



The regional geochemical baseline soil survey of southern New Zealand: Design and initial interpretation



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ABSTRACT

A multivariate geochemical baseline survey of soils from southern New Zealand has been completed. Soil samples were collected from 0 to 30 cm 'A-depth' and 50–70 cm 'B-depth' at 348 sites on an 8 km-spaced grid covering 40,000 km² of the Southland and southern Otago regions. The sub-180 μm fraction of all samples was analysed by inductively coupled plasma mass spectrometry following aqua regia (partial) digestion for 65 elements, and by Leco CS320 element analyser for total C and S. Sub-sets of the samples were analysed by XRF for 12 oxides/elements. Significant chemical variation in the soil samples can be linked to variations in source geology, soil type, climate and topography. Relatively high concentrations of certain elements (e.g. S, P, Pb, Hg, Cd), particularly in the A-depth, are attributed to anthropogenic sources such as fertilisers, paints, vehicle emissions or industrial emissions. Other elevated element concentrations, especially those in B-depth samples, are probably natural with high As, Bi, Sb and W reflecting proximity to Au mineralisation, Pt and Re near PGE mineralisation, and accumulation of heavy mineral-associated elements such as Cr in alluvium-derived soils related to the effects of both source material and hydraulic effects on flood plains. This study provides an important baseline that will benefit government, environmental, agricultural, forestry and mining sectors through improved regulatory guidelines and understanding of the regional geochemical landscape. This survey design, with minimal modification, is suitable for a national geochemical baseline survey for New Zealand.

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1. Introduction

Geochemical datasets for soil and other surficial materials are an important component of environmental baseline studies. They can be used to assess the extent of anthropogenic activity superimposed upon natural influences (Plant et al., 2001). They are applicable to a wide variety of environmental and economic purposes such as the setting of environmental regulatory limits (Cohen et al., 2012; Darnley et al., 1995), soil fertility (Clare, 1981), forensic studies (Reimann and Caritat, 2012), public health (Plant et al., 2001), agriculture (Webber, 1981), forestry, water supply and irrigation (Purchase and Fergusson, 1986), waste disposal, mineral exploration and mining (Ward et al., 1977; Ward and Brooks, 1978), industrial pollution (Deely et al., 1992) and transport and urbanisation (Fergusson et al., 1980). A number of regional, national and continental-scale geochemical baseline soil surveys have been conducted in several parts of the world, including Europe (Cohen et al.,

2011; Rawlins et al., 2012; Reimann et al., 2011a; Salminen et al., 2005), China (National Soil Survey Office, 1998), Australia (de Caritat and Cooper, 2011) and North America (Smith et al., 2013). There has been significant work in New Zealand to understand soil distribution, development and properties. For example, Landcare Research has synthesized soil surveys over most of New Zealand into a single data layer: the Fundamental Soils Layers, which shows important chemical attributes such as minimum pH and total Carbon (soils.landcareresearch.co.nz/contents/SoilData_FSL_Maps; accessed 14 April 2016). This is being replaced by S-map: the digital soil spatial information system for New Zealand (Lilburne et al., 2004). S-map online (smap.landcareresearch.co.nz; accessed 14 April 2016) currently shows soil type, drainage, depth and moisture content amongst other factors for some parts of New Zealand. Numerous soil chemical studies have been undertaken from selected sites in New Zealand for a variety of purposes (e.g. Childs et al., 1983; Kirkman et al., 1994), including the 500 soils project which sampled across New Zealand (Sparling et al., 2004 and references there-in) with 511 sample sites (excluding Southland and Westland) and which focussed on soil quality measurements (such as total C and

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N) rather than contamination or chemical baseline aspects. Yet, despite a long history of soil-related research in New Zealand, there has not been a systematic, grid-based national or regional study of the chemical composition of New Zealand soils, until now.

New Zealand represents a unique setting with respect to determining the natural geochemical baseline of soils. Unlike many other regions, New Zealand is sparsely populated and has a relatively short history of human occupation and land-use disturbance. Furthermore, significant tracts of New Zealand are designated as National Park (10% by area), and have had very minor anthropogenic modification. About 20% of New Zealand is public conservation land, with varying but generally low levels of anthropogenic influence. The relatively pristine nature of around a third of New Zealand's territory means that the natural geochemical background of its soils can be established and compared to

soils in other areas with similar geological conditions that have been affected by anthropogenic activities.

A regional, grid-based geochemical baseline soil survey has been completed in the southern part of New Zealand's South Island (Martin et al., 2015; Fig. 1). This paper presents the background, chemical results, methodology and quality assurance and quality control (QAQC) approach for the first New Zealand regional survey and presents highlights of the chemical data. These results have been examined for the adequacy of the survey design to show expected geochemical patterns, for example from underlying geology or anthropogenic input, and how the choices of survey design (such as sample spacing and analysis method) affected the chemical results. Finally, the suitability of the survey design for application to a national New Zealand survey will be assessed.

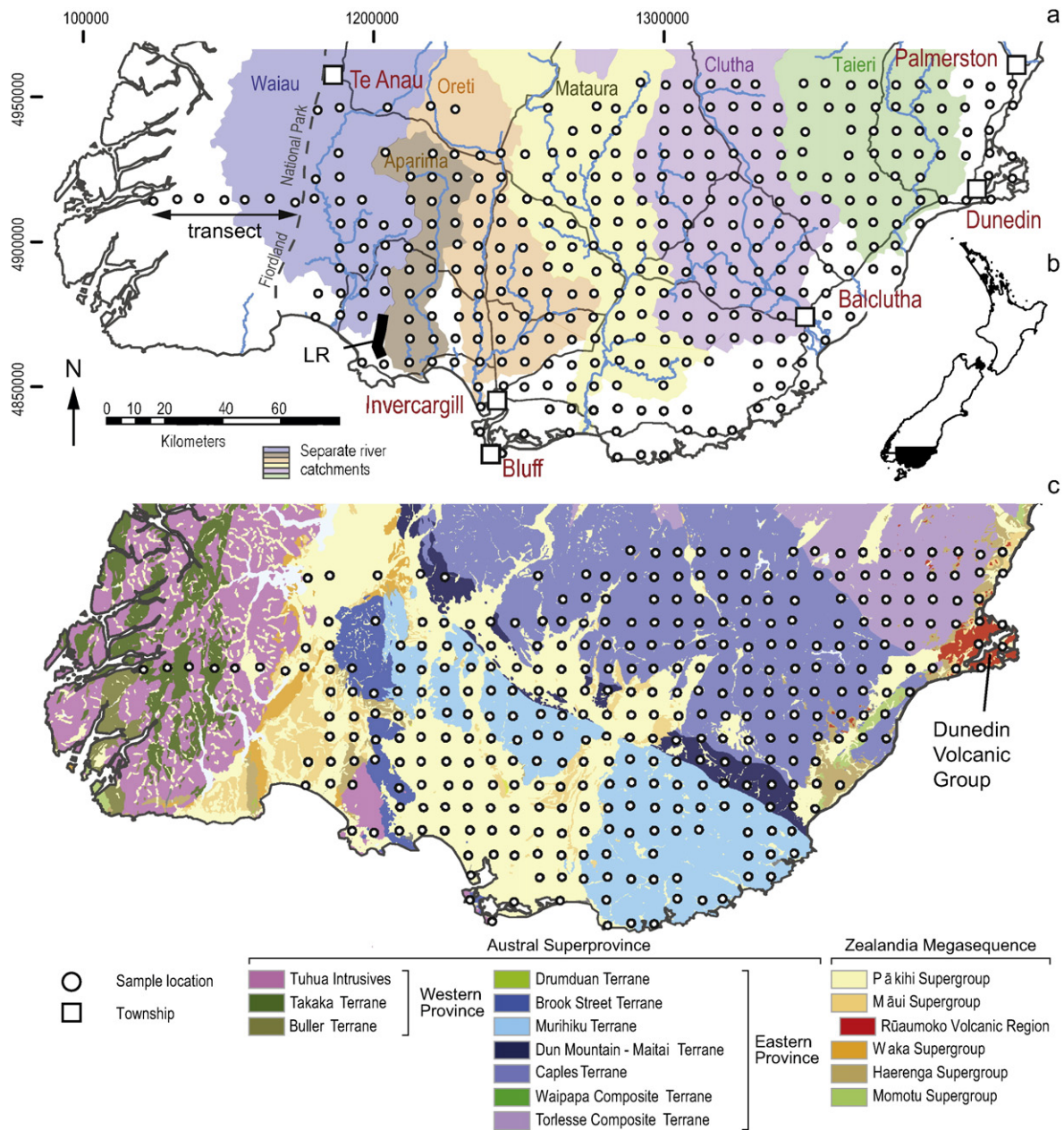


Fig. 1. Diagrams of soil sample locations in the southern South Island of New Zealand with river catchments and geology. a. Soil sample locations with major townships, roads, rivers and river catchments marked. Fiordland National Park is to the west of the dashed line and was sampled along one, west-east transect. LR = Longwood Range. b. Coastline of New Zealand showing the survey location. c. Soil sample locations with major lithostratigraphic units after Edbrooke et al. (2015) shown. The composition of each unit is summarised in Table 1.

2. The survey area

2.1. Geology, soil type, land use, climate and physiography

The area selected for the survey covers most of the Southland Region and southern part of the Otago Region, in southern New Zealand. The northern extent of the survey area terminates just south of the townships of Palmerston in the east and Te Anau in the west (Fig. 1a). The survey area extent was chosen in part because of its diversity of geology, land use, climate and topography. The geology of the survey area includes nine of the major terrane-level divisions of New Zealand's pre-Late Cretaceous metamorphic and igneous basement (Austral Superprovince, Mortimer et al., 2014; Edbrooke et al., 2015). In this survey, soils were sampled above the Buller, Takaka, Rakaia, Caples, Dun Mountain-Maitai, Brook Street and Murihiku terranes and the Tuhua Intrusives (Fig. 1b; Table 1). Each basement terrane is characterised by rocks of distinctive age and composition that relate to specific periods in the formation and evolution of Gondwana (Table 1). There are calc-alkaline volcanic, island arc igneous and volcanoclastic sedimentary rocks, continental-sourced quartzo-feldspathic metasedimentary rocks, I-, S- and A-type plutonic rocks and ultramafic ophiolite rocks. Soils were also sampled above younger (Late Cretaceous – recent) cover rocks and sediments that overlie the basement rocks (Zealandia Megasequence, Mortimer et al., 2014). These cover rocks are derived primarily from erosion of the basement rocks, and include siliciclastic and carbonate sedimentary rocks (Māui, Haerenga and Momotu supergroups), volcanogenic and volcanic rocks (including the Dunedin Volcanic Group), and widespread fluvio-glacial sediments of the Late Cenozoic Pākihi Supergroup (Table 1).

The southern South Island has a wide variety of soil types that have been influenced by local factors such as the rock type that the lithic material was sourced from, elevation and relief, climate (including total rainfall, temperature and wind), organisms, vegetation type and anthropogenic influences. Over 175 unique soil types have been recognised in the intensively farmed areas of southern New Zealand, which have been grouped into 15 major soil orders (Table 2; Fig. S1a). The survey sampled across nine of the fifteen different major soil orders with Brown soils (49%), Pallic soils (25%) and Recent soils (9%) predominant (Molloy and Christie, 1988) (Table 2). Three locations sampled 'urban soils', which are mapped separately, in a manner that precludes classification into any one major soil order.

The survey area has a cool temperate climate and a moderately high rainfall, with the greatest precipitation in Fiordland National Park (Fig. 1a) in the west (>4000 mm/year), and the lowest rainfall in parts of inland Otago Region (250–500 mm/year; Fig. S1b; NIWA, 2012). The

Table 2

The New Zealand soil orders at the sample sites.

Soil orders	#
Brown soils	171
Melanic soils	11
Pallic soils	88
Recent soils	32
Gley soils	17
Podzol soils	17
Ultic soils	5
Organic soils	3
Urban soils [¥]	3
Semiarid soils	1

#: number of sites; ¥: 3 samples collected within city boundaries are not yet assigned to one of the 15 New Zealand soil orders - they are described as 'urban' soils.

elevation of the survey area ranges from sea level up to 2300 m above sea level. Major drainage systems traverse the area, including the major south-draining rivers and catchments of the Waiau, Aparima, Oreti, Mataura, Clutha and Taieri (Fig. 1a). These river systems traverse many geological units, and several have headwaters and catchment areas at high elevations to the north of the survey area. Surficial materials deposited by these rivers during the Quaternary have been derived from varying sources, both from within the survey area, and further north. Soil development in southern New Zealand has also been affected by past fluctuations in climate. Several major glacial events occurred during the Quaternary, with glacier ice from the mountains to the north advancing to the northern fringes of the survey area, and sea level encroaching from the south and east during interglacial periods (Suggate, 1990; Turnbull and Allibone, 2003). During this period, the land was probably subjected to multiple cycles of soil development, erosion, rejuvenation and revegetation (Molloy and Christie, 1988). New Zealand's climate has remained relatively unchanged since the last glacial period c.14,000 years ago, and many of the soils in southern New Zealand date from this time.

A variety of different land-use types exist across the sampled survey area. The predominant use of land is classified as exotic grassland (76%; Fig. S2; Landcare Research Land Cover Database, retrieved 18 November 2015 from <https://iris.scinfo.org.nz/>) which largely represents farmed pastures (mostly for sheep, beef, deer and dairy farming). A significant proportion (12%) of land with native vegetation (alpine grassland, native forest and native scrub) was also sampled within the survey area, as well as exotic forests (mostly *Pinus radiata*) 8%. The remaining 4% of land uses sampled were urban (both built up and parkland), cropped farmland and exotic scrub.

Table 1

High-level geological units underlying the sampled sites.

Underlying geological unit	#	Unit description
Zealandia megasequence		
Pākihi SG	118	Pliocene-Quaternary sediment including alluvial gravel, sand and silt, glacial till
Māui SG	6	Oligocene-Miocene basalt, phonolite and trachyte lava flow, intrusive rocks
	15	Miocene-Pliocene sedimentary rock dominated by sandstone & mudstone
Haerenga SG	7	Paleocene-Eocene sandstone and mudstone
Momotu SG	1	Late Cretaceous-Paleocene breccia, conglomerate and sandstone
Austral superprovince		
Rakaia Tn	25	Triassic schist
Caples Tn	93	Triassic greywacke grading to schist
Dun Mtn-Maitai Tn	1	Permian ultramafic rock, partly serpentinitised
	0	Permian basalt
	6	Permian-Triassic sedimentary rock
Murihiku Tn	63	Triassic-Jurassic volcanoclastic sedimentary rock
Brook Street Tn	6	Permian volcanogenic sedimentary rock, limestone, basalt, andesite, gabbro, diorite
Tuhua Intrusives	4	Devonian-Carboniferous and Mesozoic granitic plutons
Takaka Tn	2	Cambrian-Ordovician metasedimentary rock, schist, and marble
Buller Tn	1	Ordovician metasedimentary rock

#: number of soil samples collected overlying this geological unit; SG: Supergroup; Gp: Group; Tn: Terrane; Mtn: Mountain.

2.2. Human history and land use

The first arrival of Māori to the area occurred in c. 1250–1300 CE. The arrival of European settlers in the 1800s increased the southern New Zealand population, but patterns have remained similar to pre-European settlement, with low population densities relative to the North Island (e.g. Holdaway et al., 2014). The current population of the survey area is c. 220,000 people, with over 70% living in the cities of Invercargill and Dunedin. Anthropogenic influences on the land as a result of human habitation include intensive agriculture (e.g. application of fertilisers, significant clearing and draining of wetlands), mineral exploration, mining (sometimes resulting in oxidised and acidified waterways from the release of metals and associated sulfides), extensive logging of native forest and the discharge of by-products from industrial, agricultural, transport and domestic sources.

3. Methods

3.1. Survey design

A systematic, 8 km-spaced grid of sample locations was used to cover the southern South Island of New Zealand (Rattenbury et al., 2014). The survey site locations were planned around kilometre map grid intersections of the New Zealand Transverse Mercator grid as depicted on Topo50 1:50,000 topographic maps. The northernmost line of samples was at 45.50° south and the survey extended to the southern and eastern coasts. The western extent of the survey is approximately the boundary to Fiordland National Park where there are few roads or walking tracks. In total, 393 sample locations were originally planned for this area (Fig. 1). In addition to the regular grid, a line of seven sites were sampled, spaced 8 km apart, extending from the western edge of the main survey area to the western coast of the South Island at latitude 45.75° south. This extension completed a transect across the South Island (Fig. 1a). A total of 348 sites were sampled, with 13% of the planned locations remaining uncollected due to access issues.

Soil was the only sampling medium. Samples were collected at two fixed depth intervals; the A-depth sample from 0 to 30 cm and the B-depth sample from 50 to 70 cm. This sampling protocol closely followed several well-established precedents (Salminen et al., 2005; Cohen et al., 2011; Reimann et al., 2014). The sampling campaign was conducted from Dunedin city with multiple collection trips occurring between December 2013 and April 2014. Approximately 80% of the sites were accessible by vehicle and the remainder required additional foot or helicopter access. The average sampling rate was seven sites per team per day. The survey collected a total of 348 sites and from these 844 samples were analysed (two samples from different depths at each location plus QAQC samples).

3.2. Sample collection and preparation

Sampling locations followed the grid-cell model, with the actual sampling location typically varying from the grid centre by up to 100 m and, on rare occasions, up to a maximum of 800 m ($\pm 10\%$ of the 8 km spacing) in some remote locations. This approach allowed avoidance of sites with obvious contamination (e.g. roads) or where there were land access difficulties. Following the procedures of Johnson (2005), at each site five samples were taken from the two sampling depths (A and B) at the four corners and centre of a 20 × 20 m square (Fig. 2a). The humus layer was removed prior to sampling. Soil was hand-augured using a stainless steel AMS 82 mm Regular auger head with extension pole and T-bar handle and the soil from the five holes combined into a single 5–10 kg sample (for both A-depth and B-depth) at the sample site (Fig. 2b). To determine site and methodological uncertainty, both site duplicates and sub-sample replicates were analysed. Site duplicates were collected c. 21 m from the original

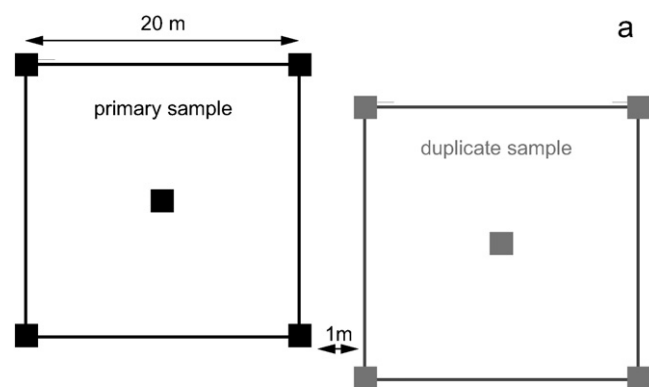


Fig. 2. The sampling methodology. a. Design of soil collection pattern at each field duplicate locality. Duplicates were collected at c. 1 in 20 randomly selected sites. b. Soil samples from the five auger holes were amalgamated in the field.

sampling location (Fig. 2b), using the same five sub-site composite sampling approach as the original sample, at one (randomly selected) in every twenty sites visited.

Location information was recorded on an application-enabled digital tablet (primary) and backed up with a paper record (Fig. 3). The routinely collected information data for each site were map coordinates, land use, slope, weather, presence of obvious contamination, soil-horizon and dominant grain size (gravel, sand, silt, clay) and at least one photograph. Samples were first air-dried, then oven-dried at 40 °C for 24 h.

Each sample was initially hand-sieved by the collection team using Endecott 200 mm diameter, 2 mm aperture woven, stainless steel wire scientific sieves. The sub 2 mm portion was split into sub-samples using a riffle splitter: four splits of c. 70 ml each were made for distribution to analysing laboratories and one split > 1 kg was retained for reference. The split sent for chemical analyses at Bureau Veritas Mineral Laboratories (BVML; formerly ACME Analytical Laboratories Ltd) in Vancouver, Canada, was further dried at 60 °C and sieved to provide a sub-180 μm fraction (the common fraction used in mineral exploration) for analysis. Around 7% of the samples were split into sub-sample duplicates.

3.3. Chemical analysis

Three analytical techniques were employed at BVML; (1) inductively coupled plasmas mass spectrometry (ICPMS) on an aqua regia partial digest, (2) X-ray fluorescence (XRF) on a fused glass bead for 12 oxides/elements and (3) a LECO CS230 element analyser for total carbon

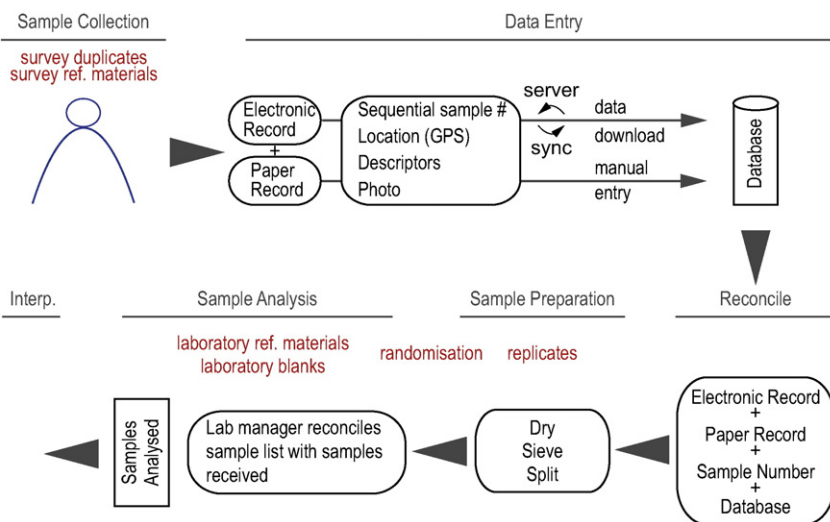


Fig. 3. A schematic diagram of the survey work flow from sample collection to interpretation (Interp.). The stages at which various quality control and quality assurance procedures are introduced are also shown. Ref. = Reference.

and sulfur. The lower and upper method detection limits (MDL) for all variables are shown in Table 3. An aqua regia partial digest was performed on 844 samples (including unknowns, duplicates and reference materials). A 0.5 g split of each sample was digested with 10 ml of a modified aqua regia solution containing equal parts concentrated HCl, HNO₃ and deionized H₂O (1:1:1) in glassware for one hour in a heating block or hot water bath. The remaining solution was made up to a standard 10 ml volume with 5% HCl. The entire sample programme was run consecutively in batches of 40 on the same PerkinElmer ELAN 9000 ICPMS instrument for 65 elements (Table 3). Laboratory XRF was also undertaken on most of the samples using a 5 g split from the sub-180 µm fraction to give total oxide/element concentrations in the sample. The samples were heated at 1000 °C to determine loss-on-ignition and then fused in a platinum-gold crucible with a lithium tetraborate flux. The molten material was then cast in platinum moulds to form fused glass discs to be analysed by XRF. The results are reported as weight percent (wt.%) oxides (non-normalised) and can be identified in this text by having oxygen in their formula (e.g. CaO) compared with results analysed by ICPMS (e.g. Ca). By convention all Fe is reported as Fe₂O₃. Determination of total C and total S was made after adding an induction flux to the prepared sample, igniting it in an induction furnace and measuring it using a LECO CS320 element analyser. LECO analyses are given the notation *tot*.

3.4. Analytical quality control

A comprehensive QAQC protocol was carried out through the entire process from collection to preparation to analysis (Fig. 3), including use of various reference materials and randomisation of samples prior to analysis (Reimann, 2005; Reimann et al., 2011b). Two survey-specific bulk soil reference materials were created: the first (GNS reference GB00121A) from surficial sediments overlying mapped Murihiku Terrane rocks in Southland and the second (GNS reference GB00156A) from soil overlying Dunedin Volcanic Group rocks on the Otago Peninsula. These materials were dried and sieved to sub-180 µm and inserted after every 20 samples in the sample batches prior to analytical sample randomisation.

Other reference materials were analysed at regular intervals, including OREAS 45EA (a lateritic soil) and DS10 (an ACME internal standard) in the ICPMS analyses; GS311-1 (Cu-Au ore) and GS910-4 (Ni-S ore) for the total C and S analyses; and SY-4(D) (diorite gneiss) and OREAS 72B (Ni-S ore) for the XRF analyses. A pure quartz standard, a flux mixture or a reagent were also run occasionally between sample analyses as a procedure blank for ICPMS, XRF or Total C and S methods, respectively. In

addition to the project reference materials, replicates and blanks, each ICPMS analytical batch of 40 included two laboratory standards (OREAS 45EA and DS10), one in-house laboratory pulp duplicate and one blank, and each XRF batch SY-4(D) and OREAS 72B.

3.5. Data processing and presentation

The data are displayed as black-and-white point source maps and colour interpolation maps, as well as comparative distributions for both the A- and B-layers via histograms, Tukey boxplots and cumulative distribution function plots (Fig. 4). Values below the lower MDL were replaced with half the lower MDL for interpolation and statistical treatment. The gridded interpolations of the point source data were based on an inverse distance weighted (IDW) technique with a 500 m cell size grid, a distance power of 1.5 and a fixed 9 km search radius. The IDW parameters chosen provided the most conservative interpretation possible whilst still creating smooth interpolations between points, and reflect the approach of a number of previous regional surveys (e.g. Cohen et al., 2011). Areas where no sample was collected were excluded prior to the interpolation. The gridded geochemical data can be portrayed as coloured maps using an equal interval colour-ramp, effective where the data show near log normal distribution, or using a quantile colour-ramp that better depicts non-linear variation (Rawlins et al., 2012). Multiple interpolations and data presentation styles were extensively experimented with. The presentation used here reflects the best and preferred method suitable for the most elements and multiple end-users. Other interpretations are possible, and the inclusion of the chemical data and co-ordinates information in Table S1 will facilitate this.

4. Results and discussion

4.1. Quality control

The data shows no time dependent variation for any element (e.g. La in Fig. 5a). Survey and laboratory reference materials also showed no time variation and around 89% of the data plot within ±30% of the expected value (or median for the project reference materials), many within ±10% of the median (Fig. 5b). Where a significant proportion of reference material values plotted outside ±30% of the expected value, it was typically for elements with values within five times the lower MDL. A notable exception is Au which has several data that plot >30% of the median for the project reference materials and which is attributed to the nugget effect (Clark, 2010). The laboratory blank analyses were below the lower MDL for all analytes.

Table 3

Median, maximum and minimum element concentrations for A-depth ($n = 348$) and B-depth ($n = 340$) soils, sub-180 μm fractions.

Analyte	Lower MDL	Upper MDL	A-depth				B-depth			
			Count	Min	Median	Max	Count	Min	Median	Max
ICPMS ppm										
Ag	0.002	100	0	0.004	0.04	0.35	0	0.003	0.04	0.15
Al	100	100,000	0	1200	15,500	52,800	0	2400	17,300	54,600
As	0.1	10,000	0	<MDL	3.7	19.7	4	<MDL	3.7	26.1
Au	0.0002	100	88	<MDL	0.0006	0.03	84	<MDL	0.0006	0.04
B	20	2000	346	<MDL	10	34	340	–	–	–
Ba	0.5	10,000	0	4.6	54.9	215	0	4.4	53.1	293
Be	0.1	1000	25	<MDL	0.3	1.7	13	<MDL	0.3	1.5
Bi	0.02	2000	1	<MDL	0.14	0.75	2	<MDL	0.15	0.59
Ca	100	400,000	1	<MDL	2700	23,000	2	<MDL	2000	26,900
Cd	0.01	2000	11	<MDL	0.08	1.31	24	<MDL	0.04	0.74
Ce	0.1	2000	0	2.5	13.5	65.8	0	2.5	15	73.5
Co	0.1	2000	0	0.2	4.6	53	0	0.4	4.8	41.1
Cr	0.5	10,000	0	2.5	12.7	211	0	2.5	13.7	243
Cs	0.02	2000	0	0.12	0.86	5.07	0	0.1	1	6.77
Cu	0.01	10,000	0	1.24	11.1	170	0	2.18	11.1	155
Dy	0.02	2000	0	0.09	0.72	3.55	0	0.11	0.78	3.49
Er	0.02	2000	0	0.04	0.34	1.82	0	0.06	0.38	1.8
Eu	0.02	2000	0	0.02	0.21	1.39	0	0.03	0.25	1.36
Fe	100	400,000	0	2700	19,400	65,300	0	2200	22,150	72,000
Ga	0.1	1000	0	0.7	5.4	18.8	0	0.7	5.7	17.2
Gd	0.02	2000	0	0.09	0.78	4.32	0	0.13	0.89	4.55
Ge	0.1	100	329	<MDL	0.05	0.2	323	<MDL	0.05	0.1
Hf	0.02	1000	196	<MDL	0.01	0.5	184	<MDL	0.01	0.45
Hg	0.005	50	0	0.009	0.06	0.68	1	<MDL	0.06	0.43
Ho	0.02	2000	0	0.03	0.14	0.75	0	0.02	0.16	0.75
In	0.02	1000	206	<MDL	0.01	0.08	167	<MDL	0.02	0.09
K	100	100,000	0	200	800	2900	1	<MDL	700	2400
La	0.5	10,000	0	1.3	5.8	69	0	1.5	6.4	58.3
Li	0.1	2000	0	0.3	14.1	43.9	0	0.3	16.2	49.1
Lu	0.02	2000	59	<MDL	0.04	0.23	36	<MDL	0.05	0.25
Mg	100	300,000	0	300	2900	19,700	0	100	3150	23,600
Mn	1	10,000	0	15	351	3773	0	12	315	3496
Mo	0.01	2000	0	0.07	0.33	2.87	0	<MDL	0.3	15.1
Na	10	50,000	3	5	70	3010	13	<MDL	60	2200
Nb	0.02	2000	0	0.14	0.9	26.7	0	0.1	0.92	8.39
Nd	0.02	2000	0	0.82	4.94	34	0	1.05	5.45	37.3
Ni	0.1	10,000	0	0.8	7.3	278	0	1.1	7.85	217
P	10	50,000	0	70	540	3330	0	40	370	2470
Pb	0.01	10,000	0	3.04	10.6	449	0	1.41	11.1	530
Pd	0.01	100	346	<MDL	0.005	0.02	340	–	–	–
Pr	0.02	2000	0	0.25	1.35	10.8	0	0.27	1.51	10.9
Pt	0.002	100	327	<MDL	0.001	0.004	320	<MDL	0.001	0.005
Rb	0.1	2000	0	1.4	11.1	24.5	0	<MDL	11.3	29.3
Re	0.001	1	306	<MDL	0.0005	0.003	280	<MDL	0.0005	0.005
S	200	100,000	17	<MDL	400	2100	101	<MDL	200	2400
Sb	0.02	2000	2	<MDL	0.11	1.66	5	<MDL	0.11	1.65
Sc	0.1	100	0	0.2	1.7	14.6	0	0.4	2.2	17.7
Se	0.1	100	42	<MDL	0.4	2.5	38	<MDL	0.4	4.6
Sm	0.02	2000	0	0.1	0.95	5.64	0	0.15	1.08	5.63
Sn	0.1	100	0	0.2	0.8	10.3	0	0.1	0.8	12.1
Sr	0.5	10,000	0	3.2	22.3	206	0	1.8	19.6	768
Ta*	0.05	2000	348	–	–	–	340	–	–	–
Tb	0.02	2000	1	0.02	0.13	0.63	1	<MDL	0.15	0.71
Te	0.02	1000	250	<MDL	0.01	0.09	238	<MDL	0.01	0.12
Th	0.1	2000	7	<MDL	0.9	6.7	2	<MDL	1.45	10.9
Ti	10	50,000	0	30	420	3730	0	30	560	3730
Tl	0.02	1000	6	<MDL	0.07	0.22	5	<MDL	0.08	0.28
Tm	0.02	2000	31	<MDL	0.05	0.31	8	<MDL	0.06	0.27
U	0.1	2000	1	0.1	0.7	2.5	0	0.2	0.7	2.5
V	2	10,000	0	4	34	291	0	3	35.5	306
W	0.1	100	302	<MDL	0.05	0.8	290	<MDL	0.05	3.1
Y	0.01	2000	0	0.51	3.21	17.9	0	0.59	3.55	17.6
Yb	0.02	2000	0	0.03	0.28	1.45	0	0.05	0.33	1.6
Zn	0.1	10,000	0	4.8	48.1	361	0	4.9	45.2	500
Zr	0.1	2000	48	<MDL	0.7	33.6	38	<MDL	0.7	17.4
XRF wt.%										
SiO ₂	0.01	100	0	25.54	59.79	78.17	0	31.59	61.62	81.14
Al ₂ O ₃	0.01	100	0	5.90	14.24	19.05	0	8.01	15.26	22.46
Fe ₂ O ₃	0.01	100	0	1.12	4.16	12.79	0	1.24	4.66	12.18
CaO	0.01	100	0	0.05	1.69	7.20	0	0.04	1.68	7.75
MgO	0.01	100	0	0.21	0.98	4.58	0	0.13	1.09	5.84

(continued on next page)

Table 3 (continued)

Analyte	Lower MDL	Upper MDL	A-depth			B-depth				
			Count	Min	Median	Max	Count	Min	Median	Max
Na ₂ O	0.01	100	0	0.29	2.61	4.20	0	0.23	2.72	4.37
K ₂ O	0.01	100	0	0.23	1.30	2.96	0	0.28	1.36	3.10
MnO	0.01	93	2	0.01	0.07	0.48	2	0.01	0.06	0.45
TiO ₂	0.01	50	0	0.31	0.72	1.39	0	0.28	0.77	1.56
P ₂ O ₅	0.01	100	1	0.02	0.18	1.05	3	0.02	0.14	0.80
Cr ₂ O ₃	0.01	10	330	0.01	0.01	0.28	324	0.01	0.01	0.38
Ba	0.01	89	4	0.01	0.03	0.25	2	0.01	0.03	0.28
LOI	0.01	100	4	4.08	59.12	13.34	3	1.67	51.5	9.78
LECO analyser wt.%										
C _{tot}	0.02	100	0	0.75	4.40	56.00	1	0.32	2.60	58.00
S _{tot}	0.02	100	63	0.02	0.03	0.10	178	0.02	0.03	0.08

Min.: minimum; Max.: maximum; ppm: parts per million; wt. %: weight percent. #: all values are below the lower method detection limit; count: number of analyses below the lower method detection limit (<MDL). ICPMS: inductively coupled mass spectrometry. XRF: X-ray fluorescence. LOI: loss on ignition. tot: denotes measurement made by Leco CS230 element analyser.

In the site and sub-sample duplicate plots, both simple X-Y and Thompson-Howarth plots (Thompson and Howarth, 1978) of most elements indicates relative sub-sample variation to be <10%, as indicated for La in Fig 5c and d. A proportion of the site duplicates plotted outside the $\pm 10\%$ precision line, indicating some natural variation at the site level beyond variation caused by methodological errors. For the vast majority of elements, geochemical variations between sites (regional changes) are an order of magnitude or more above site and methodological variability. This demonstrates that high precision and low methodological variability were achieved, confirmed that the sample

preparation method and analytical technique were appropriately chosen and implemented, and the data fit-for-purpose.

4.2. Element concentration variation

A summary of the minimum, median and maximum values for all elements analysed for both the A-depth and B-depth is presented in Table 3. The full compilation of chemistry data is included in extra supplementary material Table S1 and the full chemistry data available online (<http://pet.gns.cri.nz>; Strong et al., in press). The data set is also

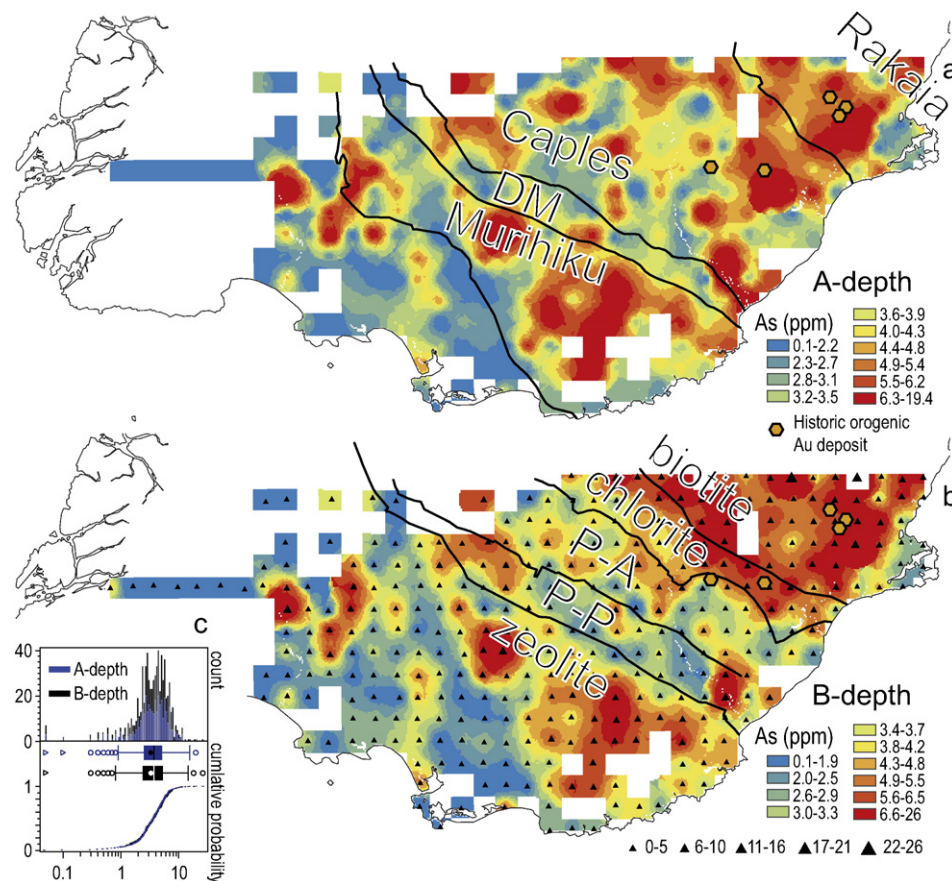


Fig. 4. Aqua regia soluble arsenic data presented as graphical plots and maps. a. Colour map (quantile) showing arsenic (As) in parts per million (ppm) for A-depth samples. The contact position between the Caples Terrane, Dun Mountain – Maitai Terrane (DM) and Murihiku Terrane is shown for comparison. b. Colour map (quantile) and black-and-white point (equal interval) source map showing arsenic (As) in ppm for B-depth samples. The transition between the garnet-biotite-albite (biotite) zone, chlorite zone, pumpellyite-actinolite (P-A) zone, prehnite-pumpellyite (P-P) zone and zeolite zone is shown for comparison. The location of selected, historically mined orogenic gold deposits is shown for comparison. c. The data variation for A-depth samples and B-depth samples is variably plotted as a histogram (top), Tukey (1977) box plot (middle) and cumulative distribution function plot (bottom).

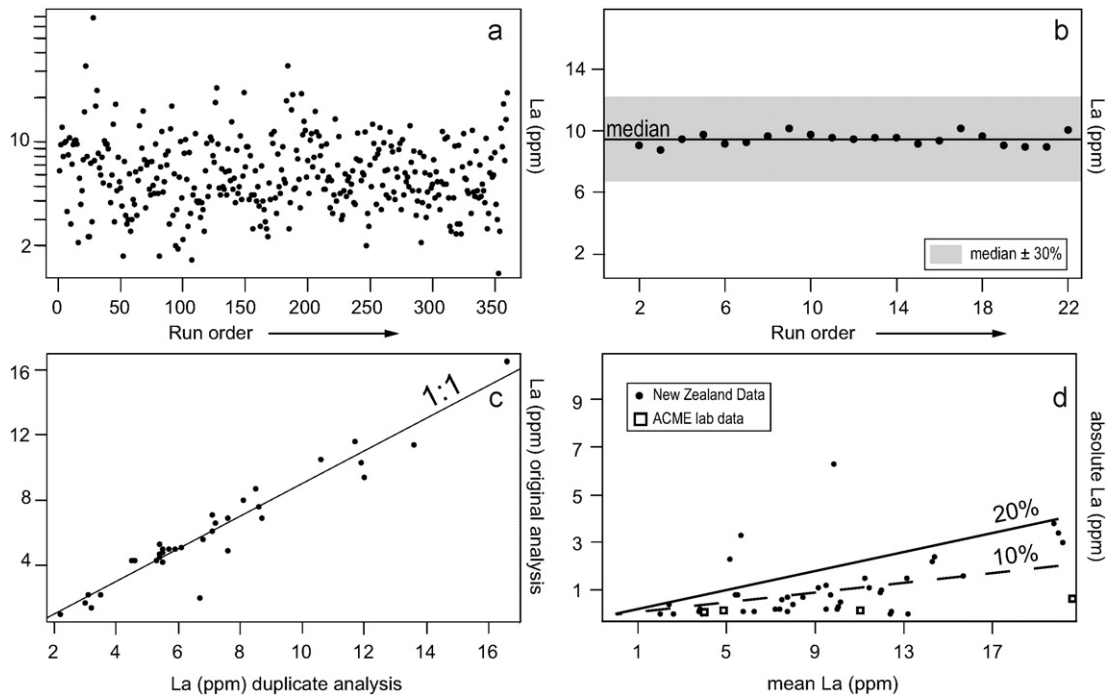


Fig. 5. Four examples of the plots used for data quality control of aqua regia soluble lanthanum (La). a. The data plotted in the order in which it was analysed in the laboratory (run order) against concentration in parts per million (ppm). b. The run order data for the survey reference material ‘GNS reference 121A’ plotted against concentration. c. The sample La concentration plotted against the field duplicate La concentration. A 1:1 relationship between the data implies perfect precision. d. A Thompson and Howarth (1978) plot using sample and sample replicate data. The mean values [(sample + replicate)/2] are plotted against the absolute difference values (sample – replicate) between the La concentration in the sample and the La concentration in the replicate of the same sample. The 10% and 20% lines are shown for comparison to the data.

presented as a series of maps and graphs in the online supplementary material (ESM 1).

4.3. Geological and geomorphic influences on element concentration variation

Metamorphic zones in the basement rocks can be differentiated by relative highs and lows in the mean and median values of specific elements. For example, the biotite and chlorite zone rocks (greenschist facies) have high As relative to sub-greenschist facies rocks in the pumpellyite-actinolite (P-A) zone and the prehnite-pumpellyite (P-P) zone rocks to the south-west (Fig. 4b). There are also relative highs in Ba, Bi, K, K₂O, Rb, Sb and U in greenschist facies rocks relative to sub-greenschist facies rocks (not shown).

Some major geological units are also characterised by relative highs and lows in the mean and median values of elements relative to other units (e.g. Fig. 4a, Fig. 6). The Caples, Rakaia and Murihiku metasedimentary basement terranes comprise >52% of the sampled survey area, and have high median As concentrations relative to the Dun Mountain-Maitai basement terrane (e.g. Fig. 4a, Fig. 6), and relative to median As values from Zealandia Megasequence rocks (Haerenga, Waka, Māui or Pākahi supergroup rocks in Fig. 6).

The median La value in Murihiku Terrane soils is higher than in the Rakaia or Caples terrane soils (Fig. 6). Soils sampled above the Murihiku Terrane also have high median values of Al, Al₂O₃, Cs, Ga, Li, Nb and P₂O₅ and moderately high values of Bi, Cu, K₂O, Mg, MgO, Mn, Mo and Sb, relative to other basement terranes. All rare earth elements (e.g. La in Fig. 6), U and Th median values are high in soils sampled from the Murihiku Terrane, relative to other basement terranes, in both the A-depth and the B-depth.

Only one sample was collected directly above mapped Dun Mountain Ultramafics Group (GB000136A/B; Fig. 7a). The A-depth and B-depth soils from this sample have amongst the highest values of Co, Cr, Cr₂O₃ and Ni, and moderately high Mg, relative to other samples in the survey. High values of Cr₂O₃ (Fig. 7a), Co, Mg and Ni are also

observed in soil samples along gravel outwash plains of the Oreti River that drains from these metalliferous basement rocks. The highest Cr contents of >200 parts per million (ppm) come from soils sampled directly above the Dun Mountain-Maitai Terrane. Soils sampled above Brook Street Terrane rocks (3% of survey area) exhibit high median

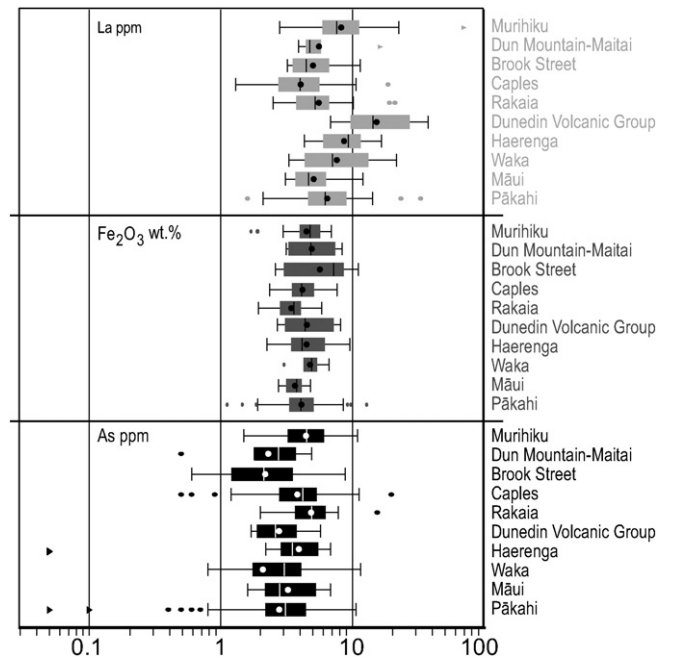


Fig. 6. Tukey (1977) box plots for aqua regia soluble lanthanum (La) in parts per million (ppm), total iron oxide (Fe₂O₃) in weight percent (wt.%) and aqua regia soluble arsenic (As) in ppm from soils samples above various underlying geological terranes, supergroups and groups.

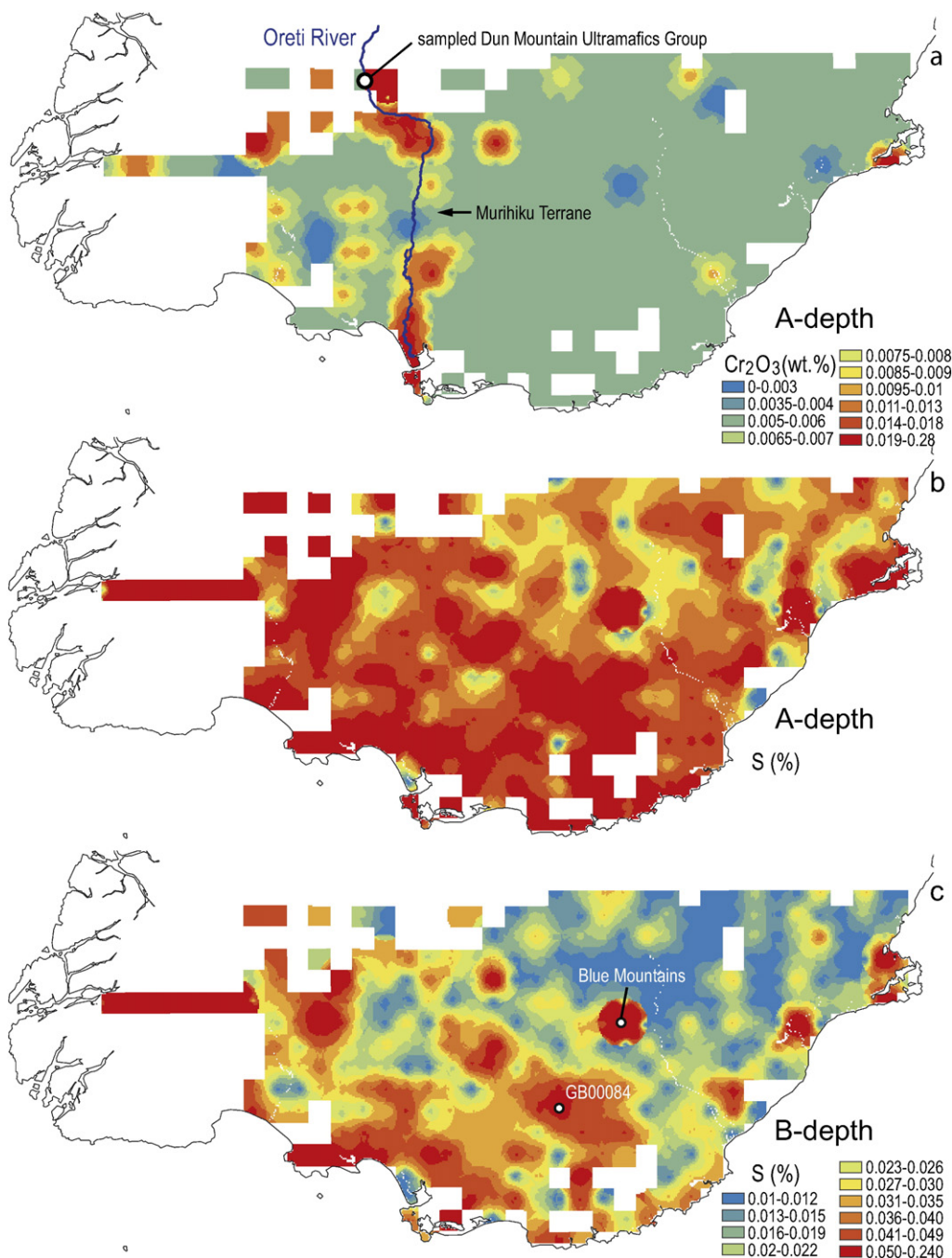


Fig. 7. Various colour maps (quantile) of element data. a. A colour map of weight percent (wt.%) total Cr₂O₃ from A-depth soil samples. Note the re-distribution of Cr₂O₃, probably in the mineral chromite, along the Oreti River from where it intersects the Dun Mountain Ultramafics Group. Colour maps of aqua regia S in the A-depth (b) and B-depth (c) as analysed by ICPMS. The colour-ramp used for the S A-depth map matches that used for the S B-depth samples to emphasise the higher concentration of S in the shallower samples. The Blue Mountains and sample GB00084 are referenced in the text.

values in Ca, Cu, Fe, Zr, Hf, Sc and V, and moderately high Ti, Mn and Mo relative to other basement terranes.

Soils sampled above the Dunedin Volcanic Group have a distinct geochemical signature characterised by high median values in Ba (ICPMS and XRF), Be, Cd, Co, Cr, La (Fig. 6), Na, Nb, Ni and to a lesser extent Ti and Mg, relative to other rock types. The Pākahi Supergroup represents New Zealand's youngest sedimentary deposits, and in the survey area is predominantly comprised of Pliocene – recent, non-marine and marine sedimentary deposits. Many of the sampling localities above the Pākahi Supergroup are unconsolidated alluvial gravels, sand, silt and glacial till, and underlie some of the youngest New Zealand soil types. Enrichment in SiO₂ is strongly correlated to the Pākahi Supergroup, though the highest

soil SiO₂ values (>80 wt.%) are associated with underlying silica-cemented, quartz pebble conglomerates of the Late Cretaceous Taratu Formation (Haerenga Supergroup; Zealandia Megasequence).

The chemistry of samples collected along the Fiordland transect (underlain by Western Province intrusives and metasediments; Fig. 1) is strongly influenced by the presence of swampy, anoxic and organic-rich conditions, leading to high organic C and S_{tot} levels (Fig. 7b, c). A sample collected from a peat bog in the Blue Mountains also displays high S_{tot} (Fig. 7c) and C_{tot} concentrations. As seen from the discussion in this section (Section 4.3), parent rock lithology is one of the largest influences on the abundance and variation of elements in southern New Zealand soils sampled in the survey.

4.4. Anthropogenic influences on element concentration variation

One of the most significant and long-standing anthropogenic influences on soil chemistry in southern New Zealand has been the application of fertilisers to boost pasture growth, which has been occurring since the 19th century (Molloy, 1980). The three primary fertilisers in use in the southern South Island are lime [CaO and/or $\text{Ca}(\text{OH})_2$], superphosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2$] and urea [$\text{CO}(\text{NH}_2)_2$], which all contain appreciable concentrations of B, Co, K, Mo, S, Se and Zn, and potentially toxic elements such as As, Cd, F, U and W (McDowell et al., 2013). The main elements associated with such fertilisers do not vary greatly in accordance with the underlying basement geology; rather their variation can be explained by differing intensive farming and fertiliser application practice over exotic grassland (Fig. S2). Many of the elements associated with agricultural fertilisers show high values in the A-depth soil compared to the B-depth soil, for example S (Fig. 7b, c), or median P_2O_5 which is 0.19 wt.% in the A-depth versus 0.14 wt.% in the B-depth. The median Mn in the A-depth is 351 ppm relative to 315 ppm in the B-depth. The highest Cd (1.31 ppm) and P (0.24 ppm) came from a single site sampled on a grass verge within 15 m of a superphosphate storage and distribution shed on a Southland farm (GB00084 – location shown on Fig. 7c).

Only 1% of soils within the survey area were collected from urban centres (Invercargill, Balclutha, Dunedin; Fig. 1, Fig. S2). Elements of concern for public health include As, B, Cd, Cr, Cu, Hg, Pb and Zn and they commonly accumulate in urban soils as a result of anthropogenic influences (Wuana and Okieimen, 2011). All A-depth soils from urban centres exhibited higher median concentrations in these elements than the median concentration of soils in non-urban areas. In the majority of cases, A-depth soil was enriched relative to median B-depth soil concentrations by 75% in As, 110% in Cd, 30% in Cr, 70% Cu and 65% in Hg. The median Pb concentration in urban soils is up to 30 times higher than the median Pb concentrations in the survey area. In particular, Pb and Hg concentrations were high around Dunedin, Balclutha and Bluff

in the A-depth (Fig. 8a), but were still below recommended safe limits for soils for New Zealand. The elevated Pb and Hg concentrations are likely to be caused by emissions from leaded petrol combustion (discontinued in 1996), heavy industry emissions and Pb-based paint (also discontinued) that were more prevalent around these urban centres.

4.5. Effects of mineralisation

Orogenic Au deposits (historical and currently mined) occur in greenschist facies, schist rocks of the Rakaia and Caples terranes (Craw and Norris, 1991; Forsyth, 2001) in the northeast of the survey area (e.g. Fig. 4). The concentration of Au in the sub-180 μm soil samples can be below the lower MDL. Where Au concentration is above the MDL, its distribution is typically more erratic than other elements due to the nugget effect (Clark, 2010). This effect leads to problems using Au as a vector to mineralisation using either presence/absence criteria or the magnitude of anomalous values. In the Caples and Rakaia terranes, Au mineralisation is also commonly associated with As, Bi, Sb and W enrichment, and Cd and Co depletion (Craw, 2002; Pitcairn et al., 2006; Figs. 4; 8b). These elements are normally above the lower MDL and are more homogeneously distributed in soil relative to Au, making them more suitable mineralisation vectors in the Caples and Rakaia terranes (e.g. Redden and Moore, 2010). These elements are commonly used for targeting mineral exploration (e.g. Grieve, 1996). Rather than providing specific targets for mineral exploration, the regional soil survey data provide statistically robust measures of most background element concentrations, so more closely spaced exploration sampling can be targeted to the areas with the most elevated background (Martin et al., 2014).

Heavy minerals such as magnetite have been eroded from the Dun Mountain Ultramafics Group rocks and re-deposited along the floodplains of the Oreti River as sedimentary components in the Pākihi Supergroup, with high concentrations of heavy mineral-associated

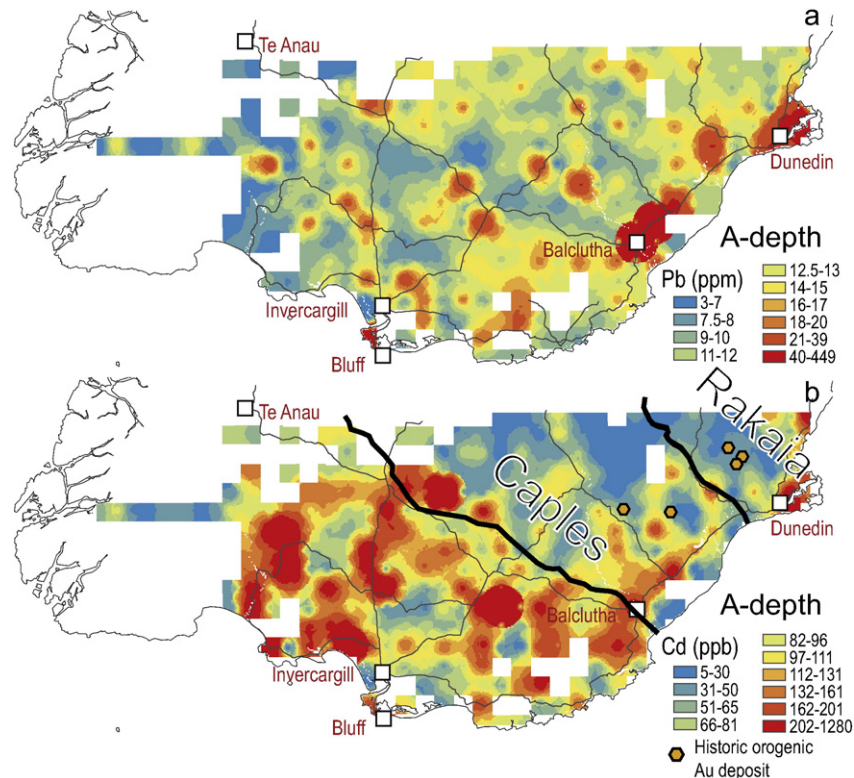


Fig. 8. Colour maps (quantile) for A depth samples of aqua regia Pb (a) in parts per million (ppm) and aqua regia Cd (b) in parts per billion (ppb). The location of the Rakaia and Caples terranes, and select orogenic gold deposits, are shown for comparison.

elements such as Cr_2O_3 , Ni and Co (Fig. 7a). This distribution of heavy minerals may prove useful in tracing sources of mineralisation. For example, platinum group element (PGE) concentrations (e.g. Pt) and other noble group elements (e.g. Re) in soils are relatively high around the Longwood Ranges (Fig. 1) which has been an exploration target for PGE mineralisation.

4.6. Comparison between aqua regia-extractable and total element values

Recovery of Na, Ca and K from aqua regia digestion is poor due to the insolubility of most aluminosilicate minerals in aqua regia. Thus measured values by the XRF method are higher than those for the aqua regia ICPMS method. For example, the median of all A-depth samples in the survey for K is 0.08 wt.% (800 ppm), whilst for K_2O the median is 1.30 wt.% (11,792 ppm K). Also, Ca concentration by aqua regia in all A-depth samples [maximum 2.3 wt.% (23,000 ppm); median 0.27 wt.% (2700 ppm)] is low compared to total CaO in all A-depth samples [maximum 7.20 wt.% (59,771 ppm Ca); median 1.69 wt.% (14,030 ppm Ca)] (Fig. 9). Concentrations in the A-depth and B-depth soil for aqua regia Ca are highest in the Brook Street Terrane areas, however, for total CaO, concentrations are highest in the Caples Terrane areas (Fig. 9).

Similar to Ca versus CaO, differences in Na versus Na_2O are observed, indicating that Na is only partially extracted during aqua regia digestion. Similar concentrations for Na occur for the two soil depths; both depths have a median aqua regia Na value of 0.01 wt.% (100 ppm). Both soil depths have high median Na values in the Dunedin Volcanics Group and the Tuhua Intrusives and low values in the Caples and Rakaia terranes, relative to other basement terranes. The total Na_2O data have high concentrations [median 2.7 wt.% (20,030 ppm Na)] relative to the Na data. Median Na_2O values are high in the Caples and Rakaia terranes, and low in the Murihiku and Brook Street terranes and the Tuhua Intrusives, relative to other basement rocks. The contrasting values in Na and

Na_2O (e.g. low aqua regia Na but high total Na_2O in the Rakaia Terrane) is interpreted to reflect higher feldspar contents in the Rakaia Terrane.

Concentrations of aqua regia Al versus total Al_2O_3 are also variable. For Al, high values are observed in the Murihiku and Brook Street terranes, relative to other basement terranes, in particular the Caples and Rakaia terranes which have the lowest median Al values. However, Al_2O_3 has high median values in the Rakaia and northern Caples terranes, as well as the Murihiku and Brook Street terranes. Median A-depth aqua regia Al is 1.55 wt.% (15,500 ppm) in comparison to median total Al_2O_3 of 14.24 wt.% (75,364 ppm Al), which clearly indicates that Al is not being released by minerals (feldspars/clays) during aqua regia digestion.

4.7. Suitability of the survey design and methodology

The majority of the measured element concentrations are above the lower MDL (Table 3). There is mappable variation in the chemistry data (e.g. Figs. 4, 9) and this variation can commonly be linked to the underlying geology suggesting it is not a laboratory artefact. The variety of chemical analyses and cross-comparison of the methods have considerable potential for assisting many societal sectors and research areas, including agriculture, environmental monitoring, local and regional government, forestry, mining and minerals exploration. The majority of the data were comparable to, or better than, standards suggested for QAQC (e.g. Fig. 5) suggesting that appropriate quality control measures were implemented throughout the programme.

The appropriateness of the survey density (8 km-spaced grid) has been tested by selecting subsets of data to mimic a 16 km-spaced and a 32 km-spaced survey (Fig. 10a, b, c). The result of this down-sampling was that for a 16 km grid, chemical variation could still be observed to vary with underlying geology, although terrane boundaries were more diffuse. Anthropogenic effects such as elevated A-depth Pb around urban centres could still be recognised (Fig. 10b). Subtler effects, such

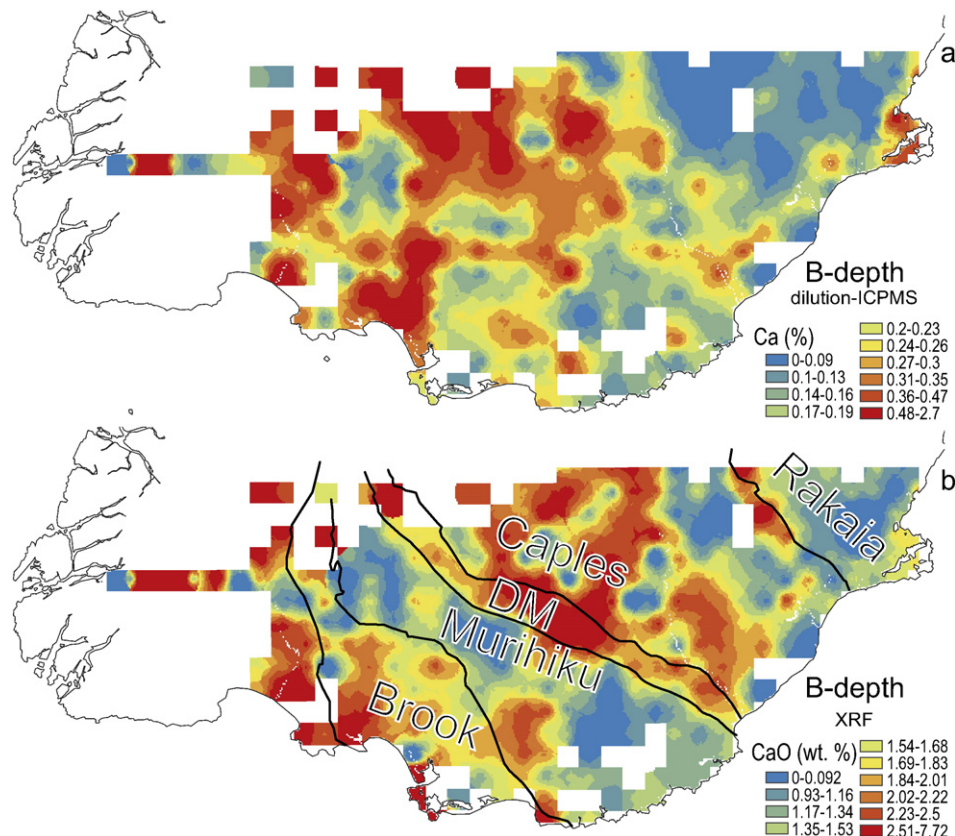


Fig. 9. Calcium (Ca) data presented as coloured maps (quantile). a. Colour map of aqua regia Ca from B-depth samples. b. Colour map of total Ca from B-depth samples analysed by XRF.

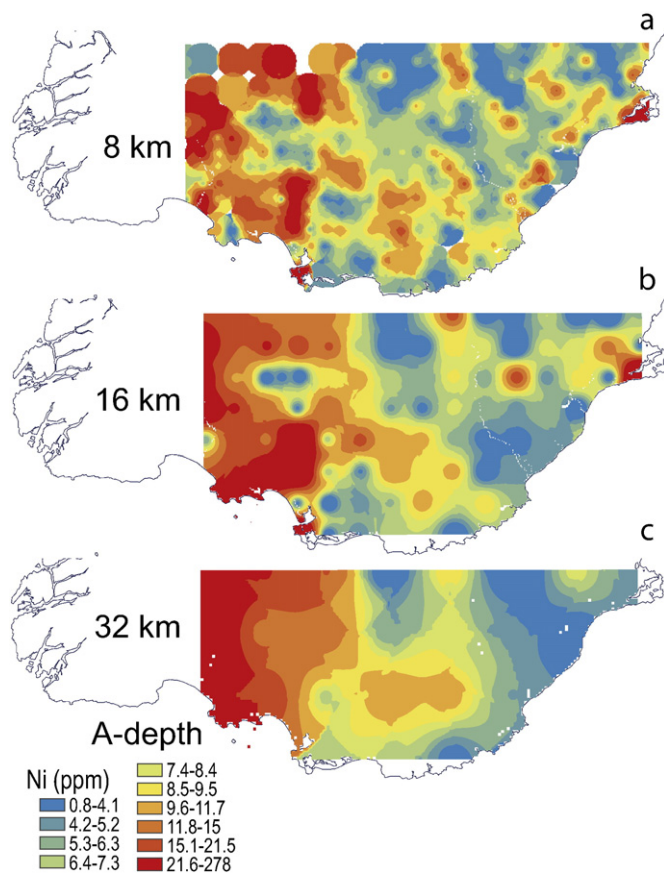


Fig. 10. Nickel (Ni) data presented as coloured maps (quantile) with different spacing between sample locations. The legend applies to each map. a. 8 km (as chosen for this survey). b. 16 km sample spacing. c. 32 km spacing.

as remobilisation of minerals within river catchments were not clearly evident. At 32 km spaced locations, terrane boundaries were not evident and chemical variation was much more general over the whole survey area (Fig. 10c).

The design elements of the southern New Zealand geochemical baseline survey largely apply to a national survey. The 8 km-spaced grid and, to a lesser extent, the 16 km-spaced grid, adequately represent the geochemical variation, and provide an acceptable compromise between area covered and resolution, for examples over little modified alpine areas versus intensely farmed regions. A larger (≥ 32 km) spacing between samples is acceptable as long as it is acknowledged that geological unit resolution and subtler effects will be downgraded or lost. Areas of marked variation in geology or land use, and urban centres, could likely benefit from samples being collected from sites at an even higher density than at the national scale. The value of collecting a very shallow soil sample, for example 0–10 cm, has been demonstrated in several studies (e.g. de Caritat and Cooper, 2011). This has not been done specifically in this project; however, a shallow soil sample (0–2 cm) is being collected in a pilot urban soil study over Dunedin City, New Zealand, in addition to an A-depth sample and a B-depth sample. The chemical results of all three depths will be compared and contrasted in this upcoming study, as will different sample fractions (sub-180 μm versus sub-2 mm).

5. Conclusions and future work

The regional geochemical baseline survey has successfully measured meaningful element concentration variation in the soil landscape of southern New Zealand. The survey design and methodology was appropriate for the regional scale of the survey and QAQC measures suggest

the survey has a high level of reliability and reproducibility. Strong regional differences were evident in the chemical data that clearly reflected the underlying geology. In specific instances, the chemistry was naturally influenced by topography and climate (e.g. swamps or peat), or showed evidence of mineral remobilisation along rivers. An anthropogenic influence was evident around urban centres (e.g. elevated Pb, Cd) and over fertilised pasture areas (higher S and P).

The aqua regia digest is ineffective at dissolving many silicates, in particular the very common feldspar group affecting analysed concentrations of Al, Ca, K and Na. Determining potential mineral hosts and forms of elements by comparison of total, aqua regia extractable and other selective extraction methods may be of some use in understanding variations in element concentration. Investigating different oxidation states of various elements may also be useful, for example Cr can be hazardous as Cr^{VI} but is relatively inert as Cr^{III} . The investigation of isotopes of certain elements (e.g. Sr, C, N, S) is under way and the subject of separate studies.

This geochemical baseline survey contains a wealth of information that will provide the basis for ongoing research of these analytical results and through further analysis of the reference soil collection housed at GNS Science. This collection can be accessed for collaborative research by contacting one of the authors or GNS Science. The data will provide a geochemical baseline for soils in southern Otago and Southland that can be used by government and industry in future planning and environmental assessments. We envisage that this study will lead to a national-scale geochemical baseline study, supplemented by urban and region specific studies, based on the survey design suggested here.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.gexplo.2016.05.009>.

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