

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

# **Application and Evaluation of Sediment Fingerprinting Techniques in the Manawatu River Catchment, New Zealand**

**A thesis presented in partial fulfilment of the requirements for the  
degree of**

**Doctor of Philosophy in Geography**

**at Massey University, Palmerston North, New Zealand**



---

**Simon Vale**

2016



## Abstract

Suspended sediment is an important component of the fluvial environment, contributing not only to the physical form, but also the chemical and ecological character of river channels and adjacent floodplains. Fluvial sediment flux reflects erosion of the contributing catchment, which when enhanced can lead to a reduction in agricultural productivity, effect morphological changes in the riparian environment and alter aquatic ecosystems by elevating turbidity levels and degrading water quality. It is therefore important to identify catchment-scale erosion processes and understand rates of sediment delivery, transport and deposition into the fluvial system to be able to mitigate such adverse effects. Sediment fingerprinting is a well-used tool for evaluating sediment sources, capable of directly quantifying sediment supply through differentiating sediment sources based on their inherent geochemical signatures and statistical modelling.

Confluence-based sediment fingerprinting has achieved broad scale geochemical discrimination within the 5870 km<sup>2</sup> Manawatu catchment, which drains terrain comprising soft-rock Tertiary and Quaternary sandstones, mudstones, limestones and more indurated greywacke. Multiple sediment samples were taken upstream and downstream of major river confluences, sieved to < 63 µm and analysed through step-wise discrimination, principle component analysis and a range of geochemical indicators to investigate and identify the sub-catchment geochemical signatures. Discrimination between the main sub-catchments was attained despite each sub-catchment containing similar rock types, albeit with varying proportions of specific lithologies. This meant that source groups were categorized as a mixture of both lithological and geomorphological sources in order to best capture the unique sediment origins. Comprehensive sampling quantified 8 geomorphological sediment sources using two mixing models; the traditional mixing model after Collins *et al.* (1997) and the Hughes *et al.* (2009) mixing model which were each optimized using a 'Generalized Reduced Gradient (GRG) Nonlinear' and an 'Evolutionary' technique providing four mixing model scenarios. These models showed good agreement attributing mudstone derived sediment (≈ 38 – 46 %) as the dominant source of suspended sediment to the Manawatu River. Sediment contributions were also estimated from the Mountain Range, ≈ 15 – 18 %; Hill Surface, ≈ 12 – 16 %; Hill subsurface, ≈ 9 – 11 %; Loess, ≈ 9 – 15 %; Gravel Terrace, ≈ 0 – 4 %; Channel Bank, ≈ 0 – 5 %; and Limestone, ≈ 0 %. Intra-storm analysis of sediment sources was investigated through hourly suspended sediment samples taken in the lower Manawatu River during a 53 hour storm event to detect changes in sediment sources. The suspended sediment samples

displayed high hourly variability which was attributed to model uncertainty and sediment pulses occurring between sampling. Mudstone proportions fluctuated  $\approx 20 - 60\%$  throughout the storm duration from a range of erosion processes, while Mountain Range sediment fluctuated from  $\approx 24 - 46\%$  and Hill Subsurface and Hill Surface both were near  $0\%$ , but approached upper values of  $\approx 23\%$  and  $\approx 24\%$  respectively. Significant shifts in sediment source proportions were observed between 2:00 – 8:00 am 29th November 2013 in relation to flow dynamics of the Pohangina River and shifting flow dominance from the Pohangina River to the Upper Manawatu. The geochemical suite was reanalysed to determine the variability of source groups and individual geochemical elements, in order to evaluate the suitability and impact of changing the geochemical suite used in estimated relative sediment source proportions. Mountain Range sediment displayed the highest average S.D. % of 39.4, followed by Gravel Terrace (S.D. % = 34.6) and Loess (28.1), while the lowest was found in Limestone (S.D. % = 18.1) and Channel Bank (S.D. % = 18.3). The highest variability of individual elements was found in the transition elements such as Cu, Ni, Cr, and Mn, as well as Ca, and Tm. Revised mixing models were run based on two geochemical tracer suites which removed elements with S.D. percentage of  $> 40$  and  $> 35$  respectively. The revised mixing model estimated Mudstone terrain to contribute 59.3 % and 61.8 %, with significant contributions estimated from Mountain Range (12.0 % and 11.4 %) and Hill Surface (11.5 % and 11.3 %) respectively, indicating that Tm, Ni, Cu, Ca, P, Mn and Cr have an influence on these sediment source estimations.

## **Acknowledgements**

I would like to express my very great appreciation to my supervisors, Associate Professor Ian Fuller (Massey University), Dr Jonathan Procter (Massey University), Dr Les Basher (Landcare Research) and Dr John Dymond (Landcare Research) for their support and guidance during this doctoral research. I am also particularly grateful for the resource and assistance given by Associate Professor Ian Smith (Auckland University)

I wish to thank Landcare Research for the financial support through the administration of the Murray Jessen Scholarship as well as financial support provided from the George Mason Charitable Trust, L.A. Alexander Agricultural College Trust Board Inc. and New Zealand Geographical Society.

I would also like to thank Dr Chris Phillips (Landcare Research) for providing me exposure to the Clean Water Productive Land Portfolio, Ms Mandy James (Landcare Research) for overseeing my placement within Landcare Research, and Dr Anja Moebis (Massey University) and John Dando (Landcare Research) for their laboratory assistance.

My special thanks are also extended to the staff based at Landcare Research Palmerston North as well as the staff and postgraduates of Physical Geography Group for providing an enjoyable and suitable working environment.

Last but not least, my deepest thanks to my family, friends, and the global community of Congress-WBN for their support, guidance and inspiration.

## Thesis Structure and Authorship

This thesis consists of four manuscripts written for publication (two accepted and two in submission) with 4 supporting chapters.

Simon Vale carried out all the fieldwork in the Manawatu between April 2012 and December 2014 and was assisted at different times by Dr Ian Fuller and Dr Jonathan Procter. Simon Vale also undertook all the laboratory work included in this thesis with some assistance by Dr Anja Moebis (Massey University), XRF technicians (Auckland University), LA-ICP-MS technicians (Australian National University), as well as Ian Smith (Auckland University) who also assisted in data preparation following XRF and LA-ICP-MS analysis.

Simon Vale wrote all the text in this thesis as the principal author in the preparation of manuscripts included in this thesis (referenced in Appendix B) with all supervisors providing general advice and editing to manuscripts.

Signed by Principal Supervisor

A handwritten signature in black ink, appearing to read 'Ian Fuller', written over a horizontal line.

Dr. Ian Fuller

## Contents

Abstract.....	iii
Acknowledgements.....	v
Thesis Structure and Authorship .....	vi
Contents.....	vii
List of Figures .....	xi
List of Tables .....	xv
Chapter 1 Introduction.....	1
1.1 General Introduction.....	1
1.2 Study Site .....	3
1.3 Catchment Character .....	4
1.4 Aims and Objectives.....	10
1.5 Thesis Organization.....	11
1.6 Summary .....	12
Chapter 2 Literature Review: Sediment Fingerprinting .....	13
2.1 General Introduction.....	13
2.2 Introduction .....	13
2.3 Catchment Sediment Processes.....	14
2.3.1 Introduction .....	14
2.3.2 Sediment Cascade .....	16
2.4 Sediment Fingerprinting .....	23
2.4.1 Introduction .....	23
2.4.2 Quantitative Sediment Fingerprinting .....	33
2.4.3 Challenges within Sediment Fingerprinting.....	37
2.5 New Zealand Research.....	45
2.6 Summary .....	46
Chapter 3 Application of a confluence-based sediment fingerprinting approach to a dynamic sedimentary catchment, New Zealand.....	47
3.1 General Introduction.....	47
3.2 Abstract.....	47
3.3 Introduction .....	48
3.4 Study Area .....	51
3.5 Material and methods .....	53
3.5.1 Sample Collection .....	53



3.5.2	Sample Preparation and Analysis .....	55
3.5.3	Data Analysis .....	55
3.5.3.1	Statistical Discrimination.....	56
3.5.3.2	Principal Component Analysis.....	57
3.5.4	Geochemical indicators .....	57
3.6	Results .....	58
3.6.1	XRF and LA-ICP-MS .....	58
3.6.2	Step-wise discrimination analysis of confluences .....	59
3.6.3	Principal Component Analysis .....	62
3.6.4	Geochemical Summary.....	65
3.7	Discussion .....	69
3.7.1	Statistical limitations of data analysis within large catchments.....	69
3.7.2	Geomorphic effects at confluences.....	70
3.7.3	Changing geological influences of sub-catchments .....	72
3.7.4	Geomorphic evaluation with sub-catchment characteristics.....	74
3.8	Conclusions.....	75
3.9	Acknowledgements .....	76
3.10	Summary.....	76
Chapter 4 Characterization and quantification of suspended sediment sources to the Manawatu River, New Zealand .....		77
4.1	General Introduction .....	77
4.2	Abstract .....	77
4.3	Introduction.....	78
4.4	Study Site.....	81
4.5	Materials and Methods .....	83
4.5.1	Sediment Sample Collection.....	83
4.5.2	Sample Preparation & Analysis .....	86
4.5.3	Geochemical Indicators .....	86
4.5.4	Statistical Discrimination .....	87
4.5.5	Multivariate Mixing Model.....	88
4.6	Results and Discussion.....	90
4.6.1	Geochemical Indicators .....	90
4.6.2	Statistical Differentiation.....	93
4.6.3	Model Comparisons.....	101
4.6.4	Sediment Contributions.....	107

4.7	Conclusion.....	109
4.8	Acknowledgements.....	110
4.9	Summary .....	110
Chapter 5 Sediment source characterization during a storm event, Manawatu, New Zealand .....		111
5.1	General Introduction.....	111
5.2	Abstract.....	111
5.3	Introduction .....	112
5.4	Study Site .....	115
5.5	Methods.....	116
5.5.1	Sediment Sample Collection .....	116
5.5.2	Sample Analysis.....	117
5.5.3	Statistical Discrimination .....	120
5.5.4	Multivariate Mixing Model .....	120
5.5.5	Storm flow hydrograph.....	122
5.5.6	Relationship between sub-catchments and storm hydrograph .....	123
5.6	Results and Discussion .....	125
5.6.1	Statistical Differentiation .....	125
5.6.2	Storm Hydrograph Adjustment.....	128
5.6.3	Sediment source proportions of hourly sediment samples.....	132
5.7	Conclusion.....	140
5.8	Summary .....	141
Chapter 6 Sediment source variability and behaviour in the Manawatu River Catchment, New Zealand .....		143
6.1	General Introduction.....	143
6.2	Abstract.....	144
6.3	Introduction .....	145
6.4	Study Site .....	146
6.5	Materials and Methods.....	148
6.5.1	Sediment Sample Collection .....	148
6.5.2	Sample Preparation & Analysis.....	151
6.5.3	Geochemical Analysis.....	151
6.5.4	Statistical Discrimination .....	152
6.5.5	Multivariate Mixing Model .....	152
6.6	Results and Discussion .....	153

6.6.1.	Geochemical Analysis .....	153
6.6.1.1.	Sediment Source Group Variability .....	153
6.6.1.1.	Sediment Source Group Interpretation.....	154
6.6.1.2.	Geochemical Enrichment and Depletion .....	159
6.6.2.	Statistical Differentiation.....	160
6.6.3.	Mixing Model Comparison .....	164
6.7	Conclusion .....	168
6.8	Acknowledgements .....	169
6.9	Summary.....	169
Chapter 7	Synthesis of Discussion .....	171
7.1	Introduction.....	171
7.2	Geochemical Characterization in Large Catchments.....	172
7.3	Geomorphological Interpretation .....	175
7.4	Storm Flow Sediment Analysis .....	178
7.5	Sediment Fingerprinting Uncertainty.....	180
7.6	Catchment Management.....	182
7.7	Summary.....	182
Chapter 8	Conclusion.....	185
8.1	Introduction.....	185
8.2	Conclusion of objectives.....	186
8.3	Future Research.....	187
References	.....	189
Appendix A	– Comprehensive summary of sediment fingerprinting literature .....	204
Appendix B	Statements of Contribution to doctoral thesis containing publications .....	235

## List of Figures

Fig. 1: Study Location Mangahao, Mangatainoka, Tiraumea, Pohangina and Oroua River .....	4
Fig. 2: Geological map of the Manawatu Catchment .....	6
Fig. 3: Map of New Zealand showing suspended sediment yields at gauging stations and mean annual rainfall isohyets after Hicks et al. (1996). Bar areas are proportional to sediment yield .....	8
Fig. 4: Spatial pattern of land-use in the Manawatu Catchment.....	9
Fig. 5: Fine sediment size characteristics including organic and colloidal ranges from Naden (2010), although does not include silicates. ....	16
Fig. 6: Overview of erosion, transport, and deposition processes operating in a slope, channel, and floodplain domain (Warburton, 2011).....	17
Fig. 7: Difference in sediment yield based on rainfall and geology; weak sedimentary rocks yielded more sediment in comparison to gneiss, granite and marble rock (Hicks et al. 1996) .....	18
Fig. 8: Summary of principal factors controlling water erosion on hillslopes and sedimentary yield to rivers, after Charlton (2008) .....	20
Fig. 9: Location of investigation area and clay mineral compositions of sediments in the major tributaries of the Murray-Darling Basin from Gingele and De Deckker (2005) .....	26
Fig. 10: $\delta^{15}N$ cycle for soil–plant–atmosphere system (Fox and Papanicolaou, 2008a) .....	30
Fig. 11: Example of depth penetration characteristics down a soil profile (as measured by cumulative dry mass) of $^{137}Cs$ , $^{210}Pb$ , and $^7Be$ in undisturbed (top row) and cultivated (bottom row) soils (Walling 2002).....	31
Fig. 12: Sediment source labelling from $^{137}Cs$ and $^7Be$ depth ratios (Wallbrink and Murray, 1993).....	32
Fig. 13: Overview of approaches used to gain provenance information from tracers (D'Haen et al., 2012) .....	35
Fig. 14: Black box approach demonstrating gap of understanding in the processes between source and sediment and how they may alter sediment tracer values (Koiter et al., 2013b) .	37
Fig. 15: Manawatu sub-catchments showing confluences with small insets of land-use and geology .....	52
Fig. 16: Typical in-channel fine sediment deposits: point bar deposition (left); trapped in the interstices of larger clasts on a bar (right); and deposited in semi-dry to dried-out pools on bars (middle).....	54
Fig. 17: Display of discriminant function results for each confluence showing upstream and downstream discriminant scores. C1-2 has 3 variables so can have both x and y axis, C3, C4 and C5 only have 2 variables.....	61

Fig. 18: Display of principal component analysis data using biplots (left) showing the sample variation and loading plots (right) showing element loading pattern for each confluence ...	64
Fig. 19: Multi-element plots of major (top), trace (middle) and REE (bottom) .....	66
Fig. 20: Th/Sc versus Zr/Sc indicating zircon enrichment for each upstream sub-catchment .....	67
Fig. 21: Particle size analysis for upstream and downstream samples including D10, D50 and D90 .....	68
Fig. 22: Simplified map showing confluence morphology .....	71
Fig. 23: Manawatu Catchment, Land-use and Geology .....	81
Fig. 24: Manawatu River Catchment showing source sampling spatial distribution and key sub-catchments .....	84
Fig. 25: Sediment sources; (A) Channel Bank; (B) Hill subsurface; (C) Hill Surface; (D) Gravel Terrace; (E) Mudstone; (F) Mountain Range; (G) Loess; (H) Limestone .....	85
Fig. 26: Normalized multi-element diagrams for Major elements (top); trace elements (middle) and Rare Earth Elements (bottom) .....	92
Fig. 27: Bracket test showing maximum and minimum tracer values by source group for selected tracers with the fluvial values indicated by the red line. ....	93
Fig. 28: Bracket test (cont'd) showing maximum and minimum tracer values by source group for selected tracers with the fluvial values indicated by the red line. ....	94
Fig. 29: Bracket test (cont'd) showing maximum and minimum tracer values by source group for selected tracers with the fluvial values indicated by the red line. ....	95
Fig. 30: Visualization of sediment sources discriminant scores for the first 3 functions. ....	100
Fig. 31: Frequency distributions from mixing model outputs for each sediment source group from each of the four mixing models; Collins-GRG, Collins-Evo, Hughes-GRG and Hughes-Evo .....	103
Fig. 32: Frequency distributions from mixing model outputs for each sediment source group from each of the four mixing models; or Collins-GRG, Collins-Evo, Hughes-GRG and Hughes-Evo .....	104
Fig. 33: Boxplot showing comparison of Objective Function statistics.....	106
Fig. 34: Study site and sub-catchment geological composition altered from Vale et al. (2016b). ....	115
Fig. 35: Manawatu River Catchment showing source sampling spatial distribution .....	117
Fig. 36: Sediment source Characteristics ; (A) Mudstone; (B) Hill subsurface; (C) Hill Surface; (D) Channel Bank; (E) Mountain Range; (F) Gravel Terrace; (G) Loess; (H) Limestone .....	119
Fig. 37: Flood Hydrograph showing sub-catchment flow curves in actual time.....	122

Fig. 38: Bracket test showing maximum and minimum tracer values by source group for selected tracers with the mean from the storm sediment indicated by the red line. ....	125
Fig. 39: Bracket test (cont'd) showing maximum and minimum tracer values by source group for selected tracers with the mean from the storm sediment indicated by the red line. ....	126
Fig. 40: Bracket test (cont'd) showing maximum and minimum tracer values by source group for selected tracers with the mean from the storm sediment indicated by the red line. ....	127
Fig. 41: Interpolated daily rainfall (mm) from the 27 <sup>th</sup> to 29 <sup>th</sup> November 2013 showing highest levels to the east of the catchment. ....	128
Fig. 42: Visualization of sediment sources discriminant scores for function 1 and function 2 (Left) and function 2 and function 3 (right). ....	129
Fig. 43: Hydrographs and Sedigraphs of; (A) Manawatu River Flow at Teachers College; (B) Time-adjusted cumulative sub-catchment flow; (C) Manawatu River Sediment load at Teachers College; (D) Time-adjusted cumulative sub-catchment sediment load (D) .....	131
Fig. 44: Mean hourly sediment source contributions during the storm event; percentage (top), sediment load (bottom) .....	133
Fig 45: Mean proportions of each sediment process throughout the storm event (dashed line) and a 5 point moving mean (bold line) .....	134
Fig 46: Suspended Sediment Concentration (SSC) – Discharge hysteresis patterns for Manawatu River at Teachers college (top) and Pohangina at Mais Reach (bottom).....	136
Fig. 47: Differentiation of sediment sources from the two dominant sub-catchment flows; A) Upper Manawatu; B) Pohangina .....	138
Fig 48: Study site and sub-catchment geological composition altered from Vale et al. (2016b) .....	147
Fig 49: Time integrated suspended sediment sampler and submerged sediment tube housing. ....	148
Fig 50: Manawatu River Catchment showing spatial distribution of the sediment sources and location of the sediment sink. Shaded areas indicate sub-catchments as marked. ....	149
Fig 51: Mean major geochemistry for each sediment source group with range displayed through shading.....	156
Fig 52: Mean minor geochemistry for each sediment source group with range displayed through shading.....	157
Fig 53: Mean REE geochemistry for each sediment source group with range displayed through shading.....	158
Fig 54: Percentage change of each element after extended exposure to river environment for Hill Surface, Hill Subsurface and Mudstone sediment sources.....	160
Fig 55: Frequency distributions for the sediment source estimations based on the S.D. < 40 % solution.....	166

Fig 56: *Frequency distributions sediment source estimations based on the S.D. < 35 % solution*.....167

Fig. 57: *Boxplot showing comparison of Objective Function statistics of the model solutions* .....168

## List of Tables

Table 1: <i>River Classification of the Manawatu Region after Ausseil and Clark (2007)</i> .....	7
Table 2: <i>Areal percentage cover of the main land cover in the Manawatu derived from the Landcover Database (LCDB) v3 after Landcare Research NZ Ltd (2012)</i> .....	10
Table 3: <i>Factors influencing bank erosion (Lawler et al., 1997)</i> .....	21
Table 4: <i>Common land-use categories in fingerprinting studies</i> .....	29
Table 5: <i>Principal sources of uncertainty within sediment fingerprinting schemes (Small et al., 2002)</i> .....	40
Table 6: <i>Sub-catchment geological composition derived from the Qmap - Geological Map of New Zealand (see Rattenbury and Isaac, 2012)</i> .....	53
Table 7: <i>Limits of Quantification (LoQ) from XRF analysis for the major and minor elements</i> .....	55
Table 8: <i>Comparison between the XRF and LA-ICP-MS concentrations values</i> .....	59
Table 9: <i>Summary table of elements that showed successful discrimination for each confluence location with elements common to each confluence indicated in bold</i> .....	60
Table 10: <i>Summary of stepwise Discriminant function analysis Wilks' Lambda value indicated by <math>\lambda</math></i> .....	60
Table 11: <i>Principle Component Analysis results showing total variance account for and the associated pattern matrix of contributing elements</i> .....	63
Table 12: <i>Geochemical Indices for average upstream sediment data plus UCC and PAAS values for comparison</i> .....	65
Table 13: <i>Comparison of mean annual suspended sediment yields estimates for Manawatu sub-catchments</i> .....	74
Table 14: <i>Geological composition by sub-catchment</i> .....	82
Table 15: <i>Sediment source characteristics for each of the sediment source classifications (cf. Fig. 25)</i> .....	83
Table 16: <i>Parameters used in the mixing model optimization</i> .....	90
Table 17: <i>Geochemical indicators for sediment sources with * Indicating the influence of an outlier</i> .....	91
Table 18: <i>Variables Entered for Stepwise Discriminant Function analysis displaying Wilks' Lambda statistic (<math>\lambda</math>)</i> .....	96
Table 19: <i>Variance explained by each function (top), and centroid values for each source and group function (bottom)</i> .....	97
Table 20: <i>Predicted group membership of samples based on discriminant function analysis values</i> .....	99



Table 21: <i>Mean source estimates with associated standard error plus standard deviation</i>	101
Table 22: <i>Structure matrix showing function contributions of selected and unselected variables</i>	102
Table 23: <i>Summary of Objective Function statistics from each sediment mixing model as well as source contributions from the 30 top-most and bottom-most sediment objective functions</i>	105
Table 24: <i>Lag-time estimates of each sub-catchment relative to Manawatu at Teachers College</i>	123
Table 25: <i>Variance explained by each function (top), and centroid values for each source and group function (bottom)</i>	128
Table 26: <i>Predicted group membership of samples based on discriminant function analysis values</i>	129
Table 27: <i>Partial Correlations controlling for sub-catchment sediment loads derived from Regression analysis</i>	139
Table 28: <i>Geological composition by sub-catchment</i>	146
Table 29: <i>Sediment source characteristics adapted from Vale et al. (2016b)</i>	150
Table 30: <i>Comparison of Mean and S.D % (underlain with bar graph representations) for analysed geochemical elements of each sediment source group</i>	155
Table 31: <i>Variables Entered for Step-wise discriminant Function Analysis</i>	161
Table 32: <i>Structure matrix showing function contributions of selected (shaded beige) and unselected variables</i>	162
Table 33: <i>Variance explained by each function and centroid values for each source and group function</i>	163
Table 34: <i>Predicted group membership of samples based on discriminant function analysis values</i>	164
Table 35: <i>Comparison of sediment source estimates with those of Vale et al. (2016b)</i>	165