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First use of a compound-specific stable isotope (CSSI) technique to trace sediment transport in upland forest catchments of Chile

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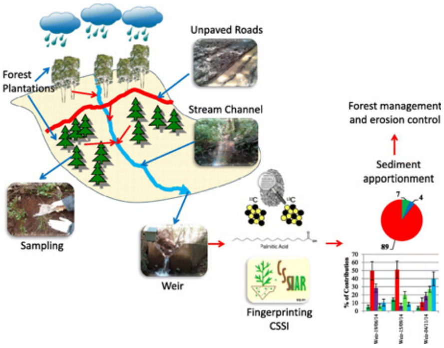
HIGHLIGHTS

- First application of CSSI fingerprinting technique in forest catchments is showed.
- Roads are the main source of sediments in non-harvested forest catchments.
- With sediment sources identified forestry managers can apply mitigation actions.
- Sampling along the stream can help to better understand sediment redistribution.

GRAPHICAL ABSTRACT



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ABSTRACT

Land degradation is a problem affecting the sustainability of commercial forest plantations. The identification of critical areas prone to erosion can assist this activity to better target soil conservation efforts. Here we present the first use of the carbon-13 signatures of fatty acids (C14 to C24) in soil samples for spatial and temporal tracing of sediment transport in river bodies of upland commercial forest catchments in Chile. This compound-specific stable isotope (CSSI) technique was tested as a fingerprinting approach to determine the degree of soil erosion in pre-harvested forest catchments with surface areas ranging from 12 to 40 ha. For soil apportionment a mixing model based on a Bayesian inference framework was used (CSSIAR v.2.0). Approximately four potential sediment sources were used for the calculations of all of the selected catchments. Unpaved forestry roads were shown to be the main source of sediment deposited at the outlet of the catchments (30–75%). Furthermore, sampling along the stream channel demonstrated that sediments were mainly comprised of sediment coming from the unpaved roads in the upper part of the catchments (74–98%). From this it was possible to identify the location and type of primary land use contributing to the sediment delivered at the outlet of the catchments. The derived information will allow management to focus efforts to control or mitigate soil erosion by improving the runoff features of the forest roads. The use of this CSSI technique has a high potential to help forestry managers and decision makers to evaluate and mitigate sources of soil erosion in upland forest catchments. It is important to highlight that this technique can also

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be a good complement to other soil erosion assessment and geological fingerprinting techniques, especially when attempting to quantify (sediment loads) and differentiate which type of land use most contributes to sediment accumulation.

1. Introduction

Land degradation is a worldwide problem that affects more than two billion people (Dotterweich, 2013; UNCCD, 2016). A major form of land degradation is water erosion, which causes a yearly loss of 1.6 billion ha of soil (Li and Fang, 2016). It is essential to improve the efficiency and effectiveness of soil management and particularly soil conservation strategies. The identification of critical areas prone to erosion or hot spots can assist in better targeting soil conservation efforts. As sediments produced by erosion also reduce water quality, it is also imperative to determine the origin of sediment runoff in order to prevent sediments from reaching river systems, lakes, and water reservoirs. In addition, optimising erosion control will not only secure agricultural and forestry production but is also an important measure to ensure the overall sustainability of land-based biomass production at affordable costs to society (Koch et al., 2013; Montanarella et al., 2016).

An industry in urgent need of more sustainable management is the forestry sector. The Food and Agriculture Organization of the United Nations (FAO) estimates that commercial forest plantations cover approximately 291 million ha worldwide (FAO, 2015). This being said, more than 1 billion ha of degraded forest land worldwide need restoration (FAO, 2011). In particular, massive lodging, the use of heavy machinery, poorly planned construction of forest roads, and the lack of appropriate drainage systems are some of the practices that most contribute to erosion in commercial forestry systems (Begus and Pertlik, 2017; Schuller et al., 2013). Therefore, commercial forestry companies in upland areas seek guidance on how to improve their practices to reduce water erosion and improve water quality. In turn, companies that produce sustainably can obtain “green” certifications, further improving their profits and market position nationally and internationally.

To reduce erosion in upland commercial forest plantations, hotspots of land degradation have to be identified. Different conventional techniques are used to identify hotspots; these include direct *in-situ* watershed based measurements of erosion and sediment redistribution, aerial photo surveys, satellite imaginary analysis, erosion modelling or tracing geochemical properties (Collins et al., 1997a; McCloskey et al., 2016; Navas et al., 2005; Yoo et al., 2005). However, the costs and time needed for long-term *in-situ* assessments are a constraint. In addition, aerial photo surveys or satellite imagery have limited utility in dense forest plantations, and they only give a snapshot in time of the situation. In Chile, commercial forests are characterised by planting and harvesting operations that occur over a time scale of 15–25 years; thus, the temporal dimension of assessments is essential. Besides using imagery, modelling can be a powerful assessment technique, but the spatial resolution of modelling may not be fine enough to inform specific management practices. Nowadays, isotopic techniques are becoming an alternative accessible and affordable tool to assess soil erosion in time and space, and these techniques are particularly useful for identifying areas susceptible to erosion. Fallout radionuclides (FRNs) such as ^{7}Be, ^{137}Cs, and ^{210}Pb can be used as tracers to estimate erosion and deposition rates at multiple geographical and temporal scales at limited cost and without major time investment (Dercon et al., 2012; Mabit et al., 2013; Smith and Blake, 2014; Taylor et al., 2013). However, it should be noted that, these FRNs cannot be used to distinguish between different types or stages of forest plantations when identifying sources of soil erosion in dense commercial forest areas (Schuller et al., 2013). Given that this is essential for understanding the impact of forest management on sediment distribution, alternative techniques are required (Reiffarth et al., 2016).

Compound-Specific Stable Isotope (CSSI) techniques based on the use of the carbon-13 (δ^{13}C) stable isotope signature of fatty acids or alkanes (in soils and sediments) can be implemented to distinguish between land use types (Hockun et al., 2016; Pisani et al., 2016; Upadhayay et al., 2017). This technique was first introduced to study the origin of estuarine sediments in 2008 (Gibbs, 2008). The main principles are that some of the compounds produced by plants can be used as labels or “biomarkers” for a specific type of soil (land use). To characterise the soil as a specific land-use, the compounds being considered as biomarkers need to be stable, long-lived, strongly bound to the soil particles, abundant, and easily measured. They also need to have a characteristic signature. In this case that unique characteristic is the δ^{13}C of certain values of the compounds produced by the different plant communities growing in the soil (*e.g.* fatty acids-FA).

For the CSSI technique, in the case of fatty acids, the biomarker compounds of choice are the even straight-chain saturated fatty acids (C14:0 to C24:0); odd carbon FA may be produced by bacteria and should be avoided (Gibbs, 2008). This group of FA is partially water soluble; such that when rainwater infiltrates ground water, the FA bind to fine soil particles, particularly clays. Degradation of FA produces other compounds which are no longer part of the pool of the FA bound to the soil. Consequently, the isotopic signature of the FA pool in the soil does not change through diagenesis (Boyd et al., 2006), although the concentration of FA in the soil may decrease (Banowetz et al., 2006). The unique isotopic values of the plant FA biomarkers can be used to identify the origin/land-use of the soil. Previous studies have determined that the CSSI technique using fatty acids is able to discriminate different types of land use including forested catchments (Hancock and Revill, 2013; Upadhayay et al., 2017). Additionally, if the CSSI values of the FA biomarkers in the source soils are known, their proportional contribution in the mixture can be estimated using mixing modelling. For the CSSI technique, the mixing model used was IsoSource, but several restrictions made it no longer the main software (Upadhayay et al., 2017). Bayesian based mixing models are currently used extensively (*e.g.* SIAR, MixSIAR). These models provide the opportunity to implement a hierarchical structure of the data (Upadhayay et al., 2017).

The Chilean forestry sector mainly focuses on fast growing “exotic” species such as *Pinus radiata* and *Eucalyptus* spp. The production of these species has increased significantly over the last 15 years, leading to a significant increase in erosion and the sediment load to river bodies. To fulfil forestry certification requirements, Chilean forest companies are required to protect catchments from the off-site impacts of forest operations. The careful placement and layout of roads and logging operations, proper planning, and the use of best management practices can reduce the magnitude of erosion and impacts on water quality (Schuller et al., 2013; Stringer and Thompson, 2000). The aim of this study was to validate the first time use of CSSI techniques for spatial and temporal tracing of sediments in commercial forest catchments located in the Chilean coastal mountain region. Complementing a previous study using fallout radionuclides (Schuller et al., 2013), the CSSI techniques used here were based on the δ^{13}C values of fatty acids in soil and sediments.

2. Material and methods

2.1. Study sites

Three upland forest catchments were selected as study sites in south-central Chile (Fig. 1) to identify sources of sediments from pre-harvest forestry operations, and to establish a baseline for future comparing

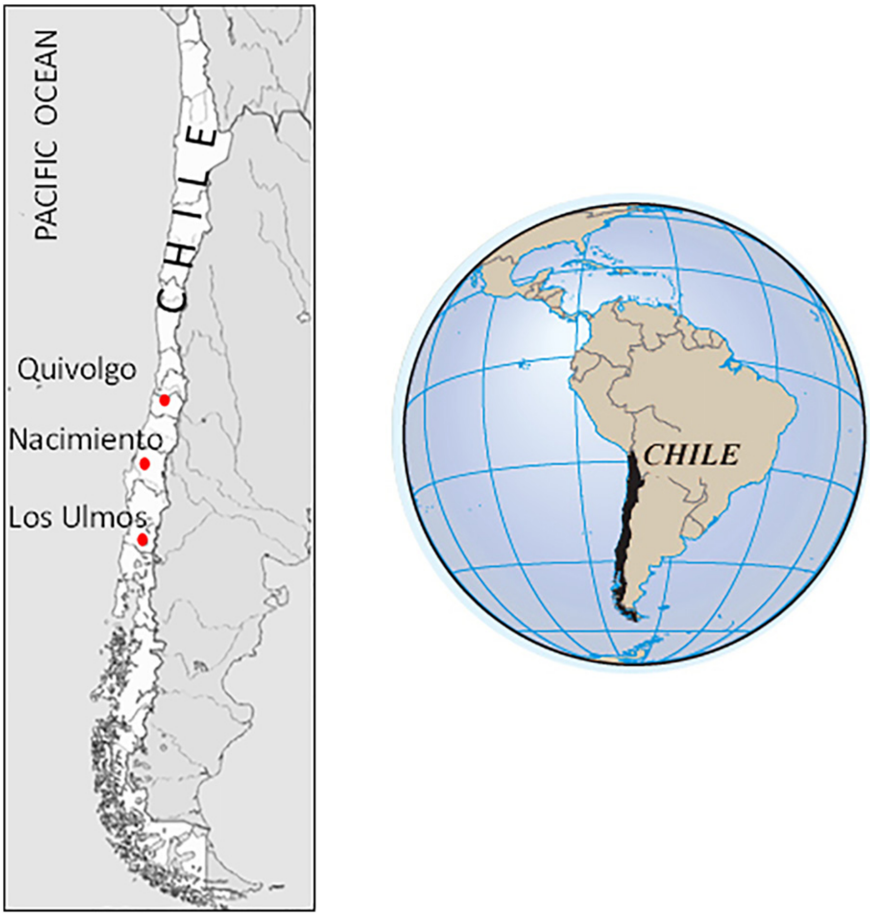

Fig. 1. Location of three studied upland forest catchments in south-central Chile: Nacimiento (37°29′ S, 72°44′ W), Los Ulmos (40°02′ S, 73°05′ W), and Quivolgo (35°23′ S, 72°13′ W).

sediment pathways after harvesting. The main characteristics of each study site are shown in Table 1. One catchment is mainly covered by *Pinus radiata*, the second is comprised mainly of pine trees and native forest (mainly species such as *Nothofagus alessandrii* and *Pitavia punctate*), and the third is a mixed plantation of *Pinus radiata* with *Eucalyptus nitens*. It is also important given the context of this study to mention that the studied catchments differ in their annual rainfall, ranging from 966 mm per year to 2500 mm per year, and their annual sediment yields, ranging from 84 up to 1182 kg ha^{-1}. Within the catchments, four potential sources of sediments were considered: unpaved forest roads, native

Table 1
Characteristics of the studied upland forest catchments in south-central Chile.

Catchment	Quivolgo	Nacimiento	Los Ulmos
Land use (%)			
Native forest	25	–	–
Unpaved forest roads	4	1	3
Pinus radiata	65	92	38
Eucalyptus nitens	–	–	32
Buffer or riparian zone	6	7	27
Plantation year	2001	1986–1987	2000
Expected year of harvesting (year)	2023	2020	2017
Annual precipitation (mm)	966	1200	2500
Period of maximum rainfall	May–September	May–July	June–July
Amount of maximum rainfall (mm month^{-1})	283	430	622
Surface (ha)	40.3	12.7	19.8
Mean altitude (m a.s.l.)	427	328	192
Mean slope (%)	44	27	18
Maximum slope (%)*	121	163	188
Mean slope of stream (%)	21	19	10
Length of main stream (km)	0.80	0.91	0.53
Length (km) and mean slope (%) of forest roads	2.4–20	0.3–33	1.4–11
Annual sediment yield (kg ha^{-1})	84	600**	1182**
Type of climate	Temperate semi-oceanic	Temperate semi-oceanic	Temperate-Oceanic
Main soil types (WRB)	Leptosol-Haplic Luvisol	Vitric Andosol	Dystric Cambisol

* 45° of inclination corresponds to 100%.
** from Schuller et al. (2013).

forest areas, buffer or riparian zones, and forest plantations (eucalyptus and/or pine trees). They were all identified as potential sources of sediments. Stream channel banks were not included as sources due to the channels were not wide (1–2 m) and the edges were right next to the riparian zones. Also the stream flows are not very high, so bank erosion is not an important source as in big rivers.

2.2. Sample collection

Fig. 2 shows where the samples were collected in each study catchment. Colour dots are related to the land use and numbers refer to the position where the samples were taken within the catchment.

Overall, in the three study sites, eighty sediment sources (soil samples) and twelve sediment deposition areas (sinks) were sampled. Sampling was conducted three times; and one to three months separated each sampling. Samples were obtained during and after the rainy season of several years (from 2010 to 2014). The difference in sampling times was due to the fact that this technique gradually gained the interest of forestry managers.

Samples from each potential sediment source and sediment sink were collected by multiple composite surface sampling (five samples were taken at 2 cm depth using metal spatulas and PVC disks) to characterise the spatial variability of the sites. Sediment sources were sampled from areas that are easily connected to the main stream. In the case of pine, eucalyptus, native forest and buffer zone areas, samples were collected using a grid pattern (samples were taken from the central point and edges of a 10 × 10 m^2) and then were mixed in a metal bucket. For the road sites, the samples were taken specifically from the downward side slope, to ensure that only sediments from the road were sampled. For the streams (sampled up-stream from the weir), the samples were collected from the centre and sides of the water channel. All samples were georeferenced by using GPS. After having removed any small tree branches, pine needles, roots, leaves, and other major objects, the samples were placed in double plastic bags and labelled accordingly.

Collection of contemporary bulk suspended sediment samples at the outlet of the catchment were trapped using a concrete v-notched weir. This type of weir reduces the flow of water allowing suspended sediments to settle. After sampling, the weir was emptied and cleaned, so that the next sample represented what happened until next sampling period.

In the Nacimiento site eucalyptus are present at the end of the catchments and are mixed with pines trees. Thus, in order to have a pure source signature of this land use samples were collected just outside of this mixing area.

2.3. Sample preparation and analysis

The samples were oven dried at 60 °C, then sieved through a 2.0 mm mesh. The extraction of fatty acids (ranging from C14 to C24) from soil samples for the Nacimiento catchment (20 g of dry soil) was performed using an accelerated solvent extractor (ASE) (Dionex ASE 200) where dichloromethane was used as the extraction solvent. The samples were heated to 100 °C and raised to a pressure of 2000 psi for 10 min; the extraction procedure was repeated twice. For the Los Ulmos and Quivolgo catchments, the following extraction methodology was applied: 20 g of dry sediment were placed into glass flasks with dichloromethane and sodium sulphate anhydrous; these were then placed on a shaker at 200 rpm for 24 h. The extracts were poured into a rounded flask and then more solvent was added to the same sediments to perform a second extraction assisted by an ultrasonic bath maintained at room temperature for 2 h. The extracts of both extraction procedures were combined, concentrated using a roto-evaporator and then dried with pure nitrogen. Afterwards, to obtain the fatty acid methyl esters (FAMEs), the dry extracts (of both procedures) were combined with a 5% BF_3/Methanol solution (for 20 min at 70 °C) and further extracted in a vortex with a 1:4 mixture of dichloromethane:hexane and water. The organic phase was placed into a 2 mL amber vial and dried with pure nitrogen before being sent for analysis.

The reason for using different extraction methodologies was that some samples were extracted with an ASE machine in New Zealand during a training course on CSSI at the National Institute of Water and Atmospheric Research (NIWA), and the rest were done at the Universidad

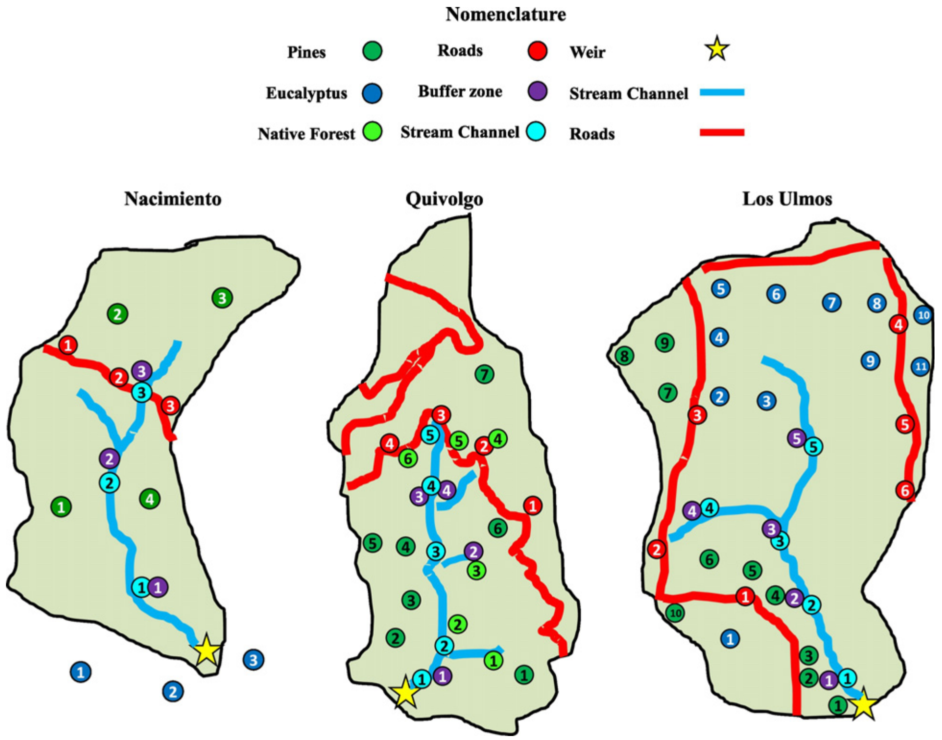

Fig. 2. Schematic location of sampling sites in the three catchments according to the respective land use (see the above legend).

Austral de Chile, Chile. Nevertheless, these techniques produce qualitative results that are not subject to extraction efficiency (fatty acid concentrations). Furthermore, the results obtained using the different extraction and drying methodologies did not differ significantly in terms of their isotopic values (unpublished results). The bulk δ^{13}C, carbon %, and the isotopic values were determined at the Stable Isotope Facilities of UC-Davis California using Gas Chromatography-combustion-Isotope Ratio Mass Spectrometry (GC-c-IRMS). The obtained δ^{13}C-FA values for the different FAMEs from the different sediment sources are presented as Supplementary information.

The methyl group added from the derivatisation process of the fatty acids using a 5% solution (v/v) of boron trifluoride in methanol (BF_3/MetOH) was corrected using the following equation (Gibbs, 2008):

$$\delta^{13}\text{C} = \frac{\delta^{13}\text{C}_{\text{FAMEs}} - (1-\text{X})\delta^{13}\text{C}_{Methanol}}{\text{X}}$$

where X is calculated using the total number of carbons of the original fatty acid divided by the number of carbons of the derivatised molecule (FAME).

These fingerprint properties were used to discriminate between the primary potential fine sediment sources in the catchment: pines, eucalyptus, roads, buffer zones, native forest and stream channels. For fingerprinting, the data were analysed using the software CSSIAR v.2.00, this software is a mixing model that was adapted from SIAR (Parnell et al., 2010) to work with isotopic values, but exclusively for soil erosion studies. SIAR is a program that works under a Bayesian approach for stable-isotopes mixing models. The mathematical advantage of SIAR over previous modelling approaches (*i.e.* IsoSource) is that it incorporates uncertainties (from several iterations) and not only absolute or average values for the δ^{13}C. This model produces simulation of plausible values that are known as posterior distributions, representing a true probability density for the parameters of interest. More details can be found in Parnell et al. (2010). Thus, CSSIAR software is an extension of SIAR running on R software that uses four packages for its proper performance: SIAR, xlsx, RDCOMClient and pixmap. This makes the CSSIAR a user-friendly software that incorporates several features described in de los Santos-Villalobos et al. (2017).

2.4. Quality assurance and quality control

Average standard deviations of reference replicate measurements no greater than ±0.5 across FAMEs were permitted. A calibrated internal standard (C12:0 or C13:0) and a reference mixture for use in both δ^{13}C-FA and bulk C calculations were added to each sample. Additionally, two reference mixtures, comprised of pure FAMEs of calibrated δ^{13}C, were co-analysed with the samples. One mixture was used for the isotopic calibration of the δ^{13}C measurements, while the other was not involved in corrections and instead served as the primary QA standard. Additional FAME mixtures were analysed to verify retention times.

2.5. CSSIAR 2.0 software validation

In order to test if the CSSIAR V2.0 model was able to decompose an artificial mixture, samples from different land uses taken in the studied catchments were combined in the laboratory in known proportions. For all samples, the percentage of carbon (%C), the bulk δ^{13}C, and the δ^{13}C-FA values were determined following the same procedure described above.

To convert the isotopic proportions to soil proportions the following equation was used:

$$\%\text{Source}_\text{n} = \frac{I_n/\%\text{C}_\text{n}}{\sum_n^1 \left({}^{I_n}/_{\%\text{C}_\text{n}} \right)} \times 100$$

where I_n is the mean feasible proportion of the “source n” in the mixture as estimated from isotopic values of carbon by the mixing model, and $\%C_n$ is the % carbon in the source soil (Gibbs, 2008). For the artificial mixtures, the soil proportions were calculated using the above formula and the respective % C for each source.

2.6. Statistical analysis

Data were analysed using a Kruskal-Wallis H test. This test was used to clarify which fingerprint properties (FAMEs isotopic values) best differentiate the possible sources. Variables were excluded from the analysis when the “*p* value” was less than 0.05 and the “H value” was higher than 5.99 (Collins et al., 1997b). To visualise the data, principal component analysis was carried out using the SIMCA-P 10 package from Umetrics, which allows one to elucidate the general behaviour of observations (samples) and variables (chemical compounds) in a complex dataset (Mudge, 2007).

2.7. Fatty acid selection

One of the key aspects of the soil apportionment calculations is the selection of the most suitable fatty acids for source discrimination (de los Santos-Villalobos et al., 2017). In this study, the fatty acid selection was carried out by evaluating the validity of the point-in-polygon criterion. This criterion is based on the following principle: for a given mixture the δ^{13}C isotopic value(s) of all suitable fatty acids plotted against each other should surround the δ^{13}C-FA values of the mixture. This would mean that the sources were selected properly and that they in fact contribute to the studied mixture. Fig. 3 shows an example of the dispersion plot of three sources and one mixture where: i) The selected fatty acids are eligible candidates to be used in the calculations when the mixture falls into the polygon formed by the δ^{13}C-FA values of the sources (Plot A); ii) The selected fatty acids are ineligible when the isotopic value of the mixture falls outside of the δ^{13}C polygon of the sources, and so other fatty acids should be selected when running the mixed model (Plot C). However, most of the time, the above selection process is visual and relies on the observer's criteria. Here we used a mathematical approach to aid the selection of criterion to determine the most appropriate fatty acids in the soil erosion calculations. Specifically, the angles that are formed by the δ^{13}C of a pair of selected fatty acid isotopic values or of the mixture(s) and the sources were used to calculate the most likely sources. Fig. 3 shows the possible scenarios and how the calculations, through an Excel spreadsheet, are used to discriminate the best fatty acids. The Excel spreadsheet was used to confirm when the mixture was inside the polygon. In Fig. 3 three different scenarios are shown: i) the angles formed by the sources and the mixture are all smaller than 180°, and thus the proposed fatty acids are suitable (Plot A). ii) When the mixture falls on a straight line between the two sources, and forms a maximum angle of 180°, the fatty acids proposed are still suitable (Plot C). Finally, iii) the value of the mixture falls outside the polygon formed by the mixtures, forming an angle greater than 180° in at least one of the triangles formed with two isotopic values of the mixtures (Plot C). In this last scenario the pair of δ^{13}C of the selected fatty acids, or at least one of them, should not be used to run the mixed model; thus, the selection of fatty acids is rejected. Based on the above-mentioned procedures, three fatty acids were selected to conduct the calculations in this study.

3. Results and discussion

A summary of the isotopic values (δ^{13}C-FA) for the sources and the mixtures can be found in Table 2. In general the bulk δ^{13}C values were very similar between samples, and greater differences were observed in the δ^{13}C values of the fatty acids. Thus, it can be seen that the identified land uses have unique isotopic signatures.

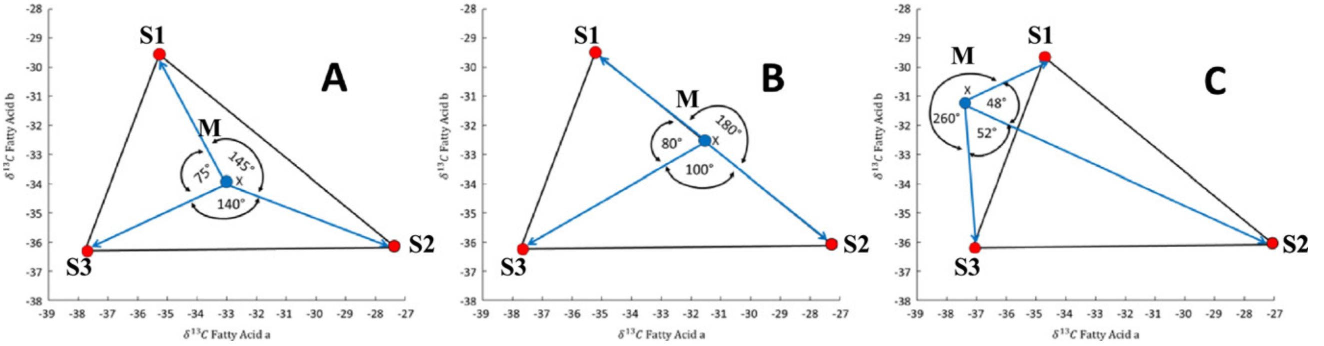

Fig. 3. Illustration of the three possible scenarios in the selection of the most suitable fatty acids. The dispersion plots depict the δ^{13}C values of two fatty acids from three sources and one mixture. The position of the red (sources) and blue (mixture) spots in the graph are based on three hypothetical scenarios.

3.1. Quality assurance and quality control

Based on the criteria explained above for the fatty acid selection, the predicted apportionment results obtained for the artificially composed soil mixtures through modelling followed the same trend as that found for the collected soil samples (see Table 3). Considering the statistical mean ± the standard deviations calculated by the mixed modelling software, the values obtained for the soil samples were within the same range in all cases. This means that the software used gave an appropriate estimate of each potential source of the sediment mixture, and these estimates were within definable limits (Gibbs, 2008).

It should be noted that it is important to select the most suitable δ^{13}C-FA to perform calculations. Here we obtained better results using three different fatty acids for each mixture (for mixture 1: C16:0, C18:0 and C18:1; for mixture 2: C16:0, C16:1, C18:1) when using four sources and one mixture. This approach was previously highlighted by other authors suggesting the use of a minimum of n-1 properties to distinguish between n sources (Reiffarth et al., 2016; Walling, 2013). It may be possible to generate more artificial mixtures to compare to the obtained results; this could be done using Mid Infrared Spectroscopy - DRIFT-MIRS - (Poulenard et al., 2012) or Fallout Radionuclides (FRN) (Schuller et al., 2013), among others (Guan et al., 2017). Nevertheless, completely uniform conditions may be difficult to obtain for all catchments due to slight differences in sampling and/ or analytical methodologies (Reiffarth et al., 2016; Upadhayay et al., 2017).

3.2. Principal component analysis (PCA)

The PCA accounted for 54%, 63%, and 79% of the variance in the data for the Nacimiento, Quivolgo, and Los Ulmos catchments respectively (Fig. 4). It indicated that the potential sediment sources had different isotopic signatures; thus, sources could be differentiated and apportionment calculations could be conducted. As stated in the introduction, one of the limitations of the FRN fingerprinting technique used in a previous study was the difficulty of differentiating between different land uses. In this study, multiple samples collected from the same source type generally clustered together. Despite this, some samples from buffer zones and roads presented different signatures within the catchments. These differences could be attributed to sediment inputs from surrounding areas or areas at higher elevations. Concerning the PCA for the Quivolgo catchment, the native forest data cluster near the pine forest data. This was expected as these samples were collected in an area that

Table 2
Summary of the average isotopic values (± standard deviation) for the sources and sinks in the studied catchments.

Fatty Acids										
Sources and deposition zones	Bulk carbon	Myristic (C14:0)	Palmitic (C16:0)	Palmitoleic (C16:1)	Stearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)	Arachidic (C20:0)	Behenic (C22:0)	Lignoceric (C24:0)
Nacimiento										
Pines	−27.3±0.2	−33.7±0.3	−30.6±0.4	−28.7±0.8	−28.6±0.4	−30.0±0.2	−31.6±0.5	n.d. -	−30.5±0.3	−31.0±0.1
Eucalyptus	−27.4±0.1	−34.2±0.6	−31.0±0.3	−30.5±0.7	−29.7±0.5	−29.6±0.4	−31.4±0.6	−33.8±0.0	−31.1±0.2	−31.9±0.5
Roads	−27.2±0.4	−33.4±0.3	−30.5±0.8	−29.8±0.8	−29.3±0.4	−29.8±1.0	−31.2±0.6	−31.0±2.2	−31.0±1.7	−31.1±1.7
Buffer zone	−27.1±0.2	−33.3±0.4	−30.3±0.5	−29.0±0.7	−28.6±0.4	−29.7±1.1	−31.9±0.9	n.d. -	−31.9±0.4	−32.4±0.6
Stream channel	−27.5±0.3	−34.3±0.5	−30.3±0.1	−31.0±0.8	−30.6±0.3	−29.4±0.2	−31.1±1.1	n.d. -	−33.0±0.1	−32.8±0.4
Weir	−27.5±0.2	−33.7±0.8	−30.2±0.7	−30.2±0.4	−30.5±0.4	−29.5±0.6	−32.3±1.2	−30.3±0.8	−32.5±0.5	−33.0±1.0
Quivolgo										
Pines	−28.0±0.3	−33.2±1.4	−29.4±1.0	−27.5±1.9	−28.0±0.9	−27.7±2.5	−28.3±0.8	−29.0±0.9	−28.2±0.8	−27.7±1.9
Roads	−27.3±0.4	−32.5±0.4	−31.3±0.8	−32.1±1.1	−29.6±0.6	−28.5±0.9	−30.0±0.5	−31.5±1.2	−29.5±0.6	−29.0±1.1
Buffer zone	−28.2±0.4	−30.9±0.6	−28.7±1.3	−28.9±0.4	−28.8±0.8	−31.3±4.6	−27.8±2.3	−31.7±0.6	−31.2±0.4	−30.8±1.0
Native forest	−28.0±2.3	−31.0±2.3	−29.3±0.8	−27.8±1.6	−29.0±0.7	−26.5±1.1	−28.5±0.9	−30.3±0.7	−29.7±0.8	−29.7±0.7
Stream channel	−28.1±0.4	−30.5±0.6	−28.7±0.4	−27.9±0.3	−28.8±0.2	−25.0±4.2	−30.2±0.8	−31.6±0.7	−30.8±0.6	−30.9±0.4
Weir	−28.3±0.2	−31.0±1.6	−29.0±0.7	−28.2±0.6	−29.3±0.4	−26.3±2.4	−28.9±0.8	−30.2±1.2	−30.2±0.1	−30.6±0.1
Los Ulmos										
Pines	−28.9±0.2	−31.6±1.3	−27.4±1.2	−28.7±1.7	−27.0±0.5	−26.4±0.9	−29.2±1.2	−29.3±0.6	−28.4±0.8	−28.7±0.9
Eucalyptus	−29.3±0.4	−35.0±1.7	−29.4±0.3	−29.8±1.3	−27.9±0.8	−27.9±0.5	−30.9±0.5	−30.0±0.5	−29.7±0.4	−29.9±0.2
Roads	−28.9±0.8	−36.8±1.5	−30.4±1.5	−30.1±1.6	−28.2±0.7	−28.0±2.6	−31.1±3.5	−31.3±1.2	−30.7±1.0	−31.2±1.1
Buffer zone	−28.2±0.3	−31.6±0.4	−29.3±0.4	−29.3±0.8	−28.8±0.6	−29.4±0.7	−30.8±0.7	−31.4±0.7	−29.8±0.9	−30.6±1.0
Stream channel	−28.1±0.3	−32.9±1.2	−30.5±0.9	−32.0±2.3	−29.1±0.4	−30.0±0.9	−32.6±1.0	−31.3±0.1	−30.5±0.4	−31.4±0.4
Weir	−28.2±0.3	−32.2±1.2	−30.1±0.4	−30.5±1.1	−29.6±1.1	−30.8±1.2	−31.6±0.4	−31.6±0.5	−30.2±0.6	−31.0±0.6

n.d.: Not detected.

Table 3
Real and predicted soil proportions from four land uses (*i.e.* sources) for two artificial mixtures using the software CSSIAR v2.00 and the respective isotopic values of the artificial mixtures and sources.

Land use	Mixture 1		Mixture 2	
	Real soil proportion (%)	Predicted soil proportion (%)*	Real soil proportion (%)	Predicted soil proportion (%)
Eucalyptus	7	6 ± 2	11	7 ± 7
Pine	8	9 ± 6	25	24 ± 1
Unpaved road	64	64 ± 12	58	63 ± 11
Native forest	21	21 ± 7	6	6 ± 9

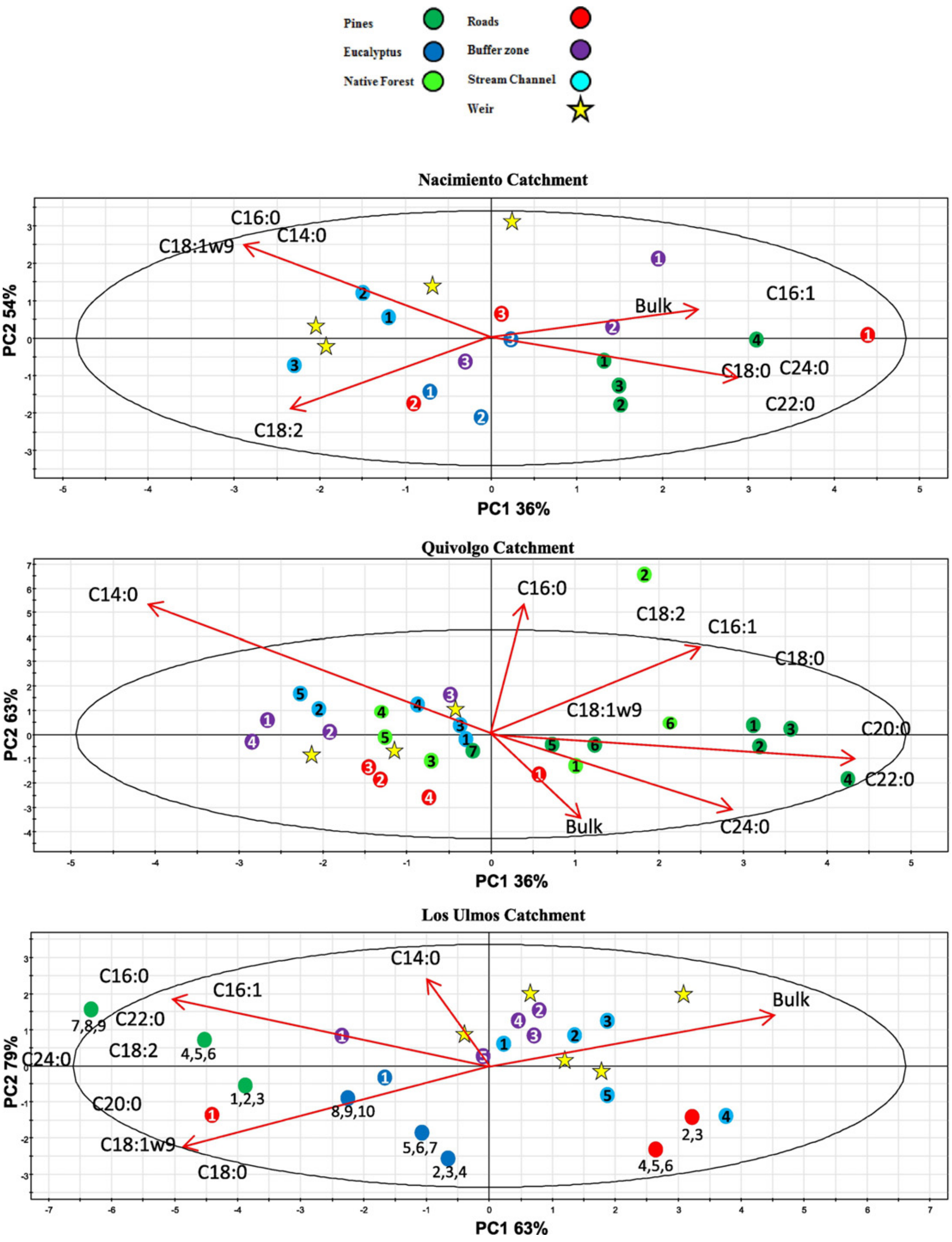

Fig. 4. Principal Component Analysis (scores and loadings) showing the distribution of the different isotopic signatures of the fatty acids for the sources, sediment mixtures, and weir samples investigated in the catchments. Note that eight samples are composed of two or three subsamples in the Los Ulmos catchment.

is surrounded by pine plantations, and the hill slopes favour the movement of soil from the pine forest towards the native forest plantations.

While samples from a given source type were generally similar, the road samples had very different isotopic signatures. Differences in road samples were particularly apparent in the Quivolgo catchment and to a lesser extent in the Los Ulmos catchment. One explanation for this might be that roads have signatures of soil that was exposed many years ago as machines must dig through the present vegetation to build them. Additionally, road samples may be influenced by the sediment and chemical properties of the surrounding vegetation. For example, sample "road 1" in Los Ulmos is entirely surrounded by pines, and in the PCA, this sample clusters together with the pine samples.

The weir samples were very similar to the stream channel samples, and this was observed for all catchments. These results suggest that the stream channel plays an important role in the redistribution of sediment.

3.3. Sediment apportionment

3.3.1. Sources of sediment along the stream channel

The variability in sediment origin within the catchments was assessed by analysing sediment samples taken from different positions along the stream channel (Fig. 5). Land uses located above the stream channel (in the high, middle and low part) were considered as sediment sources. Using this approach, it was found that the sediments from the stream channels of all three catchments (up-stream from the weir at the outlet of the studied catchment) mainly originated from the unpaved forest roads; specifically, 20 to 98% of the soil originated from roads (See Fig. 5). Samples taken from the upper part of the catchments had the highest percentages of soil originating from roads due to the proximity to the frequently transited road. The wide variability in rainfall, the different length and slope of the roads, and the periods when sampling was conducted did not change this pattern.

For the middle and lower parts of the stream channel, the mixed model calculations showed that the other land uses, such as pines and native forest, contributed sediment in Los Ulmos and Quivolgo. In Los Ulmos, the buffer riparian zone was identified as a significant contributor (based on the samples taken at positions 1, 2, and 3 in the stream channel). Nevertheless, it is not likely that the buffer zone is a significant source of sediments but rather an area of sediment transit and trapping. Therefore, the buffer zone covered by native forest was treated as a mixture and additional calculations were performed to clarify the origins of the sediments found in this area. This resulted in the finding that the main sediments in the buffer zone were rather sediments coming from a very steep road nearby. These additional calculations confirmed that the buffer zone itself was not a source for sediments, but was a transition zone for the sediments coming from the upper slopes. Calculations done

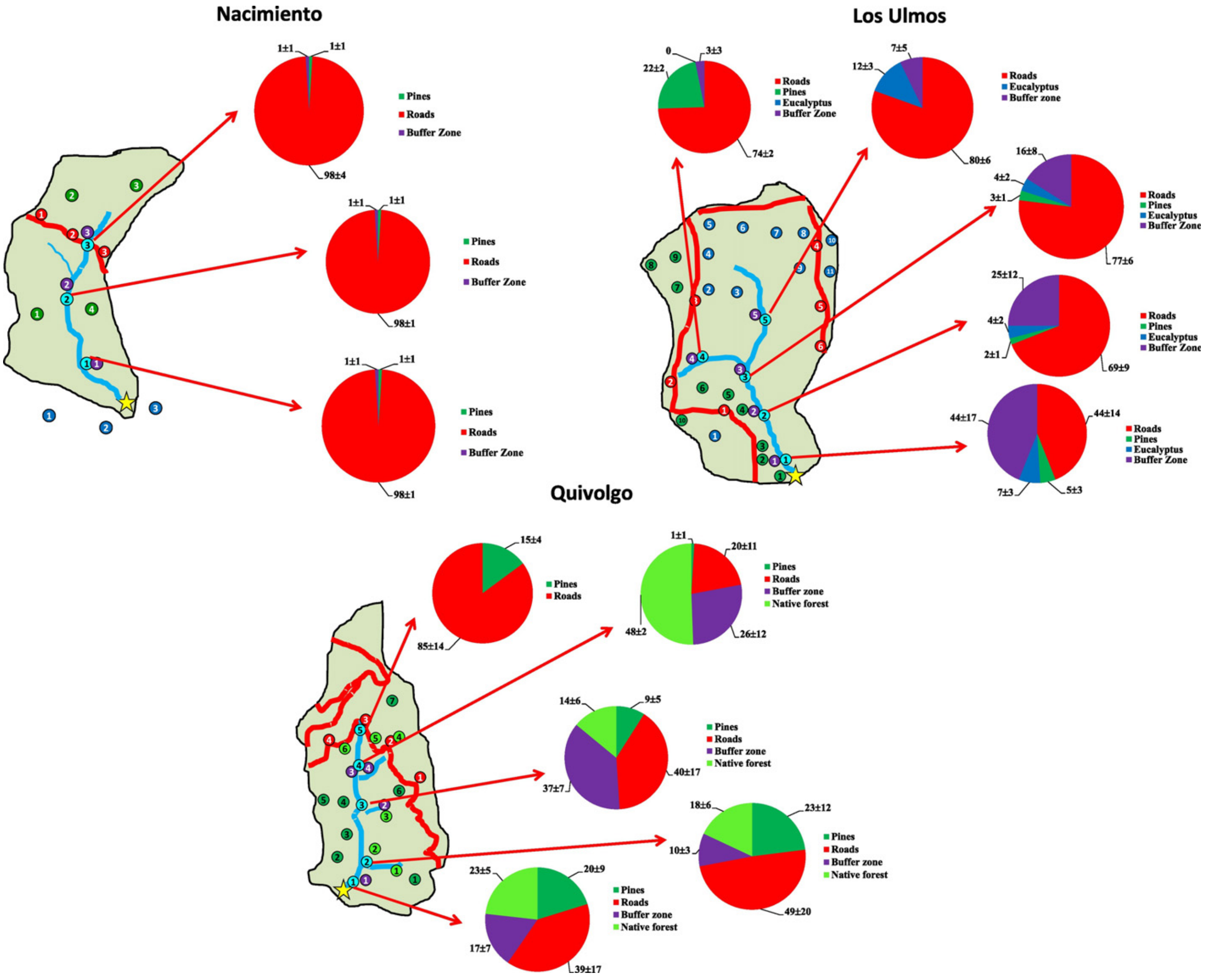

Fig. 5. Sediment apportionment for samples taken along the stream channels (excluding the weir samples) in the three studied catchments (± values represent the standard deviation obtained by the mixed model).

without this land use (buffer zone) as a source (data not shown) showed that roads are the dominant source of sediments in all catchments. In Quivolgo, the upper part of the catchment was dominated by sediments from roads as stated above. The intermediate and lower parts were more influenced by the other land uses such as pine, buffer zones, and native forest; nevertheless roads were the dominant source of sediments. Conversely, in Nacimiento, roads were the main source of sediments throughout the stream channel.

The sampling strategy used, with different sampling positions along the stream channel proved to be essential to understand the processes of sediment transport along the stream. Without this approach and having only one position sampled at the outlet of the catchments (weir), the main erosive processes, *i.e.* road degradation, would have been underestimated. Subsequently, the strategy for reducing sediment loads in the stream would not have been correctly identified, as sediment transport mechanisms may have been interpreted as a natural processes that are difficult to manage. In fact proper management, implementation, and maintenance of forest roads, can reduce the amount of sediment originating from forest roads (Begus and Pertlik, 2017), and this is especially true in areas with steep slopes and high rainfall intensity.

Because the catchments have not yet been harvested, the soils are stable and vegetation (*e.g.* pine needles) creates a soil cover that protects the soil from direct rainfall that causes soil erosion (Li et al., 2014). Therefore, sediment pathways may significantly change when clear-cut operations take place. However, this study only looked at the temporal variation in sediment origin under pre-harvest conditions.

3.3.2. Temporal variation in sediment origin

Analysis of the weir samples, representing the sediments deposited between two sampling time points, showed that the main source of sediments was roads regardless of temporal period (see Fig. 6). These results were in agreement with those found for sediments collected along the stream channels (see Fig. 5). Furthermore, it can be concluded that the origin of sediments in a non-harvested catchment and with a mature forest do not change throughout the year.

During the wet season in Quivolgo (see Fig. 6 for Quivolgo, the first two samples were taken during the rainy season), sediments were mainly derived from roads. At the ending of the rainy season (see Fig. 6, third sample for Quivolgo catchment) all land uses contributed equally to the origin of sediments. Conversely, in Nacimiento, the roads dominated the sediment contributions during both the wet and the dry season. In Los Ulmos, the contributions were shared between roads and the buffer zone. Nevertheless, we have previously highlighted that buffer zones are often a transition area that is mainly comprised of by road sediments; thus, the high contribution of the buffer zone in Los Ulmos could be masking greater proportions of soil originating from roads.

By multiplying the proportion for each land use by the total sediment yield, it was possible to estimate the amount of sediment coming from each land use type within the catchments. When considering the large differences in yearly sediment yields among the three studied catchments, (ranging from 84 up to 1182 kg ha^{-1} and correlated with differences in rainfall $-R^2 = 0.88$, $n = 3-$; Table 1), the total sediment yield from the main source, *i.e.* roads, is very different from catchment to catchment. Specifically, the yields in the driest and wettest catchments differed by a factor of fourteen. However, it is difficult to know if rainfall is the only driver for these differences as only three catchments were studied. To understand the specific role of the other catchment characteristics, such as catchment slope gradients, and road length or road slope gradient, more analysis must be done. Additionally, it should be noted that the Quivolgo catchment had a very low sediment yield compared with the other catchments (considering that amount of rain was relatively similar to that in Nacimiento). This can be explained by the state of the soil, which is extremely eroded (Leptosol-Haplic Luvisol). Furthermore, the stream channel is very stable and does not transport much sediment.

3.4. Forest management and sediment redistribution

As commercial forest plantations in Chile cover about 2.5 million ha and resources for soil conservation are limited, it is important to have tools that can assist in identifying hotspots of erosion. The large impact that forest plantations can generate on water quality during forest road construction or logging can be mitigated only when sediment sources are identified. Here the studied catchments were characterised by low sediment contributions from forest plantations and higher contributions from roads. This was expected as forests were not harvested at the time of the assessment, and the soil was covered with vegetation (Schuller et al., 2013). In Chile, forest plantation roads are mainly bare soil, and in some cases covered with some layers of gravel to stabilise them. Studies have highlighted that unpaved roads contribute 20 to 60 times more sediment than undisturbed forest and 10 times more sediment than harvested areas (Motha et al., 2003). This may be explained due to the hydrophobicity that exotic plantations cause on the surface of the soil (Doerr et al., 1998). On the other hand, (Ensign and Mallin, 2001) suggest that this situation can dramatically change (roads as a main source of sediments) when clear cut and heavy machinery is used. Clear-cutting has been shown to deteriorate water quality even when a 10 m buffer zone is left. According to previous studies in the Los Ulmos and Nacimiento catchments (comparing the pre-harvest and post-harvest scenarios), the amount of sediment yields after clear-cutting were three to seven times higher compared to pre-harvest conditions (Schuller et al., 2013).

Here the CSSI technique allowed use to determine the partial contribution of different land use types to sediments deposited in stream channels. These techniques have been shown to be useful in assessing soil erosion in forestry catchments and targeting improved management of sediment sources (Hancock and Revill, 2013). In addition, it is important to highlight that the CSSI technique can also be very useful to determine sediment yields. The contribution percentage can seem to be a big number (*e.g.* 80% coming from roads), but this percentage can be a partial contribution of a small or big amount of sediment yields.

Moreover, forest management practices, road infrastructure, and erosion mitigation and its efficiency are also influenced by other factors such as soil type. In this study we had three different types of soil, from stable Andosol to very erosive Leptosols, which are very different in terms of stability; this stability can influence sediment delivery.

4. Conclusions

This paper validates for the first time the use of $\delta^{13}C$ signatures in fatty acids for establishing base line information regarding the spatial and temporal character of sediment pathways in upland commercial forest catchments under pre-harvest conditions. This technique is shown to be useful, efficient, and cost-effective when identifying areas susceptible to soil erosion and sources of sediments in forest catchments. Although the studied sites were limited in size, with a maximum of 40 ha, here we illustrate the importance of not relying on just one sampling at the outlets of catchments. Sampling along the stream channel may be additionally justified due to the fact that the original signal of the sediments in the stream channel may alter, as sediment transport is limited by the flow speed of the stream. Hence, sampling sediments that are carried by the streams from the upper part of the three catchments helped clarify the origin of the sediment transported by the water. With this sampling approach, we found that sediments mainly originated from the roads; thus efforts should be focused to control or mitigate soil erosion in these areas.

Seasonal sampling did not show any significant differences, and roads were the main source regardless of sampling time. However, further investigation needs to be done when extreme events occur, such as when there is extreme rainfall or forest fires as other studies have found that these events modifying the amount and sources of sediments (McIver

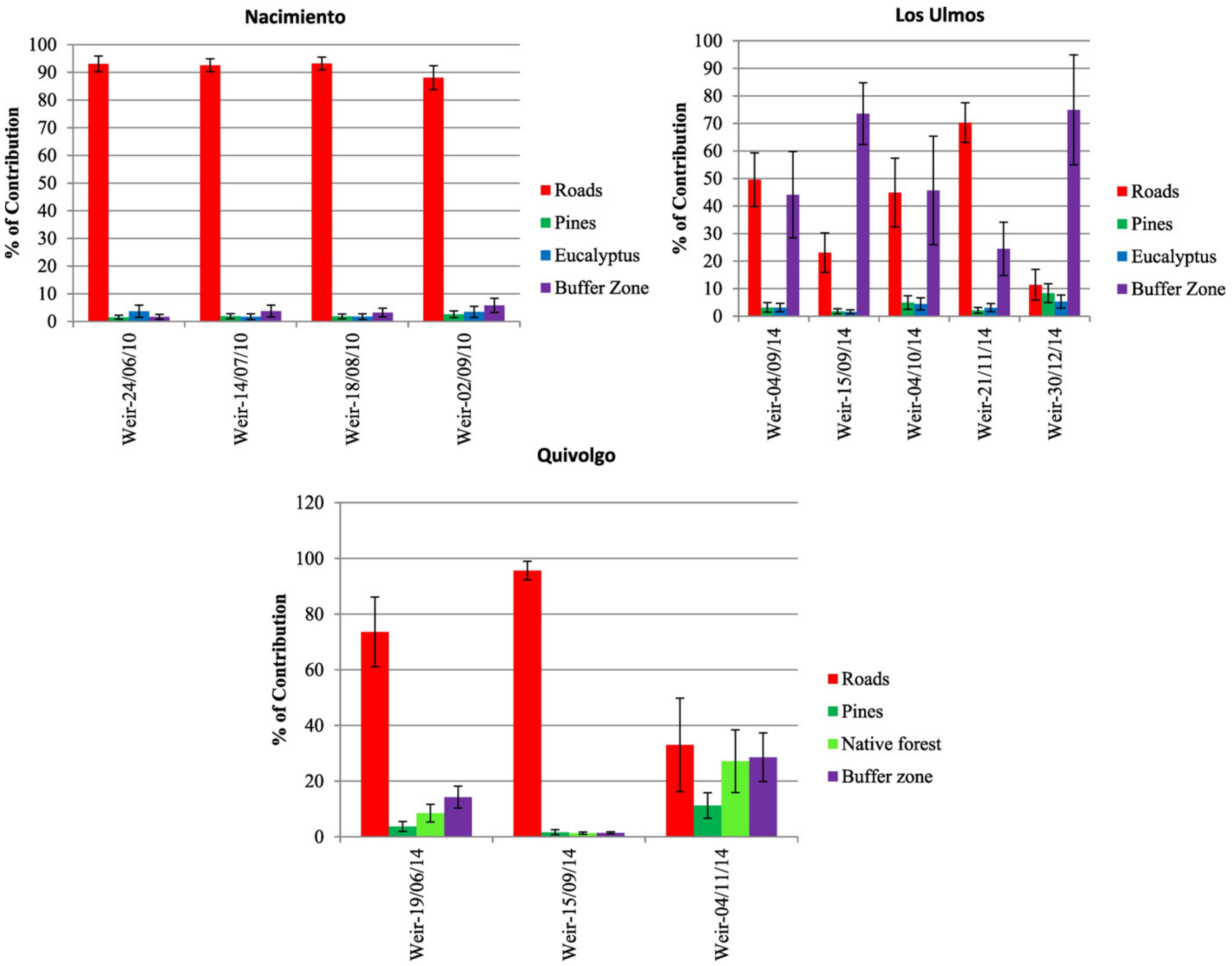

Fig. 6. Temporal variation in sediment origin for samples taken at the outlet (weir) of the three studied catchments (error bars represent the standard deviation obtained by different iterations from the mixed model).

and McNeil, 2006) or cause an enrichment in δ^{13}C signatures (Araya et al., 2017).

It is important to highlight that the technique used in this study can also be a complement to other isotope fingerprinting techniques (Guan et al., 2017), especially when differentiating between specific land use contributions. Future studies employing complementary techniques, such as using the δ^{13}C of *n*-alkanes or using hydrogen isotopes, should focus efforts to extend the abilities of mixed models to differentiate between sediment sources in order to help mitigate soil erosion and land degradation. In addition, the uncertainties of soil apportionment calculations can be reduced by correcting the isotopic proportions to soil proportions using amount of the biomarkers and not only the organic carbon content.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.09.163.

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We would also like to dedicate this study to all people that lost their possessions during the forest fire that affected a vast territory in central Chile during February 2017, where one of the study sites (Quivolgo catchment) was also entirely burnt.

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