Applied Geochemistry 82 (2017) 15–24

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Stable isotopes reveal human influences on southern New Zealand soils

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ARTICLE INFO

Article history:
Received 27 November 2016
Received in revised form
30 April 2017
Accepted 2 May 2017
Available online 5 May 2017

Handling Editor: Prof. M. Kersten

Keywords:
Stable isotopes
Carbon
Nitrogen
Sulphur
Anthropogenic impact
Regional survey
Soil
New Zealand

ABSTRACT

A multi-isotopic soil study across a southern New Zealand transect has been undertaken as part of a geochemical baseline survey to identify human impacts on New Zealand's landscape and characterise different land uses and anthropogenic effects. Carbon, nitrogen and sulphur isotopes from two soil depths (0–30 and 50–70 cm) were acquired across a variety of land uses (including pristine national parks, urban centres, intensively farmed pastoral land), climates (dry <500 mm annual rainfall to wet >6000 mm annual rainfall), altitude (sea level to >2300 m above sea level) and soil parent material lithology (sandstone, schist, basalt). Detrital organic matter accumulated more in lowlands than at higher altitudes with higher carbon and nitrogen contents found in river valleys. Carbon isotopes clearly differentiated between drier higher altitude or open pastoral sites (more positive values) and wetter forested sites (more negative values). Nitrogen isotopes reflect anthropogenic human influence with elevated values around urban and intensively farmed sites, and lower values characterising indigenous forests and pristine sites. Sulphur isotopes either show more positive values, typical of fertilisers, rain or sea spray in open pastoral sites, or more negative values consistent with weathered geological sources such as metamorphic sulphides found in schist in some river valley sites. The study demonstrates that regional isotope studies are a potential tool to understand the long and short term impacts on landscapes, and may be useful for future mineral exploration, urban health studies, agricultural site remediation, and land use control and regulation.

1. Introduction

Regional geochemical baseline studies have been widely used to examine the geological and anthropogenic contribution of specific elements to soils. They provide an important tool to determine environmental baselines and undertake economic mineral exploration. Large scale regional, national, and continental scale soil studies have been undertaken in Europe (Cohen et al., 2012; Rawlins et al., 2012; Reimann, 2005; Salminan et al., 2005), China (National Soil Survey Office, 1998; Jiao et al., 2010), Australia (de Caritat and Cooper, 2011) and North America (Smith et al., 2013). These integrated studies have provided important databases and geochemical maps for public, economic, environmental and regulatory interests in both urban and rural areas. These international baseline studies are being used to monitor the impact of human activities and provide strategies to protect urban and rural environments against contamination or pollution (Kelly et al., 1996). More recently they are being integrated into forensic provenancing and traceability studies to provide ground-truthing and checks on agriculture systems (Lark and Rawlins, 2008; Martin et al., 2012; Font et al., 2015).

Recently, a systematic grid-based regional multivariate geochemical study has been undertaken for the first time in the southern South Island to evaluate the usefulness of regional baseline mapping across New Zealand landscapes (Martin et al., 2016, Fig. 1). The outcomes from this study will benefit government, environmental, agricultural, forestry and mining sectors by providing key geochemical baselines which can improve regulatory guidelines and understanding of the regional geochemical landscape. This study builds on work reported by Martin et al. (2016) by undertaking a multi-element stable isotope study of these southern South Island soils across a regional transect with the aim of

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http://dx.doi.org/10.1016/j.apgeochem.2017.05.006
0883-2927/

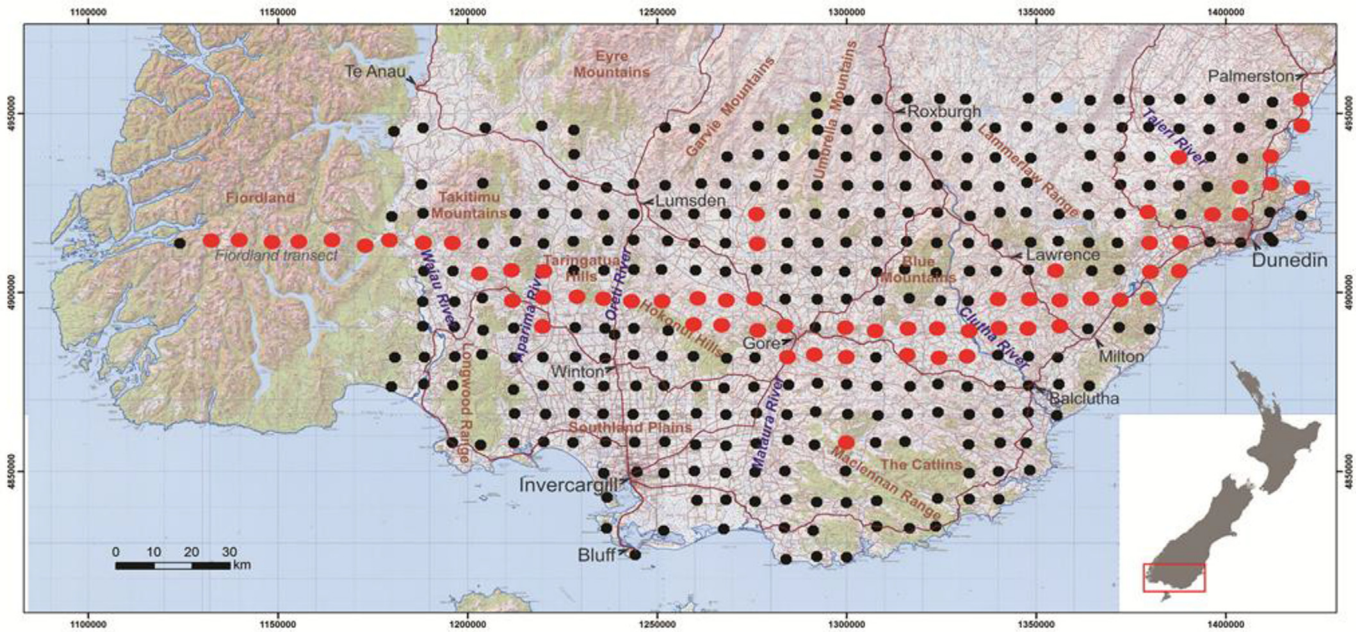

Fig. 1. Southern South Island survey area. The multi-isotope transect (this study) is represented by red dots (n = 67 sites) while the black dots represent sites sampled in the geochemical survey but not analysed for isotopes (Martin et al., 2016). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

understanding anthropogenic and natural influences across a diverse landscape.

Environmental stable isotopes (^{13}C, ^{15}N, and ^{32}S) are more commonly used in conjunction with hydro-chemical data to study regional groundwater patterns (Oetting et al., 1994; Porcelli and Baskaran, 2012), specific geological formations for petroleum (Ridgley, 2002), environmental contamination (Miljević and Golobočanin, 2007; Rogers et al., 2012) or minerals exploration (de Caritat et al., 2004) rather than the natural baseline attenuation of soils. Our novel study uses two different soil depths to assess the geological and anthropogenic availability and origin of carbon, nitrogen and sulphur. We determine soil carbon, nitrogen and sulphur isotope baselines for future environmental and ecological studies, particularly for nutrient and energy uptake where these elements are transferred into ecosystem components (grass, plants, herbivores, carnivores). Moreover, New Zealand's primary agriculture based industries could benefit significantly from the authentication and traceability tools which could be developed for regional or country of origin provenancing.

New Zealand is a unique environment to study environmental anthropogenic impacts due to its isolated location in the southern hemisphere, its sparse population (with the arrival of Europeans only some 200 years ago) and its predominant cover of either indigenous forest or pastoral agriculture. Currently around 39% of New Zealand's land cover is pastoral agriculture, 9% in exotic forest and more than 50% under native land cover, primarily tussock and forest in upland areas (Mudge et al., 2014).

Low population density and areas of intensive pastoral farming in the southern South Island result in specific influences and impacts on the landscape which are unique to this region. Combined with a diverse pre to Late Cretaceous metamorphic and igneous basement geology, which is carbon and nitrogen poor but in places sulphur-rich, human effects which typically accumulate the fertilizer-derived nutrients, N and S, in organic matter, allowing areas of human modification to be easily distinguished (using elemental and isotopic abundance) from pristine terrain.

New Zealand's landscape is dominated by C3 plants which fix carbon dioxide using the ribulosodiphosphatecarboxylase (RuDP carboxylase) enzyme. These C3 plants discriminate against the heavier carbon isotope (^{13}C), and hence the isotopic fractionation from atmospheric CO_2 (−8‰) is more pronounced (C3 plants: −33 to −24‰) than in C4 (C4 plants: −16 to −10‰, grasses, corn, cane sugar, etc) and CAM (CAM plants: −20 to −10‰, pineapple, orchids, cactus etc) plants which use phosphenolpyruvatecarboxylase (PEP carboxylase) and undergoes photosynthesis up to six times faster than C3 plants.

In forested canopies, atmospheric CO_2 (−8‰) is transferred through respiration into leaves. When these leaves are incorporated into topsoil, the fresh leaf litter accumulation retains the more negative $\delta^{13}C$ values before slowly being bacterially degraded (and isotopically fractionated) towards more positive $\delta^{13}C$ values as ^{12}C is preferentially consumed over time and the soil profile is built up with age (Natelhoffer and Fry, 1988).

While carbon isotope values ($\delta^{13}C$) of topsoil can indicate current C3 and C4 plant cover (Deniro, 1985), it can also be used in conjunction with increasing soil depth as; a proxy for past habitat according to vegetation type, the atmospheric composition at the time that the carbon was stored (Suess effect; Revelle and Suess, 1956), and identifying more recent land-use change.

Carbon isotopes can even indicate climate change effects as they are negatively correlated with shade and water use efficiency (Farquhar and Richards, 1984; Farquhar et al., 1989; Seibt et al., 2008; Brookman and Ambrose, 2012; Rawlence et al., 2016). Usually more positive $\delta^{13}C$ values are biased towards drier and open ecosystems due to stomatal closure in response to evaporative demand causing decreased photosynthetic discrimination (Bowling et al., 2014), while more negative $\delta^{13}C$ values are typical of wetter closed-canopy forests (Kohn, 2010).

Natural abundance of nitrogen isotopes ($\delta^{15}N$) provides a good insight into large-scale terrestrial ecosystem inputs and N-cycling, along with changes in water-nitrogen interactions. Nitrogen soil isotopes ($\delta^{15}N$) are frequently used to investigate synthetic