		**0.89**	**0.88**
	KW-H	3	0.89	0.84
	PCA	3	0.71	0.71
	GA-DFA 1	3	0.81	0.69
2000–2010	GA-DFA 2	4	0.76	0.74
	GA-DFA 3	5	0.77	0.77
	Average		**0.79**	**0.75**
	KW-H	3	0.91	0.81
	PCA	3	0.79	0.83
	GA-DFA 1	3	0.90	0.90
1958–2000	GA-DFA 2	4	0.90	0.90
	GA-DFA 3	5	0.91	0.91
	Average		**0.88**	**0.87**
	KW-H	3	0.87	0.84
	PCA	3	0.88	0.88
	GA-DFA 1	3	0.88	0.88
Pre-1958	GA-DFA 2	4	0.91	0.91
	GA-DFA 3	5	0.90	0.89
	Average		**0.89**	**0.88**

[a] –5000 model iterations.
[b] –30 000 model iterations.

ease of comparison, only the composite fingerprint with the highest percentage correct discrimination of the two catchment sediment sources selected by each GA-DFA run (i.e. using 3, 4 or 5 properties in each signature) is presented in Table 7. It can be observed that the percentage of catchment source samples classified correctly by the GA-DFA composite signatures did not improve by increasing the number of fingerprint properties in each composite signature for both sites. Inclusion of high numbers of individual tracers in composite signatures can improve signature discriminatory power but clearly this must be considered in the context of the overall need to minimise un-mixing model errors. This point is discussed further in a subsequent section. Most of the optimum composite fingerprints were unable to achieve the minimum threshold of 85% correct discrimination used by most sediment source fingerprinting studies (Collins et al., 1997a, 2010a; Owens et al., 1999; Stone et al., 2014; Walling et al., 2008). Consequently, a higher degree of uncertainty is associated with the estimates of sediment source apportionment given the weaker source discrimination using the datasets collected here.

4.3. Mass balance model performance

Fig. 3 shows the relationship between the two GOF estimators used to compare model performance based on the different sets of composite fingerprints. The R^2 values of 0.86 and 0.87 show that the differences between the two GOF estimators is small in the case of the dataset used here. Regardless, the GOF estimator represented by Eq. (5) was adopted for inclusion in further data processing. The GOF of each composite fingerprint, using Eq. (5), for the two Monte Carlo analyses (Table 8) shows that increasing the number of individual fingerprints included in the composite signatures from 3 to 5 did not result in a better model GOF. This is contrary to findings of some studies that have reported that uncertainty in sediment source fingerprinting can be reduced by increasing the number of tracers (Martinez-Carreras et al., 2008; Sherriff et al., 2015). Increasing the number of model iterations from 5000 to 30 000 per floodplain core section, did not improve the model efficiency in predicting the measured tracer property values of the floodplain sediment samples. In fact, most of the model GOF estimates were exactly the same for both sets of repeat iterations. These results support the use of ≤5000 model iterations reported by many previous sediment source fingerprinting studies (Collins et al., 2010a, 2012, 2013; Pulley et al., 2015a; Smith and Blake, 2014; Stone et al., 2014; Wilkinson et al., 2013). The lowest GOF (average GOF of 0.79 and 0.75 for 5000 and 30 000 iterations, respectively), was recorded for the upper-most sediment slice at Site 2.

The output probability density functions of the 5000 and 30 000 iterations were plotted and used to estimate relative frequency-weighted average median contributions (Collins et al., 2012a) from the individual sediment sources and to estimate uncertainty ranges of the predicted median source proportions. The pdfs for each composite fingerprint signature using 5000 iterations are shown in the supplementary material provided online. The pdfs and the predicted median contributions from each source (Table 8) show that the range of feasible contributions of sediment from surface and subsurface sources was very broad (1–100%). According to Collins et al. (2010a) the usefulness of source apportionment data generated using Monte Carlo routines depends upon how narrow the contribution ranges are for specific sources. However, in situations where large ranges exist, it is informative to take account of such ranges in estimating relative frequency-weighted average median source proportions (Collins et al., 2012a). In this case, the final estimate of the relative frequency-weighted average median source contributions was generated on the basis of a weighting (cf. Collins et al., 2014) combining the GOF and corresponding

Table 9
Summary of the predicted median source proportions (%). Single values represent the overall relative frequency-weighted average medians; ranges represent the full uncertainty in the median contributions predicted by the Monte Carlo repeat runs of the mass balance model.

Sediment	Signature	5000		30,000	
Site 1		Surface	Subsurface	Surface	Subsurface
2000–2010	KW-H	49	51	49	51
		0–100	0–100	0–100	0–100
	PCA	45	55	45	55
		0–100	0–100	0–100	0–100
	GA-DFA 1	75	25	75	25
		0–100	0–100	0–100	0–100
	GA-DFA 2	67	33	67	33
		0–100	0–100	0–100	0–100
	GA-DFA 3	78	22	78	22
		0–100	0–100	0–100	0–100
	Weighted average[a]	**49**	**51**	**49**	**51**
1958–2000	KW-H	52	48	52	48
		0–100	0–100	0–100	0–100
	PCA	46	54	46	54
		0–100	0–100	0–100	0–100
	GA-DFA 1	55	45	55	45
		0–100	0–100	0–100	0–100
	GA-DFA 2	50	50	49	51
		0–100	0–100	0–100	0–100
	GA-DFA 3	47	53	48	52
		0–100	0–100	0–100	0–100
	Weighted average[a]	**49**	**51**	**49**	**51**
Site 2 2000–2010	KW-H	25	75	26	74
		0–100	0–100	0–100	0–100
	PCA	53	47	53	47
		0–100	0–100	0–100	0–100
	GA-DFA 1	18	82	31	69
		0–100	0–100	0–100	0–100
	GA-DFA 2	30	70	48	52
		0–100	0–100	0–100	0–100
	GA-DFA 3	29	71	30	70
		0–100	0–100	0–100	0–100
	Weighted average[a]	**31**	**69**	**43**	**57**
1958–2000	KW-H	61	39	60	40
		0–100	0–100	0–100	0–100
	PCA	66	34	64	36
		0–100	0–100	0–100	0–100
	GA-DFA 1	58	42	58	42
		0–100	0–100	0–100	0–100
	GA-DFA 2	74	26	74	26
		30–100	0–75	0–100	0–100
	GA-DFA 3	75	25	75	25
		30–100	0–75	0–100	0–100
	Weighted average[a]	**61**	**39**	**63**	**37**
Pre-1958	KW-H	46	54	46	54
		30–100	0–75	0–100	0–100
	PCA	45	55	46	54
		30–100	0–75	0–100	0–100
	GA-DFA 1	45	55	48	52
		30–100	0–75	0–100	0–100
	GA-DFA 2	63	37	63	37
		30–100	0–75	0–100	0–100
	GA-DFA 3	58	42	58	42
		30–100	0–75	0–100	0–100
	Weighted average[a]	**52**	**48**	**52**	**48**

[a] Estimated using a weighting factor combining the GOF (Eq. (5)) and % discriminatory power for each signature.

discriminatory power (%) of each composite signature (Table 9). Only composite signatures that yielded a GOF higher than 80% were used to estimate the overall relative frequency-weighted average median source proportions. The GOF minimum of 80% has been used as a measure of reliability of mass balance model results in various fingerprinting studies (Martinez-Carreras et al., 2008; Collins et al., 2010a; Evrard et al., 2011).

For floodplain core Site 1 for the periods 2000–2010 and 1958–2000, there was perfect coincidence in the model solutions using the sets of 5000 and 30 000, both yielding surface and subsurface weighted average median contributions of 49% and 51%, respectively. For the floodplain core Site 2, the weighted average median contributions from surface and subsurface sources were estimated at 31% and 69% respectively using 5000 model iterations and 43% and 57% respectively, using 30 000 model iterations. For the 1958–2000 period, surface and subsurface sources respectively contributed 61% and 39% using 5000 model iterations and 63% and 37% using 30 000 iterations. The model solutions using the sets of 5000 and 30 000 iterations for the period before 1958 yielded the same weighted average median contributions of 52% and 48%, respectively, for surface and subsurface sediment sources. These results suggest that for this dataset, the estimated source

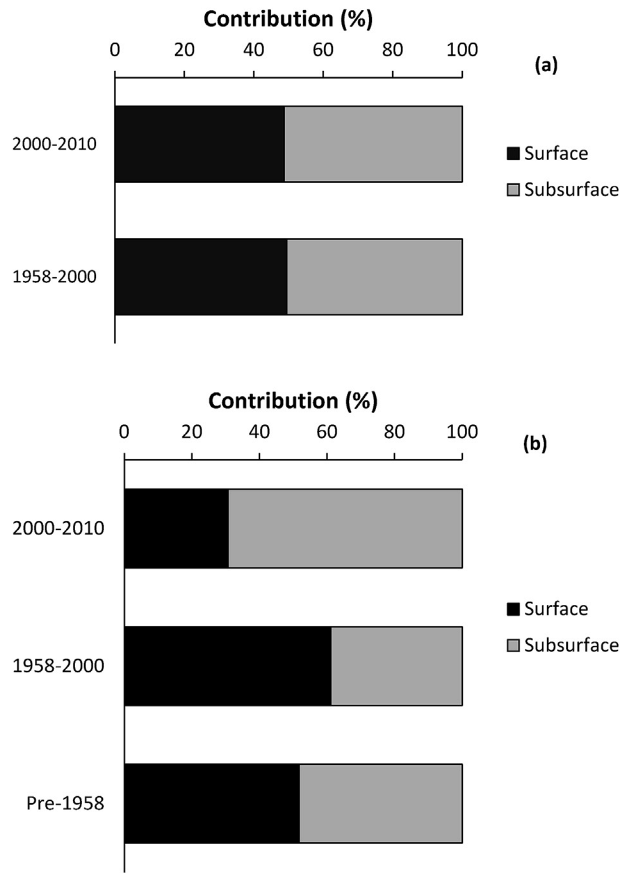

Fig. 4. The overall estimate of the relative frequency-weighted average median contributions from surface and subsurface sources to floodplain sediment samples collected from Site 1 (a) and Site 2 (b).

contributions are not highly sensitive to the number of un-mixing model iterations used in the Monte Carlo routine.

4.4. Source apportionment and interpretation

The results shown in Fig. 4 (only results of 5000 iterations are shown) reflect the final weighted median contributions from surface and subsurface sources to the sediment cores collected at two sites 35 m apart on the same floodplain. While increased sediment contributions from subsurface sources is an indicator of gully or stream bank erosion and that from surface sources reflects sheet and inter-rill erosion (Hancock and Revill, 2013; Wallbrink et al., 1996), previous research in the catchment has shown that rill and gully erosion were increasingly becoming more severe (Kakembo and Rowntree, 2003; Kakembo et al., 2009). Thus subsurface sediment sources are most likely to be indicative of rill and gully erosion rather than stream bank erosion. For Site 1, the sediment record representing the period from 1958 to 2000 and 2000–2010 shows no change in sediment contribution from surface and subsurface processes. On the other hand at Site 2, the sediment record reflects a decrease in sediment mobilized by rill and gully erosion from 48% before 1958 to 39% of the deposited sediment between 1958 and 2000. However, between 2000 and 2010 there was a sudden rise in the contribution of sediment from rill and gully erosion sites (69%). This abrupt change in sediment source is surprising and should be interpreted in the context of the high uncertainty indicated by the lower model GOF for the sediment samples represented by this period (Table 7).

The large differences in the predicted sediment source estimates for each time period between the two proximal sediment cores in the same floodplain reflects some of the uncertainties associated with the use of floodplain sediment cores in sourcing investigations. Sediment deposition on floodplains is known to exhibit high spatial variability in response to variations in microtopography, vegetation and distance from the main river channel (Owens et al., 1999; Walling and He, 1997). Areas closer to the river channel may experience slightly higher deposition rates while areas near the floodplain margin are likely to have lower deposition rates (Owens et al., 1999). The first site was located at a slightly higher landscape position (~30 cm) than Core 2, which was additionally situated near to the site of a former channel. Thus, the overbank deposition at the sites of the two cores could have happened at different times and been associated with different flood events. Overall, the results underpin the need to take replicate cores from depositional sinks to capture any spatial variation in the properties of deposited fine-grained sediment and indeed the chronology of that deposition.

The only long term published research from the study catchment and surrounding areas that documents the soil erosion status since 1938 (Kakembo and Rowntree, 2003) indicated that only after the mid-1970s did severe forms of soil erosion and gully erosion become widespread coinciding with increased land abandonment and a period of extreme rainfall events. Thus, the role of subsurface processes is not expected to be dominant before the mid-1970s. A recent study (Manjoro et al., 2012a) covering the period 1998–2008 showed that severe soil erosion including gully erosion increased simultaneously with the increase in bush encroachment on representative hill slopes in the upper part of the study catchment. Recent field observations in the study catchment have indicated that although gully erosion is very severe especially in the upper part of the catchment, in spatial terms, the area affected is less than that affected by surface processes. Thus, the sudden change in sediment source predicted by the tracing results for recent sediment at Site 2 do not agree with alternative evidence for the study area. This example reminds users of the need to interpret source fingerprinting estimates on the context of alternative data sources for soil erosion and sediment delivery.

5. Conclusion

This study, based on a single catchment in South Africa, has explored the uncertainties in sediment source fingerprinting associated with increasing the number of properties in composite signatures, increasing the number of repeat model iterations and the use of two sediment profiles collected from the same floodplain sediment sink. Although some research has indicated that increasing the number of fingerprints in mass balance modelling will improve the GOF with measured sediment tracer values, we found that increasing the number of individual fingerprint properties included in the composite signature did not result in a higher model GOF. Given the potential counterintuitive performance of a widely-used GOF estimator, we adopted an alternative. It was also noted that increasing the number of repeat model iterations did not significantly change uncertainty ranges in modelled source proportions nor improve the GOF. Accordingly, the model results based on 5000 iterations were used to assess the importance of subsurface processes in the study catchment. The temporal patterns of sediment source contributions from surface and subsurface processes predicted for the two sediment cores were very different despite the cores being collected in close proximity from the same floodplain sink. Although only two sediment cores were used in this study, the results show that sediment apportionment results can vary even using historical sediment collected in close

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proximity. Although floodplain sediment has been proven to be an important source of proxy historical data for environmental processes including soil erosion (Collins et al., 1997b; Owens et al., 1999), the spatial variability of sediment deposition on floodplains means that floodplain cores collected from the same depositional unit may produce different sediment records. The sediment source contribution estimates from this study are not consistent with the available published data on erosion processes and thereby highlight the potential limitations associated with using floodplain cores to reconstruct catchment erosion processes and associated sediment source contributions in complete independence of alternative data sources.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2016.07.019.

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