Clarifying the waters: A critical analysis of turbidity and its role in environmental monitoring in New Zealand

"The real dirt in turbidity"

Christina Bright

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Abstract

Turbidity is widely-used as a water quality indicator to infer the mass of suspended sediment (SS) transported through riverine systems, and is inexpensive, readily available, and can be easily deployed to record continuous measurements. However, using turbidity as a surrogate for SS concentration (SSC) is frequently confounded by the composition of riverine suspended material, and the particle size and shape of sediments. Presented as a series of research papers, this thesis provides a distinctly Southern Hemisphere perspective of sediment, organic matter, organic carbon, and turbidity across southern New Zealand, and offers a critical reflection on the role of turbidity in environment monitoring. The suspended material of southern New Zealand rivers under base flow was mostly comprised of inorganic suspended material, although the total composition also includes variable amounts of organic material (<10%, and up to 50 – 80%). The proportion of organic to inorganic particulate material in southern New Zealand is significant under certain land covers, and contributes a significant proportion of particulate organic carbon flux to the Southern Oceans (0.04 – 2.7 t km^{-1} a^{-1}). In addition, different catchment morphologies and lithologies have a propensity to discharge different particle size distributions of inorganic sediment. These differences in particle sizes are most likely a function of underlying lithology from in channel attrition. This thesis has also identified that specific turbidity (turbidity normalised to mass concentration of particulates) is a potentially effective metric to indicate a 'non-standard' light attenuation response (that is, greater turbidity per mass of SS). Specific turbidity is shown through both in-field measurements and laboratory experiments to be affected by organic composition (particulate and dissolved) and the particle size distribution. Multiple regression analysis of catchment characteristics show that suspended particulate material composition and particle size are linked to discharge and flow behaviour, landcover, and lithology. The application of these findings is applied to monitoring SSC with turbidity across New Zealand by examining the specific turbidity for 77-monitoring stations. It is evident that organic composition and particle size have a notable effect on SS-turbidity ratings across New Zealand, which has limitations for the comparability, and relevance of SS data derived from turbidity when used as a regulatory tool. This thesis shows that although turbidity is pragmatic, its use in SS monitoring is problematic.

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Common Abbreviations

CDOM	Coloured dissolved organic matter
DOM	Dissolved organic matter
DOC	Dissolved organic carbon
FPM	Fine particulate matter
POC	Particulate organic carbon
POM	Particulate organic matter
PSD	Particle size distribution
SS	Suspended sediment
SSC	Suspended sediment concentration
SSY	Suspended sediment yield
TOC	Total organic carbon
TSM	Total suspended material
UFPM	Ultra-fine particulate material

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1 Introduction

Human agency has had a pervasive influence on the state of waterways globally, through extensive land use transformation, intensification, and displacement of indigenous vegetation covers. The consequence of such changes has resulted in substantial degradation of waterways globally (e.g., Peters & Meybeck, 2000; Walling, 2008; Rodriguez-Blanco *et al.,* 2013), and these effects have been acutely felt across New Zealand (e.g., Quinn *et al.,* 1997; Basher, 2013; Larned *et al.,* 2016; Julian *et al.,* 2017). Threats to water security for human use, and for habitat protection have never been greater, with all major indigenous freshwater species in New Zealand now listed as either endangered or under threat (Dunn *et al.,* 2017). The disturbance of the land, through anthropogenic transformation, is particularly acute and degrades water quality, especially as an increase in particulate material is displaced from hillslopes into the conveyance systems of the dense network of rivers and streams across New Zealand.

Particulate material transported by rivers is comprised of inorganic and organic materials, and is indicative of the processes affecting the terrestrial environment (e.g., physical weathering, biological production, anthropogenic disturbance) and the processes controlling the amount and timing of material carried by rivers to other water bodies (e.g., climate, hydrology, seasonality) (Schlesinger & Melack, 1981; Meybeck, 1982; Hope *et al.,* 1994). It is important to understand *how* particulate materials are transported by rivers over these different spatial and temporal scales, during land use disturbance, and the effect this has on yields of particulate material that cascade through the fluvial system. Soil loss and the associated transport of nutrients have serious impacts on downstream environments and water quality, namely water clarity, and as such has received considerable attention (e.g., Walling, 1988; Wood & Armitage, 1997; Owens *et al.,* 2005; Hicks *et al.,* 2011; Wohl *et al.,* 2015; Upadhayay *et al.,* 2017). Particulate material in rivers, therefore, is a reflection of soil loss, bank and gully erosion, and landslides, as the armouring vegetation is degraded through forest clearance, heavy grazing, or mechanical disturbance (e.g., Ryan, 1991; Glade, 2003; Croke & Hairsine, 2006; Hughes *et al.,* 2012; Kamarinas *et al.,* 2016).

Evidently, ensuring good land use management can, in part, be achieved by managing how much particulate material is transported through river networks. The objective of this thesis is to examine, in detail, how much particulate material is conveyed through rivers in southern New Zealand in relation to inorganic suspended sediment, and how different landscape units contribute to the overall suite of particulate materials in rivers, how it is monitored, and how the use of surrogates of particulate material may be affected by differences in particulate composition, size, and optical properties. The surrogates (turbidity and specific turbidity) are the focus of this work as the current environmental management framework in Aotearoa New Zealand is specified in terms of turbidity in regional water plans (Harding *et al.,* 2016). Through this thesis the applicability and limitations of turbidity are explored, although it is recognised that turbidity is a pragmatic surrogate for quantifying suspended sediment, and by inference, land disturbance.

Suspended sediment is not easily measured, and several surrogate technologies have been developed to infer suspended sediment, typically optical water quality and visual clarity indices. Turbidity is one of the most common surrogates, as it is easy to measure with readily available sensors that are cost efficient and easy to install in-situ, with suitable laboratory based portable instruments available (Ankcorn, 2003; Kitchener *et a.,* 2017; Rymszewicz *et al.,* 2017). The term turbidity describes the optical clarity of river water (Gao *et al.,* 2008; Kamarinas *et al.,* 2016; Kitchener *et al.,* 2017), and distinctly differs from its common counterpart, visual clarity (Davies-Colley *et al.,* 2014). Despite being deployed in similar applications, both are used in different environmental monitoring scenarios, and the uptake and use of turbidity is more common. The most appropriate use of turbidity is to develop a site-specific and bespoke rating of suspended sediment concentration to turbidity (herein referred to as an SSC-turbidity rating) by pairing concurrent in-situ measurements of turbidity and SSC. However, when turbidity is used in this way as a surrogate, little regard is given to the organic matter, dissolved substances, and particle properties that control the optical expression of river water. This presents a significant challenge to obtaining continuous records of suspended sediment, particularly if the intrinsic characteristics of suspended sediment are not static over time, or space, and therefore can introduce noise in SSC-turbidity relationships (Collins *et al.,* 2011; Grove *et al.,* 2015). Noise leads to bias in the delineation of the landscape controls on suspended sediment generation and transport at spatial and temporal scales. These measurement discrepancies are largely manageable when using turbidity as a bespoke surrogate for one location. But when SSC-turbidity ratings are

extended to greater spatial scales, particularly where there may be heterogeneity in landscape units, sediment supply, and in-channel attrition, it may not be appropriate to translate SSC-turbidity ratings to other locations or events within the same catchment, let alone, to other catchments. Of greater concern, however, is when turbidity is used as an absolute threshold for environmental compliance that is common practice across New Zealand (Ryan, 1991; ANZECC, 2000). Thus, this thesis also provides a critical rationale for why turbidity may not be suitable as an absolute measure of suspended sediment and is highly susceptible to interference from other riverine material, namely organic particulates, coloured dissolved organic matter or changes in particle size.

There is, therefore, a growing tension between the pragmatic use of turbidity in environmental management situations, and what are understood as the science deficiencies of the method. Turbidity is an efficient surrogate for suspended sediment (with caveats), but a lack of understanding for when turbidity is not an appropriate metric has resulted in the default use of turbidity across different landscape units, and for regulatory frameworks in New Zealand. This thesis addresses these gaps in knowledge by exploring the environmental characteristics that lead to imperfect suspended sediment and turbidity monitoring, and provides a critical rationale for when and where turbidity is an appropriate surrogate.

1.1 Thesis Overview

Chapter Two is a broad introduction to suspended sediment and particulate organic matter, light attenuation, and turbidity and the relevant theory of their use and derivation; and surmises the relevant suspended sediment research within the New Zealand context. The chapter concludes with a description of the research strategy for this thesis and the specific research questions. The specific research questions are addressed in Chapters Three to Seven and are written as stand-alone journal articles. Each of these articles contains specific theory and methods as relevant to the specific research question being addressed. As research articles these chapters also include stand-alone results and discussion sections. The references, however, are compiled together at the end of the thesis. It should be noted that each of these individual article chapters has some duplication of introductory and theoretical content and methods across the chapters.

Chapter Three addresses the relevance of turbidity interference from POM in an indigenous tussock grassland catchment (C*hionochloa rigida*) and a catchment undergoing forest clearance in the Glendhu Experimental Catchments, Eastern Otago. This chapter sets the scope for the subsequent chapters and research projects that were developed, and was published in the *Journal of Hydrology (New Zealand)* in 2016. Chapter Four describes how the organic component of suspended sediment flux varies between agricultural and indigenous land covered catchments, from a region wide study of POM during baseflow conditions across southern New Zealand. The paper has been accepted for publication in *Geomorphology* (December 2019).

Chapters Five and Six both describe the effect of turbidimeter interferences and different light attenuation responses. Chapter Five evaluates the effect of organic matter on light attenuation and turbidity and quantifies the effect of POM and CDOM on SSC-turbidity relationships. The influence of particle size and shape, and their influence on nephelometric turbidity is discussed in Chapter Six. Chapter Five was published as a research article in *River Research and Applications* (2018), and Chapter Six was submitted to the *International Journal of Sediment Research* in 2019 and is currently under review. The final research article is presented in Chapter Seven, and examines turbidity, suspended sediment and other optical measures of water clarity measured as part of the New Zealand National River Water Quality Network (NRWQN). The article examined the influence of catchment characteristics on suspended sediment–turbidity ratings across New Zealand. Chapter Seven was submitted to *River Research and Applications* in 2019, and is currently under review.

The significance and key findings of the thesis are summarised in Chapter Eight, which provides a synthesis of the five research articles, and bridges the individual research papers together. The synthesis also considers future research opportunities and critically reflects on the limitations of turbidity and its application in environmental monitoring in New Zealand. The continued use of turbidity for monitoring suspended sediment is discussed, particularly with respect to generating greater awareness for the trade-off between pragmatic use of turbidity and its methodological limitations. The research questions, and the outcomes of the thesis are summarised in Chapter Nine (Conclusions).

2 Muddying the Waters: A Review of Suspended Particulate Material in Rivers

Catchments and their rivers are dynamic and respond to both natural and anthropogenic impacts and are the primary transport pathway within catchments (Hedges, 1992; Belmont *et al.,* 2014). Therefore, the particulate materials transported by rivers can be indicators of disturbance across spatial and temporal scales, and reflect the response of natural vulnerability to erosion, or erosion that is enhanced by anthropogenic disturbance. The following sections describe the inorganic (Section 2.2) and organic (Section 2.3) components of the particulate material transported by rivers and identify where understanding is lacking. How these parameters are measured is described, particularly in relation to turbidity that is used in suspended sediment monitoring (Section 2.4). The general implications described are that turbidity responds to more than the presence of just sediment in river waters (Section 2.5). This observation is often stated, but is not well explained, and has critical implications to the use of turbidity that must be better understood. An account of suspended sediment research in New Zealand is provided, identifying a critical need for further research (Section 2.6). The chapter concludes with a statement of the research questions (Section 2.7) and research strategy (Section 2.8).

2.1 Riverine Suspended Particulate Material

Suspended inorganic sediment and particulate organic matter (POM) are the two components of riverine suspended particulate material and their relative proportions in any given catchment are dependent on a number of factors, including catchment characteristics (e.g., topography, soil and regolith type), climate (e.g., amount and timing of precipitation, seasons), and catchment hydrology (e.g., storm flows), although inorganic material (i.e., suspended sediment) is usually dominant (Hicks *et al.,* 2004). The release of suspended sediment to waterways from outside the fluvial environment relies on supply, and occurs primarily due to physical weathering processes, such as erosion; or human disturbance like

road construction, forest clearance, and land tilling (e.g., Dymond *et al.,* 2017). This material is then mobilised by surface water via overland flow pathways to surface waterways; but can also be temporarily stored, held in transit on riverbeds, banks and floodplains, before being re-entrained when storage zones are inundated by river flows, and critical transport thresholds are reached (Grabowski *et al.,* 2011). Instream stored sediment is preferentially sorted based on sediment properties (e.g., particle size and mineralogy, that control the mass, density, and settling velocity), so that for material in suspension sand will settle first followed by silt and clay. In this way, hydrodynamics controls the particle size distribution of sediments in suspension based on thresholds for entrainment and deposition (McCave, 1984; Grabowski *et al.,* 2011; Koiter *et al.,* 2013) (Figure 2.1 a-b).

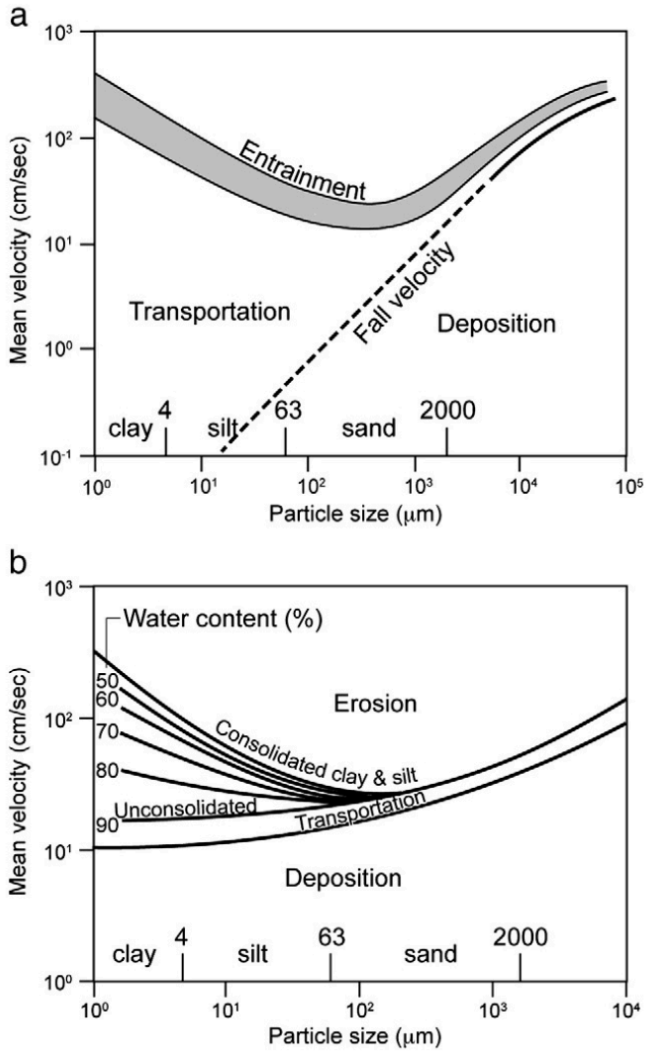

Figure 2.1 The a) Hjulström and b) Postma diagrams that describe the thresholds for entrainment and erosion according to particle size (Source: Grabowski et al., 2011).

The residence time of sediment within a river channel operates in equilibrium between in-channel sediment, and adjacent sediment stores, with processes that control transport competence and entrainment (Phillips *et al.,* 2007; Belmont *et al.,* 2014). Often the processes that cause a shift in this equilibrium are of most importance to environmental managers. For example, sediment transported by riverine systems has the potential to accumulate behind dams and other structures, where a reduction in stream flow velocity reduces stream competence. Such features operate to dampen or accelerate the occurrence of erosion, scour, and deposition. The effects of changing sediment fluxes is frequently observed at the coast, as beach erosion is linked to a reduction in riverine sediment supply, whereas excessive loading of riverine sediment can cause smothering of estuaries and the sea floor (Hicks *et al.,* 2004). Excess fine sediment either in fluvial, estuarine, or near shore zones therefore represents a natural hazard (Anthony & Julian, 1999) by either:

- clogging riverbed sediments and reducing habitat function (Ryan, 1991; Wood & Armitage, 1997);
- silting up harbours and estuaries affecting shipping and navigation (Rovira et al., 2014); or
- degrading cultural and social values and use of fresh and coastal waters (Newcombe & Jensen, 1996).

For these reasons, suspended sediment is a key water quality indicator for human use of rivers and harbours, as well as understanding ecosystem decline. Additionally, sediment flux and yields are the indices used to understand physical weathering processes and catchment denudation (e.g., Carey *et al.,* 2006; Larsen *et al.,* 2014), as well as land use disturbance impacts (e.g., Ryan, 1991; Hicks *et al.,* 2000; Basher, 2013; Croke & Hairsine, 2006).

Globally, the delivery of suspended sediment to oceans has been estimated in the order of 15–20 $x10^9$ t per year (Holeman, 1968; Milliman & Syvitski, 1992; Walling & Webb, 1996; Ludwig & Probst, 1998; Farnsworth & Milliman, 2003; Syvitski *et al.,* 2003). High relief islands in the Asia and the Oceanic regions are considered significant sediment producers, due to active tectonic margins that are dominated by small mountainous rivers (Milliman & Syvitski, 1992; Ludwig & Probst, 1998). In recent global assessments, sediment delivery by rivers to the coastal ocean is recognised as being controlled by both natural and anthropogenic influences (Walling, 2008; Vanmaercke et al., 2015; Wohl *et al.,* 2015). However, such anthropogenic impacts were not considered in early assessments, and

therefore assessments of 10–15 x10^9 t per year are conservative predictions of global yields (Milliman & Meade, 1983; Milliman & Syvitski, 1992; Ludwig & Probsts, 1998). Anthropogenic influence can also mediate sediment yields, for example, it is estimated that 15% of global discharge is impounded by large dams, therefore stalling the delivery of sediment (Nilsson *et al.,* 2005). In contrast, increases in yield from areas disturbed by industries, such as agriculture, forestry, mining, and construction are likely exacerbating sediment yields (Walling & Webb, 1996; Krishnappan *et al.,* 2009). Ultimately, the variability in global suspended sediment yields will likely increase as climate change alters precipitation patterns, the severity of storms, and reduce snow accumulation and melt seasons, that will result in deviations from current suspended sediment yields (e.g., Walling, 2008; Lewis & Lamoureux, 2012; Rodriguez-Blanco *et al.,* 2016; Zhou *et al.,* 2017).

Growing interest in the use of suspended sediment data has focused on understanding the physical and chemical properties of fine grained-sediment, soil erosion and supply limitations, sediment transport pathways, and in-channel storage and remobilisation, which are all essential to the efficient implementation of soil loss and erosion mitigation programmes. Research related to acquiring accurate sediment data has recognised the relationships between sediment and important sediment-related attributes, such as suspended sediment concentration, deposited sediment, visual clarity and turbidity, and light penetration (Foster, 1992; Clifford *et al.,* 1995; Davies-Colley & Smith, 2001). The properties of suspended sediment that allow the transport of other environmental nutrients and contaminants has raised interest in establishing the supply or transport limitations on particulate materials, employing new sediment source tracking technologies for sediment source discrimination in non-homogenous environments (e.g., Gibbs, 2008; Walling, 2013; Belmont *et al.,* 2014). These studies generally apply source-tracing techniques on land use types (e.g., Gibbs, 2008; Upadhayay *et al.,* 2018), or geochemical properties (e.g., Collins *et al.,* 2017; Koiter *et al.,* 2013; Vale *et al.,* 2016), and specific assessment of the processes that control concomitant transport is scant. Additionally, the approach is generalised to defining source end-members and constructing mixing models to explain sediment origin in the landscape, but generally do not account for in-channel attenuation, abrasion, or attrition that may transform the sedimentary signatures. Despite these limitations, suspended sediment is regarded as a complex mixture of terrestrially-derived material with important biogeochemical functions, behaving as a vector for transport of eroded mineral material and

the associated transport of nutrients, and organic compounds (Baldwin *et al.,* 2002; Owens *et al.,* 2005).

2.2 Particulate Organic Matter

The migration of organic matter from hillslopes (primarily as soil organic matter) with other organic litter and leaf debris occurs simultaneously with the erosion of mineral material (e.g., soil and regolith), resulting in the delivery of both particulate materials to the fluvial environment (Hicks *et al.,* 2004; Sanchez-Vidal *et al.,* 2013). Consequently, total riverine suspended material contains portions of both particulate inorganic and organic material. The relative proportions of each informs the understanding of water quality parameters like water clarity, the processes of erosion and deposition, biological cycling, ecological function, chemical transformations, and the flux of nutrients and contaminants. Riverine organic material transported with sediment contains organic nutrients that accounts for 90 – 240 Mt a^{-1} of carbon globally (Schlesinger & Melack, 1981; Lyons *et al.,* 2002) and is a significant component of the global carbon budget.

Particulate organic matter (POM) yields are less well documented than suspended sediment and are often implicitly described in carbon flux studies that report yields of particulate organic carbon (POC) and dissolved organic carbon (DOC) (e.g., Meybeck, 1982; Ittekkot, 1988). Understanding POM flux and dissolved organic matter species has played a significant role in developing the River Continuum Concept (Figure 2.2). The concept provides a framework for understanding the regulatory mechanisms for biological equilibrium (Vannote *et al.,* 1980), although does not specify the key landscape characteristics that enable delivery of organic matter from the terrestrial environment. While the River Continuum concept is highly cited, the concept has also been widely criticized (e.g., Winterbourn *et al.,* 1981). What is known is inferred from carbon cycle studies that describe the ratio of DOC to POC as a means of establishing the dominant forms of carbon flux (Schlesinger & Melack, 1981; Meybeck, 1982), and by doing so have identified the proportion of POM that comprises the suspended load in rivers primarily in relation to hydrological variations only. This is a considerable gap within the existing knowledge, as understanding POM and POC flux in association to landscape types and land use practices is particularly relevant in disturbed landscape, like New Zealand, and informs Research

Questions Two, Three, and Four which aims to connect fluvial POM to POC yield across diverse catchments (see: Section 2.6).

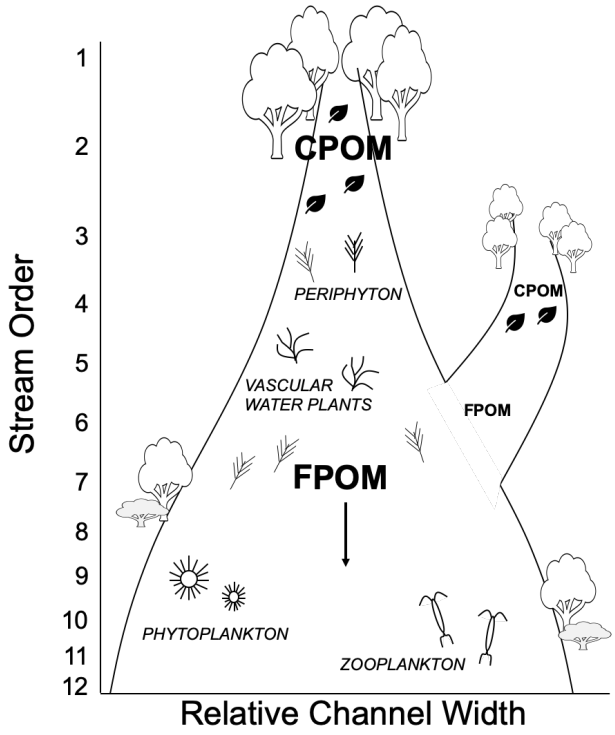

Figure 2.2 River Continuum Concept defining the coarse particulate organic matter (CPOM) and fine particulate organic matter (FPOM) that are derived from a number of terrestrial and in-stream sources longitudinally along a river channel (Adapted from: Vannote et al., 1980).

Particulate organic matter is most easily determined by a loss-on-ignition method whereby suspended material samples are dried at 105ºC in a convection oven for up to 24 hours, followed by weighing, and then incinerated in a muffle furnace at temperatures between 375 and 600 ºC, and reweighed (Grove & Bilotta, 2014). Weight lost is equivalent to the organic portion of the total sample. POM proportions of TSM vary significantly, being as low as 1–2.5% (e.g., Ittekkot, 1988; Ittekkot & Arain, 1996; Lyons *et al.,* 2002; Gomez *et al.,* 2003; Wu *et al.,* 2007; Zhang et al., 2009), or much higher at 45–70% (e.g., Naiman, 1982; Hasholt & Madeyski, 1998; La Husen, 1994; Golladay, 1997; Schallenberg & Burns, 2003; Madej, 2015). Those studies showing higher proportions of organic matter are usually observed in forested catchments with a higher availability of organic material (e.g., Golladay, 1997). Specific yields of carbon (and organic matter) are highly dependent on ecosystem type and specific environmental characteristics, therefore large variability in specific yields are

observed globally; 1.0 – 23.4 g C m^{-2} yr^{-1} is estimated across global forests (tropical, temperate, boreal), grasslands, tundra, and wetlands (Schlesinger & Melack, 1981).

Global carbon fluxes include both dissolved and particulate forms, which are regulated by atmospheric processes, vegetation and soil production, biogeochemical exchanges, hydrology, in – stream retention and production, climate, and geology. The effect of these complex interactions between the atmosphere-hydrosphere-lithosphere-biosphere all influence the amount of POC produced within and alongside river corridors, and DOC-POC ratios (Hope *et al.,* 1994). As POM is incredibly important to the provision of POC (and DOC) in the fluvial system, understanding the POM transported by rivers, therefore, has important applications to the study of biological systems, nutrient cycles, and study of fluvial suspended sediment behaviour (Golladay, 1997; Goni, 2006; Hatten *et al.,* 2012; Madej, 2015). Particulate carbon can also be analytically determined using a total carbon analyser, by measuring in duplicate the same sample, one with a pre-treatment of filtering through a 0.45 µm glass fibre filter to determine the dissolved organic carbon (DOC); and the second sample analysed without filtering to determine the total organic carbon (TOC) (see: Standard Method 5310B, Reckhow, 2006). The POC is determined as the difference between the total and dissolved carbon measurements. If all components are known (including POM), then this data can then be used to calculate the van Bemmelen factor, which is the ratio of POC to POM (Pribyl, 2010). The van Bemmelen factor ranges from 1.4 – 2.5, with a value of 2 typical of most organic matter, that is approximately half of the organic matter is comprised of carbon (Pribyl, 2010). Therefore, studies that focus on POC and DOC can be used to infer yields of POM. The use of van Bemmelen factors to estimate POC in New Zealand is limited, and in general this technique has more commonly been applied to global soil organic carbon assessments (Pribly, 2010; Grove & Bilotta, 2014). In Pribyl's (2010) review of studies reporting global van Bemmelen conversion factors, no examples were reported for New Zealand. This is a considerable limitation associated with understanding carbon export in association to fluvial POM across New Zealand, as others have shown that carbon export is highly relevant in New Zealand, particularly in POC form (e.g., Gomez *et al.,* 2003; Carey *et al.,* 2005).

To better understand carbon flux from organic matter, this thesis calculates a van Bemmelen factor for southern New Zealand and estimates carbon yields (see: Research Question Three in Section 2.6). Furthermore, there is a disconnect between studies focused on suspended sediment and organic particulates as there is little overlap between studies that focus on both

fluxes. Most often sediment related research is concerned with environmental impacts, and catchment denudation (e.g., Croke & Hairsine, 2006; Larsen *et al.,* 2014), whereas organic matter and carbon studies are concerned with carbon cycling processes, sequestration and carbon burial (Schlesinger & Melack, 1981; Lyons *et al.,* 2002; Gomez *et al.,* 2003; Carey *et al.,* 2005). There is a need for greater understanding of the relationship between fluvial sediment and organic matter, and the processes that control the inorganic-organic mix of riverine suspended particulate matter, and informs the development of Research Questions One and Two, that are addressed in Chapter Four.

2.3 Water Clarity and Surrogate Technologies

The concentration of sediment and other fine materials determines water clarity and visual appearance, ultimately affecting the provisioning of ecosystem services, such as the penetration of light and photosynthesis. Insufficient light in riverine ecosystems can result in fish mortality and affect macroinvertebrate community composition (Davies-Colley & Smith, 2001; Wood & Armitage, 1997; Davies-Colley & Wilcock, 2004; Krishnappan *et al.,* 2009; Julian *et al.,* 2013; Osadchyy *et al.,* 2016). In addition, reduced visual range has a considerable effect on the human perception of recreational water bodies, cultural and aesthetic values, and human health, and therefore limits are often set on optical clarity related parameters in regulatory frameworks (Davies-Colley & Close 1990; Smith *et al.,* 1997; Davies-Colley & Smith, 2001; Sadar 2004). Optical clarity and suspended sediment are monitored primarily using proxies, as to observe and collect sufficient suspended sediment data is a resource intensive process. Manual collection of sediment data requires frequent site visits, particularly at higher flows, followed by time-consuming laboratory processing (Larsen *et al.,* 2001).

Early approaches to estimating sediment yields were to rate sediment concentration to discharge through simultaneous sediment and stream flow gaugings, and were used to develop SSC-discharge rating curves (e.g., Adams, 1979; Adams, 1980; Duvert *et al.,* 2012). These approaches are convenient, since subsequent estimations of sediment transport can be made from discharge measurements alone, but have considerable sources of uncertainty, in particular, because suspended sediment does not peak concurrently with peak discharge (Wass & Leeks, 1999). It is common for suspended sediment to peak prior to peak discharge

and is the basis of hysteresis analysis of suspended sediment concentrations over hydrographs (Hughes *et al.,* 2012; Landers & Strum, 2013; Harington & Harington, 2014; Pietron *et al.,* 2015) (Figure 2.3b). In some instances, however, sediment supply and delivery conditions within a catchment may equally produce a sediment peak after peak discharge (e.g., Hafia, 1984; Walling & Webb, 1986; Harington & Harington, 2014; Pietron *et al.,* 2015) (Figure 2.3c), so that even a sediment rating that just considers the ascending limb of a hydrograph may substantially underestimate sediment concentrations. As such, the suspended sediment-discharge relationships within rivers are controlled by many complex processes (Hudson, 2003; Lefrançois *et al.,* 2007; Harington & Harington, 2014). In these regards discharge is a flawed surrogate for suspended sediment transport (Warrick, 2015). Rather, continuous in-field techniques that can determine changes in suspended sediment over hydrographs have greater application for quantifying suspended sediment where hysteretic responses occur. The most common of these surrogates is turbidity, as opposed to other optical water quality parameters, such as visual clarity, which have successfully been assessed for use as a surrogate for SSC but are harder to monitor over continuous time scales (Davies-Colley *et al.,* 2014; Slates *et al.,* 2014).

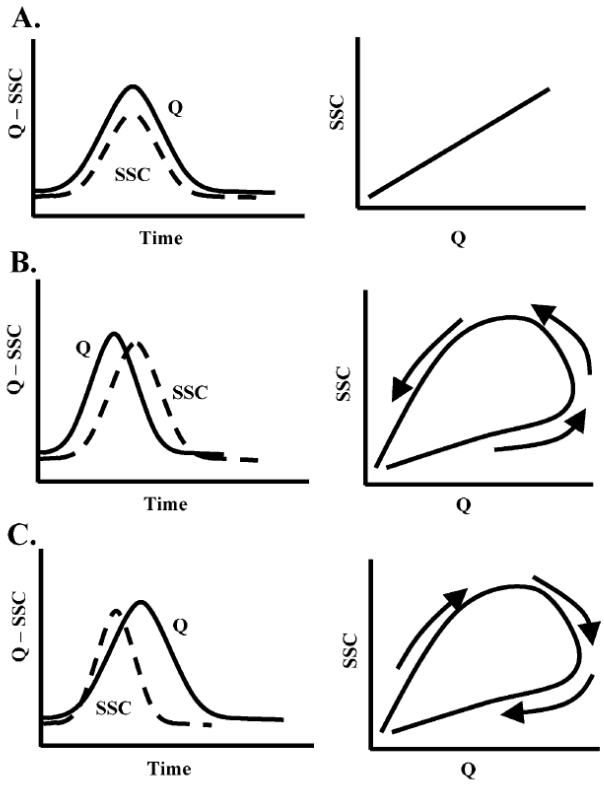

Figure 2.3 Common relationships between discharge (Q) and suspended sediment concentration (SSC) describing the a) linear trend, b) anti-clockwise, and c) clockwise hysteretic responses (Source: Hudson, 2003).

Turbidity is the most common surrogate technology that allows for continuous monitoring, however, other techniques include laser diffraction, pressure difference and acoustic sensors (Gray & Landers, 2014) (Table 2.1). Laser diffraction is used to measure the particle size distribution of suspended sediment and infers SSC based on scattering angles. Pressure difference methods requires simultaneous measures of pressure, and the difference is converted to a density value used to infer SSC, whereas acoustic sensors use the backscatter generated from acoustic waves to infer sediment characteristics (SSC, particle size distribution, and shape) (Larsen *et al.,* 2001; Gray & Glysson, 2003; Gray & Landers, 2014) (Table 2.1). Not one single surrogate is suited to the application of all continuous sediment monitoring needs, and no one technique is necessarily capable of estimating SSC under all conditions (Gray & Glysson, 2003; Gray & Lander, 2014). However, surrogates do provide a means of collecting data at higher temporal and spatial resolutions, and likely proves more useful to researchers and regulators than a limited number of more accurate suspended sediment measurements (Gray & Glysson, 2003), therefore this trade-off is typically made. Of all surrogates, turbidity offers a relatively rapid and inexpensive method for determining water clarity and suspended sediment concentration in comparison to the other surrogates described above, and is used extensively in environmental monitoring (Gippel, 1995; Ziegler, 2002; Ankcorn 2003; Gray & Glysson, 2003). Given the wide use of turbidity in New Zealand in regulatory monitoring (e.g., Hicks, 2011b) and sediment research (e.g., Ryan, 1991; Ballantine *et al.,* 2015), there is a need to assess the reliability and validity of using turbidity as a surrogate for suspended sediment across national-level monitoring networks (see: Chapter 7).

Table 2.1 Summary of surrogate technologies for monitoring suspended sediment (Sources: Gray & Glysson, 2003; Gray & Landers, 2014).

Description	Advantages	Disadvantages
Turbidity		
Optical expressions of a sample that causes light rays to be scattered and absorbed rather than transmitted in straight lines.	Ubiquitous; Technology is well established; Calibration is straightforward; Most affordable; Laboratory and in-situ measurement	Unrepresentative of cross-sectional SSC variability Saturation of turbidity signal common; Sensitive to biological fouling and grain size composition colour shape of sediments; Lack of consistency between commercially available instruments
Laser Diffraction		
Instruments exploit the principles of small angle forward scattering angles to infer particle size distribution (PSD) Using PSD sediment concentration (SSC) can be inferred.	Continuous PSD measurements; Calculated SSC are not affected by variability in PSD; Laboratory and in-situ measurement; Unaffected by changes in particle size	Biological fouling; Unrepresentative of cross-sectional SSC variability; Saturation of laser-optic signal; Cost
Pressure Difference		
Simultaneous measurements from pressure transducer sensors arrayed at different depths in a water column. E.g., bubbler technology. Pressure difference is converted to a water density which SSC is inferred from after correcting for water temperature.	Representative of a vertical column's SSC; Robust technology; Accuracy improves with SSC; Simple and straightforward theory	Unrepresentative of cross-sectional SSC variability; Assumes near constant SSC in the vertical; Less suited to low SSC environments; Sensors must be submerged, and therefore vulnerable to flow level changes; Spurious data with turbulent flow
Acoustic		
SSC determined using back scatter and attenuation of acoustic signals. E.g., acoustic doppler velocity. Acoustic waves passing through water-sediment mixture will scatter and attenuate. Backscatter and attenuation relate functionally to sediment characteristics (SSC, PSD, and shape).	Acoustic meters are robust; Require little cleaning and maintenance; Measure a large portion of the flow; Can measure a high temporal resolution; Multifrequency can quantify PSD and SSC	Sensitive to biological fouling, PSD, grain size, composition, colour and shape; Wavelength defines sensitivity to sediment parameters – limited range; Limited at low concentration; Complex algorithms

2.4 Turbidity and Light Attenuation

Turbidity describes the optical clarity of water measured by light attenuation and the degree of light scattering caused by suspended materials in a water sample (e.g., clay, silt, sand, and organic matter, CDOM, and other micro-organisms) (Gippel 1995; Sadar, 1999; Sadar 2004; Ankcorn 2003; Kitchener *et al.,* 2017; Rymszewicz *et al.,* 2017). The particulate materials that give a scattering effect, and light attenuation (as measured by turbidity) are controlled by a range of catchment characteristics (i.e., physiography in Figure 2.4) and human activities, that have distinct water quality implications. Therefore turbidity and light attenuation are a useful and important metric of stream health (Figure 2.4). In environmental management, turbidity is used as a 'first warning' indicator for identifying areas in catchments where targeted soil erosion may be required. Or, is also used to assess where risk associated with soil erosion may be elevated. Environmental scientists use turbidity to derive SSC and study ecological processes, as changes in turbidity typically relate to predictable changes in suspended particulate matter concentration (Gray & Glysson, 2003).

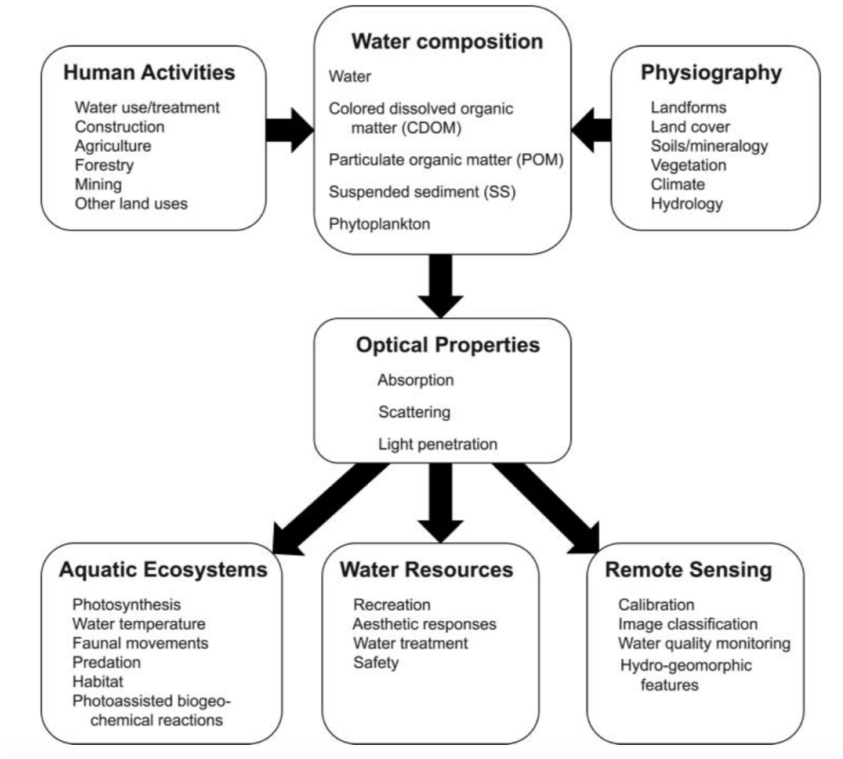

Figure 2.4 Relationship among catchment characteristics and independent processes that control optical water quality, and the related water quality outputs and applications of optical water quality data (Source: Julian et al., 2013).

Turbidimeters vary in the type of light source used (e.g., infra-red LED versus tungsten white light) and the position of the detectors in relation to the incident light that define the degree of scatter and light attenuation (Figure 2.5). Instruments with different optical design therefore may yield different results (Figure 2.6) (Sadar, 1999). Nephelometric turbidity sensors are a popular optical sensor used as the measurement of light scattering at 90º (± 30º) (Figure 2.6) to the light source increases linearly as SSC increases (Sadar 1999; Davies-Colley & Smith, 2001; Sadar, 2004). Nephelometric turbidimeters are calibrated to a formazin standard made from a synthetic polymer and measured in units specific to the method and light source type (e.g., NTU, FNU, FAU) (Sadar, 1999; Ankcorn, 2003). Two international methods specify the general regulatory methods available, EPA 180.1 and ISO 7027, although other methods include GLI Method 2, which is less frequently used as it applies to a specific type of instrument (Ankcorn, 2003). Method EPA 180.1 specifies a white light tungsten filament lamp that measures light attenuation within the visible light spectrum at 400 – 600 nm, whereas method ISO 7027 specifies use of an infrared LED light at 860 nm (Sadar, 1999), and there are a number of instruments available that meet requirements of either EPA 180.1 or ISO 7027 methods.

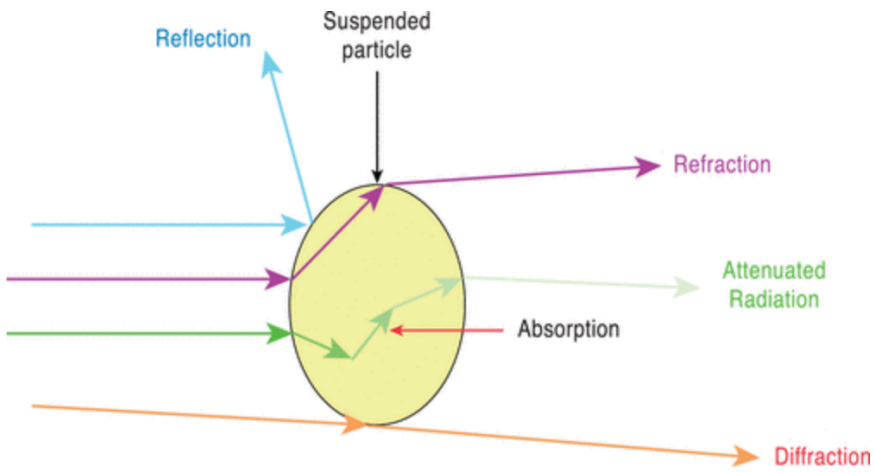

Figure 2.5 The scattering and absorption effect of suspended particulates that define the light attenuation response of water (Source: Kitchener et al., 2017).

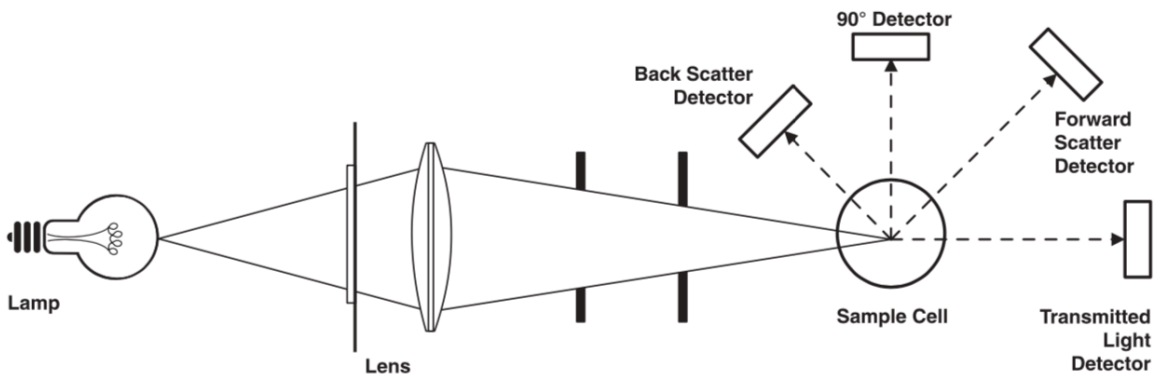

Figure 2.6 Typical optical design of turbidimeters (Source: Sadar, 1999).

Turbidimeters and the sensors used to measure turbidity can be more or less sensitive to the non-homogenous and optically distinct components of the suspended particulate matter and CDOM depending on the optical design of the instrument, as shown in turbidimeter sensor comparison studies (e.g., Gippel, 1995; Davies-Colley & Smith, 2001; Ziegler, 2002; Barter & Dees, 2003; Lewis *et al.,* 2007; Rymszewicz *et al.,* 2017). Optical effect, and light attenuation is sensitive to differences in composition, size, shape, density and refractive index of suspended materials (Sadar, 1998; Gippel, 1995; Davies-Colley & Smith 2001; Ziegler, 2002; Sadar, 2004; Omar & MatJafir, 2009) (Figure 2.5). Organic and inorganic material range from clay sized plate-shaped minerals < 1 µm, to sand sized spherical minerals and irregular shaped organic debris (> 63 µm) (Hicks *et al.,* 2004), and therefore the light attenuation effect of inorganic suspended sediment (clay, silt, and sand), POM, and CDOM contribute to turbidity differently. Turbidity is not directly related to, nor calibrated with, a particular type of particle, and rather measures the net combined optical effect of particulate and dissolved materials in relation to formazin standards (Gray & Glysson, 2003). The formazin standard therefore does not reflect the range of particles that exist in the environment and poses issues when using turbidity to infer the characterises of natural suspended particulates (Gippel, 1995; Davies-Colley & Smith, 2001). Therefore, the relationship between turbidity and SSC, and use of turbidity as a surrogate for SSC, depends strongly on composition and the particle size distribution of suspended materials, and is often catchment or location specific (Gippel, 1989; Lewis *et al.,* 2007). Non-linearity and noise of SSC and turbidity relationships is the result of optical variability (La Hussen, 1994; Ziegler, 2002; Davies-Colley & Nagels 2008; Omar & MatJafir, 2009). This inherently produces interference when the desired use of turbidity measurement is to predict SSC.

Variability in turbidity response is an acknowledged limitation of turbidimeter instruments by manufacturers (e.g., Sadar, 1999; Sadar 2004; Gray & Landers, 2014), however, it is generally overlooked by users (Gippel, 1989). Recognition for the practical limitations of nephelometry is growing (e.g., Ziegler, 2002; Kitchener *et al.,* 2017; Rymszewicz *et al.,* 2017) although in limited uptake since few studies quantify the impacts of noise in SSC-turbidity relationships on suspended sediment monitoring (Barter & Dees, 2003; Hicks *et al.,* 2004; Lewis *et al.,* 2007; Dymond *et al.,* 2017). Furthermore, there is no comprehensive account in current research of the effect that problematic turbidity measurement has on use of turbidity in suspended sediment monitoring, and where this is most influential. Therefore, Research Questions One and Five (Section 2.6) address these concerns directly and links the problematic use of turbidity to environments where these impacts are most profound. In particular, the scale of effect that irregular turbidity scatter caused by mixed sample composition, particle size and the shape can have on SSC-turbidity relationships is explored. Understanding these behaviours is crucial to understanding the relationship between turbidity and suspended sediment that is otherwise subjective and not well understood.

2.5 Suspended Sediment in New Zealand

New Zealand produces high riverine loads of sediment, even by global standards, due to the supply-dominated landscape and history of land disturbance since European settlement (Hicks *et al.,* 2011; Dymond *et al.,* 2017). Subsequently, significant work has attempted to quantify the yields of sediment and the temporal and spatial variation of suspended sediment since the late 1970s (e.g., Adam, 1978; Griffiths, 1981; Griffiths, 1982; Griffiths & Glasby, 1985; Dymond, 2010; Hicks *et al.,* 2004; Hicks *et al.,* 2011; Dymond *et al.,* 2017). Early studies of New Zealand's sediment yield were estimated at 389 Mt a^{-1} using annual suspended sediment yields determined from regional studies (Griffiths, 1982; Griffiths & Glasby, 1985). Hicks and others expanded on this approach by developing a NZ-wide sediment model that linked landscape units, rainfall, and geology to a generalised sediment yield model (Hicks *et al.,* 1996; Hicks *et al.,* 2003; Hicks *et al.,* 2011). By using an adjusted empirical method with additional data, a revised estimate of New Zealand's sediment yield was downscaled to 209 Mt a^{-1} that amounts to approximately 1.7% of global sediment delivery to the ocean (Hicks *et al.,* 2011) (Figure 2.7).

Rainfall variation in the South Island is a significant contributor to sediment yield (Hicks *et al.,* 1996), whereas in the North Island where rainfall variation is less, geological factors have more control over sediment yield. Relative to global standards (e.g., Holeman, 1968; Millian & Meade, 1983; Ludwig & Probst, 1998), New Zealand is a significant contributor of suspended material to the ocean on a unit area basis (Hicks *et al.,* 2011). In terms of total flux, Asia and the larger Pacific islands contribute around 70% of the global sediment budget, as sediment yields are much higher than for other global drainage basins due to high rainfall and tectonism (Griffiths & Glasby, 1985). A comprehensive review of suspended sediment research in New Zealand by Hicks *et al.,* (2004) summarised that land use, vegetation cover, and land disturbance were likely the main factors underpinning sediment yields. Despite the acknowledged variations due to rainfall and geological factors, national sediment yields incorporating land use or vegetation cover factors has not occurred. Improved understanding on the generation and transport of fluvial suspended sediment based on such catchment characteristics is crucial to understanding the erosivity parameters that exert control over sediment yield, for example land disturbance.

Figure 2.7 Map showing distribution of high to low specific suspended sediment yield (as t km^{-2} yr^{-1}) from New Zealand's rivers (Source: Hicks et al., 2011).

Monitoring for suspended sediment across New Zealand began in the 1950s and was carried out by the Ministry of Works as a way of understanding soil loss and erosion. Focus shifted to hydroelectric generation in the 1960s and 1970s (Hicks *et al.,* 2004), and in the 1980s and 1990s research was more focused on understanding sediment yields associated with land disturbance from land cover conversions in small catchments and the impact of soil loss on terrestrial landscapes (e.g., Quinn & Stroud, 2002). Up until the late 1990s there was a general gap in the collection of nationwide sediment data. In response to this, the New Zealand suspended sediment record was expanded and the New Zealand National River Water Quality Network (NRWQN) was established in 1989 measured sediment mass concentration although it was quickly switched out for cheaper alternatives like turbidity (Smith & Maasdam, 1994; Ballantine *et al.,* 2014). In recognition of a lack of suspended sediment data, monitoring for total suspended solids (TSS) was temporarily added back into the NRWQN network in 2011. Turbidity and visual clarity were related to TSS across the national record and proved useful as surrogates for TSS (or SSC) across New Zealand (Davies-Colley, 2013; Ballantine *et al.,* 2014). However still, these studies recognised scatter in relationships between TSS and turbidity (Davies-Colley, 2013; Ballantine *et al.,* 2014). Suspended sediment data is now more readily available throughout New Zealand, although largely through specific research projects focused at the catchment scale (Hicks *et al.,* 2004), and this data is sporadic in space and time (e.g., Griffiths, 1982).

Recent efforts in New Zealand to control the amount of anthropogenic sediment transported by fluvial systems and reduce impacts on downstream receiving environments has focused on reducing soil erosion at the catchment scale, employing mitigation techniques at targeted locations, such as riparian management and erosion control planting (Dymond *et al.,* 2017). More recent sediment yield estimation models such as SPARROW (e.g., Elliott *et al.,* 2008) and SedNetNZ (e.g., Hughes & Croke, 2011) have been developed with rainfall and geology as main controls, but also include other recognised controls on sediment yield. Nevertheless, there is still paucity in the collection of national sediment data (Ballantine *et al.,* 2014), and surrogates like turbidity are used despite little understanding of the challenges associated with the use of different turbidity methods.

The recognised need for a national approach for improved management interventions was reflected in the development of the National Policy Statement for Freshwater Management (2014) (NPS-FM) (Harding *et al.,* 2016). As part of this strategic environmental

management framework a National Objectives Framework (NOF) set limits on identified water quality variables, although sediment was not included as an attribute with set limits, rather the water quality implications related to reduced water clarity from increased sediment are recognised (Rouse & Norton, 2017). Sediment became the focus of the 2017 amended NPS-FM, followed by further recognition of the gap in understanding New Zealand's vulnerability to soil loss and increased sedimentation in rivers, signifying the lack of information still surrounding the impacts of sediment in New Zealand freshwater systems (Ministry for the Environment & Stats NZ, 2018). The 'Action for Healthy Freshwaters' package released by the Government in late 2019 includes proposed amendments to the NPS-FM and NOF that would see a limit set on suspended sediment as measured by turbidity. Furthermore, a National Environmental Monitoring Standard (NEMS) has been developed to support turbidity data collectors and users and sets protocols for the measurement of turbidity. Therefore, New Zealand provides a setting in which the use of turbidity for monitoring suspended sediment can be examined and evaluated. Despite movement towards standardised measurement, there remains a dearth of information related to the relevance of where and when turbidity is an appropriate surrogate for suspended monitoring. The present study addresses this gap in understanding and investigates the use of turbidity in suspended sediment monitoring for New Zealand.

2.6 Thesis Aim and Research Questions

There is a clear divide in the understanding of suspended sediment and organic particulates as separate components within fluvial systems. A growing body of research has identified the relevancy of both components in relation to water clarity and the optical expression of water, although much remains to be understood with regards to the landscape characteristics that control the inorganic-organic mix of suspended particulate matter, and the combination of catchment processes. Therefore, this thesis assesses the implication that suspended sediment is only one component of riverine suspended material that is fluxed through riverine systems, and the organic component (known as POM), can be a significant portion of the suspended flux across certain landscapes. Given its high sediment yields, New Zealand therefore provides a case for the study of both inorganic and organic fluxes that are particularly relevant to assessing the environmental impacts of riverine suspended material.

The compositional variations within riverine suspended material gives rise to suspensions with different particle sizes and shape that controls light attenuation and, therefore, turbidity measurement. Although these effects are acknowledged, there is a dearth of information that quantifies the effect these have to the use of turbidity as a surrogate in suspended sediment monitoring. Despite the considerable investment in monitoring with surrogates like turbidity, to improve the relevancy of sediment data more information on sediment properties and optical nature of the organic component is required. New Zealand's freshwater community is moving towards improved monitoring strategies, with focus being placed on sediment as a major water quality contaminant. New Zealand currently uses turbidity to monitor SSC and is in the process of establishing more regulated methods for the use of turbidity in suspended sediment monitoring (as discussed in Section 8.3), as such this research provides a useful contribution to the regional management of suspended sediment in New Zealand rivers, with applications to global use of turbidity in monitoring and research programmes. Therefore, this thesis aims to validate the effects of riverine suspended material composition and particle size on light attenuation responses and turbidity, and the general implication of this on use of turbidity in suspended sediment monitoring.

The specific research questions posited in this thesis are:

RQ1: Is POM an important component of stream suspended load, and does it affect suspended sediment-turbidity relationships?

RQ2: How much POM is fluxed by southern New Zealand rivers, and what is the association of this POM to suspended sediment and carbon flux?

RQ3: How much POC is discharged through rivers in Southern New Zealand and what is the POC yield for 84 southern New Zealand catchments?

RQ4: What extrinsic and intrinsic catchment characteristics control POM concentration and POM proportions?

RQ5: What effect do organic composition and particle size have on turbidity measurements derived from different nephelometric methods (EPA 180.1 and ISO 7027)?

RQ6: What influence do catchment characteristics have on suspended sediment–turbidity ratings across New Zealand?

2.7 Research Strategy

The approach of this thesis is to examine the relationships between suspended sediment, turbidity, and organic matter through a multiscalar, field-based approach. Previous research (Bright, 2015) was a pilot study into assessing changes in suspended sediment and nutrients associated with forest clearance, using the Glendhu Experimental Catchments in Eastern Otago, as a case study. Through this work, it became evident there was a poor relationship between turbidity and suspended sediment, and this directed further research into the nature of particulate material, its organic components, and how different types of carbon may act as interferences to establishing SSC-turbidity ratings. The findings from this initial small-scale study were then used to frame the main research agenda for this thesis. Scaling up from the pilot study, the approach of this thesis has been to conduct a series of investigations that highlight the scenarios in which turbidity is an imperfect predictor of SSC, and determines the landscape characteristics under which POM is most relevant (Figure 2.8).

As a part of a regional-scale assessment of SSC, POM and turbidity, seven high order southern New Zealand catchments were sampled to link in-river measurements of particulate material with variations in land use. Field based-studies were carried out to highlight the challenges of measuring SSC in landscapes displaying different characteristics. Additionally, laboratory experiments were employed to draw connections between the broad fluxes of suspended sediment and POM, and the properties of these particulate materials that give water a characteristic optical effect. Laboratory based experiments were carried out to mimic the conditions under which natural suspended material varies in controlled settings. The combined approach of field based and laboratory studies employed in this thesis allow for an examination of the effect that organic matter, coloured dissolved organic matter (CDOM), and particle size and shape have on light attenuation and turbidity measurement.

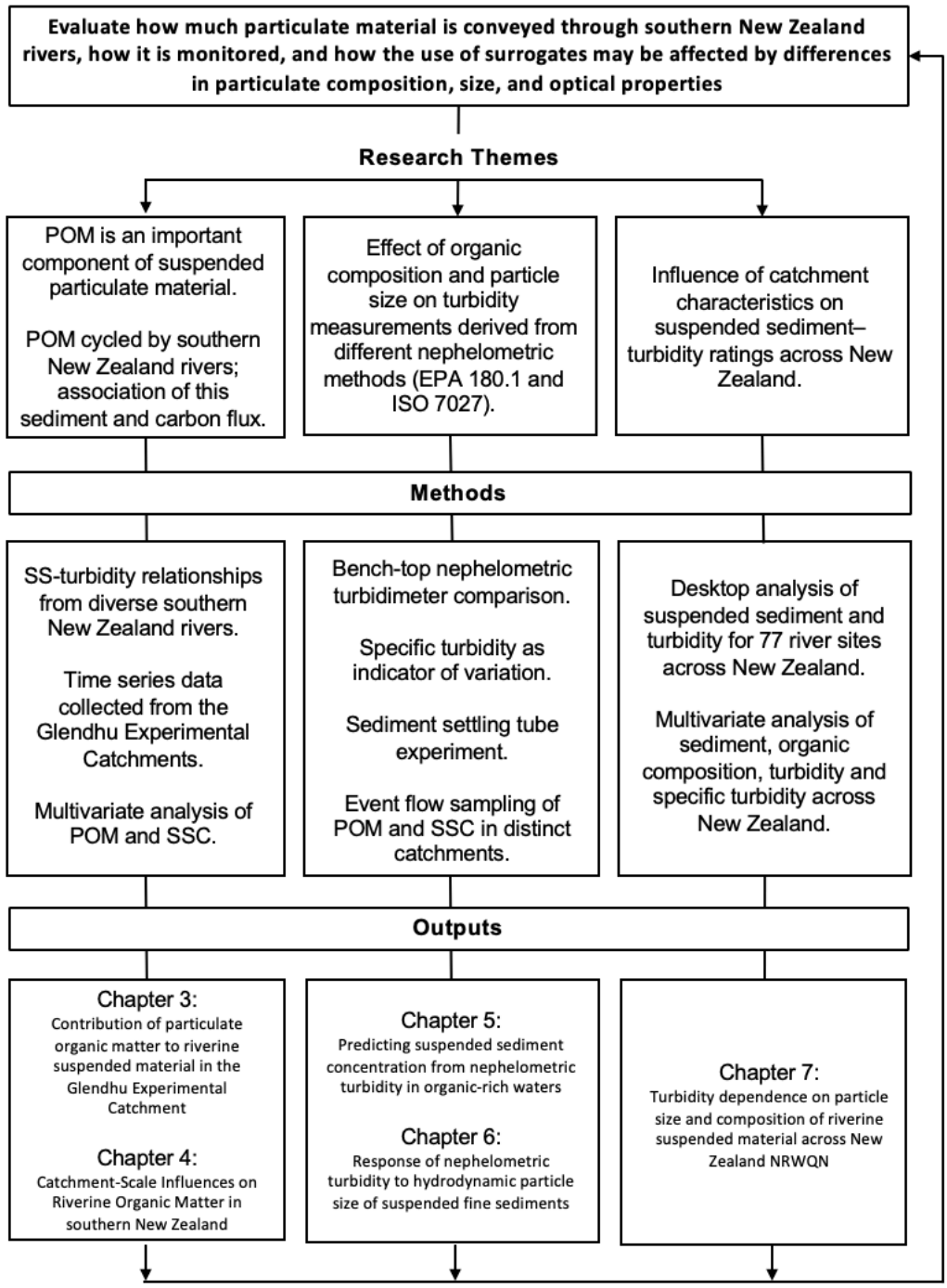

Figure 2.8 Overview of thesis research strategy with research themes, and the experiments carried out to understand the behaviour of suspended sediment, particulate organic matter and turbidity in a variety of catchments across southern New Zealand, and nationally across New Zealand's National River Water Quality Network (NRWQN).

As explained in this chapter, there is a clear mandate for research within New Zealand to examine the role of turbidity within regulatory settings, its use as proxy for suspended sediment, and to illustrate the potential factors that make turbidity a poor surrogate. Furthermore, investigation of the organic matter fluxes in relation to carbon export and the concomitant transport of this with inorganic suspended sediment is required, and crucial to the further understanding of suspended riverine materials. The following five chapters explore these issues as a series of research papers.

3 Contribution of Particulate Organic Matter to Riverine Suspended Material in the Glendhu Experimental Catchment

Research article published in the *Journal of Hydrology (NZ)* in 2016[1]. See Appendix 11.2.

3.1 Abstract

Turbidity is a widely-used water quality indicator that is used to infer the volume of suspended sediment transported through riverine systems. In New Zealand, regional limits on turbidity are a component of water plans, where excessive turbidity is often used to indicate land disturbance. Turbidity of river water is a function of both organic and inorganic constituents. Measurement of inorganic suspended sediment is common; however, to date there has been little work determining how much of the total suspended material in rivers may be organic material, and how this affects relationships between suspended particulates and turbidity. The objective of this study was to determine what portion of total suspended material occurs as particulate organic matter and what effect this has on the relationship between suspended sediment and turbidity. Particulate organic matter was determined by a loss on ignition method that supplemented traditional methods for determining suspended sediment concentration. In the Glendhu Experimental Catchments, Otago, New Zealand, particulate organic matter contributed 45% of the total suspended material from a tussock catchment and 60% of the total suspended material from a forested catchment, although concentrations were highly variable: 0.6–20.3 mg L^{-1} (equivalent to 10-80%) in the tussock catchment and 0.7–39.7 mg L^{-1} (equivalent to 23-95%) in the partially cleared forested catchment. These data suggest that particulate organic matter can represent a large portion of total suspended material in these catchments. The presence of dissolved organic material

[1] Minor changes to the narration of this research article have been made to improve coherency between chapters. The use of 'proxy' has been replaced with 'surrogate', for where turbidity is described in the use of estimating suspended sediment concentration.

may also interfere with turbidity measurements, and contribute to uncertainty in deriving turbidity-suspended sediment relationships in organic-rich rivers.

3.2 Introduction

Quantifying the amount of particulate material in rivers and streams is an important aspect of monitoring water quality because it is associated with the transport of nutrients, contaminants, pesticides, heavy metals, and pathogens (Griffiths, 1981; Walling, 2005; Gray & Gartner, 2009; Hughes *et al.,* 2012). Total suspended material (TSM) is composed of organic and inorganic fractions, and both types of suspended material are important contributors to stream water turbidity (Figure 3.1).

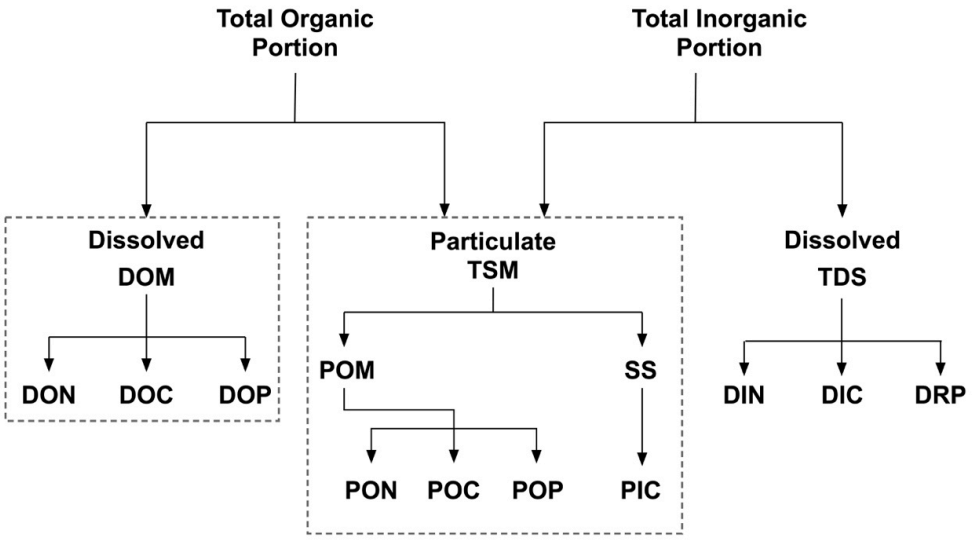

Figure 3.1 Diagram of dissolved and particulate constituents in river water with an emphasis on carbon contributions. The dissolved and particulate components comprise of organic and inorganic portions that may occur as dissolved (i.e., <0.7 µm) or particulate (>0.7 µm). Elements in the dashed box potentially affect turbidity. Abbreviations: DOM = dissolved organic matter, which comprises dissolved organic: nitrogen (DON), carbon (DOC), and phosphorus (DOP); TSM = total suspended material, which comprises particulate organic matter (POM) and (inorganic) suspended sediment (SS). POM also contains particulate organic: nitrogen (PON), carbon (POC), and phosphorus (POP), although POC is the dominant fraction. SS comprises dissolved elements, of which particulate inorganic carbon (PIC) is a small contributor. The dissolved fraction is usually referred to as total dissolved solids (TDS) and comprises many ions including nutrients (e.g., dissolved inorganic: nitrogen (DIN), carbon (DIC), and phosphorus (DRP)).

Turbidity is an inverse measure of water clarity, therefore turbidity increases due to the presence of suspended material, gases and some dissolved substances (Ziegler, 2002). The scattering, or attenuation, of light caused by the suspended material in a water column provides a basis for turbidity measurements (Ziegler, 2002; Jastram *et al.,* 2010). Unlike suspended sediment concentration (SSC), turbidity is relatively easy to measure and determined using turbidimeters in the laboratory, or in situ via a range of instruments. Three basic types of turbidity instruments are typically used: turbidimeters (nephelometers), spectrophotometers, and multiparameter instruments with submersible sondes that can accommodate a turbidity sensor (USGS, 1998). How turbidity data are applied (e.g., for assessing drinking water quality) and the specific site characteristics often define what type of instrument is most suitable (USGS, 2005). In New Zealand turbidity is commonly employed by unitary and regional authorities to assess the clarity of rivers for recreational, habitat and cultural use, as mandated by the National Policy Statement for Freshwater Management (NPS-FM) (2014). Turbidity is also commonly used as a surrogate for determining the SSC of stream water as changes in turbidity relate to a predictable change in SSC (Gippel, 1989; Gippel, 1995, Gray & Gartner, 2009; Hicks *et al.,* 2011), which is important for water uses where sedimentation is a concern (e.g., hydroelectricity generation, irrigation, fisheries management and ecosystem health). However, the organic and inorganic components of TSM affect measurements of turbidity differently (Table 3.1), and the use of turbidity to predict changes in SSC should be approached cautiously. Riverine sediment is recognised as an attribute that needs to be managed as a part of regional resource management plans (as outlined in the National Objectives Framework supplement to the NPS-FM, 2014). As a result, regional authorities use turbidity as a water quality attribute in their monitoring of freshwater systems and limit setting in regional plans.

Table 3.1 Components of total suspended material (TSM): Dissolved Organic Matter; Particulate Organic Matter (POM); and Suspended Sediment (SS) and how these variables affect turbidity (Adapted from: Gippel (1989) and USGS (2005)).

Component of Total Suspended Material (TSM)	Examples	Effect on turbidity
Dissolved Organic Matter	Fluvic acid, humic acid, lignosulphonic acid, tannic acid	Taint water with a characteristic yellow-brown colouration. Affects absorption of light
	Ionic forms of minerals	Nil effect
Suspended/Particulate Organic Matter (POM)	Pollen, micro-organisms, seeds	Variation in colour, shape, size, surface area, density and refractive index. Affects wavelength of light.
Suspended Sediment/Inorganic Matter (SS)	Products of weathering (e.g., quartz, kaolinite)	Variation in colour, shape, size, surface area, density and refractive index. Affects wavelength of light.

In New Zealand several studies have drawn attention to the use of turbidity as a surrogate measure for suspended sediment (SS) (e.g., Davies-Colley & Close, 1990) and have demonstrated the use of a number of other surrogate variables for determining SSC, like visual clarity (e.g., Davies-Colley, 1988; Davies-Colley & Close, 1990; Davies-Colley *et al.,* 1997; Ballantine *et al.,* 2015; Hughes *et al.,* 2015). These studies have identified that the relationship between turbidity and suspended material is complex, and that other variables such as water colour, presence of organic acids, and organic detritus affect the accurate measurement of SSC (e.g., US-EPA, 1993; Gippel, 1995). Therefore, the optical properties of water are not only dependent on the SSC, but also the presence of organic material.

Scatter in SSC-turbidity relationships results from a number of variables, including sediment properties such as shape, surface area and density, as well as the organic matter content of suspended load (USGS, 2005). Furthermore, these variables also depend on hydrologic factors such as season and discharge (Gippel, 1989; Gippel, 1995; Jastram *et al.*, 2010). In addition, the colour of stream water produced by the presence of dissolved organic material also affects turbidity by altering the wavelength of light detected by turbidimeters (Gippel, 1989; Davies-Colley & Close, 1990). Organic acids are readily leached from peaty soils (Fiedler *et al.,* 2008) and wetlands, and are a feature of acidic brownwater streams that drain indigenous forests on the West Coast of the South Island (Collier, 1987; 1988), and in the peat-rich areas of the North Island of New Zealand. Thus, the relationship between SSC and turbidity is typically bespoke to each catchment contingent on its rainfall, weathering resistance and soil characteristics (Gippel, 1989; Griffiths, 1981; Hicks *et al.,* 2011);

however, most established relationships between turbidity and SSC rarely account for how much of the suspended portion occurs as organic material. Thus, work is required to assess whether organic material is a significant portion of suspended load, and what effect this may have on turbidity measurements.

Studies that have assessed the concentration or portion of suspended material as particulate organic matter (POM) have mostly focussed on the contribution of particulate organic carbon (POC, which is a subset of POM; Figure 3.1) to determine the flux of carbon to the oceans and sequestration (e.g., Scott *et al*., 2004; Coynel *et al.,* 2005a; Hilton *et al*., 2008). A preliminary study of the POC portion of total suspended material (TSM) in New Zealand was undertaken by Lyons *et al.* (2002) by determining the portion of POC using a loss on ignition method. Three South Island rivers, the Cropp, Haast and Hokitika, were found to have <0.5% of TSM present as POC (Lyons *et al*., 2002). Similarly, a study of 10 large catchments in the North and South Islands quantified the portion of TSM as POC as less than 1%, with POC yield ranging from 1–81 t km^{-2} yr^{-1} (Carey *et al*., 2005). By comparison, Gomez *et al.* (2003) reported POC ranged from 0.4–4.0% of TSM concentration in the Waipaoa River, Gisborne. These previous New Zealand studies typically investigated large, steep catchments that were generally >350 km^2. However, overseas studies have reported that POC may be dependent on catchment scale, declining as catchment size increases (Madej, 2015), so the New Zealand studies described above may not adequately reflect the POC flux in smaller headwater catchments. Furthermore, the studies by Lyons *et al.* (2002) and Carey *et al.* (2005) had small data sets, basing the calculations of POC on 16 and 12 discrete grab samples, respectively, during summer in largely pristine alpine catchments, and may not be representative of different land uses or seasonal variations. Additionally, the few studies undertaken in New Zealand have not focussed on the potential relevance that POM and POC may have to measurements of turbidity and SSC.

To investigate the potential influence of POM on turbidity records, as well as the temporal variations in POM concentration and portion of TSM, a study was undertaken in the Lammerlaw Ranges, Otago. In this paper, POM concentration, and POM as a percentage of TSM, is assessed to determine whether POM is an important component of stream suspended load, and whether it affects SSC-turbidity relationships. Additionally, factors that may control the percentage of TSM that is contributed as POC, such as rainfall, discharge and seasonal variations, are also considered.

3.3 Method

The Glendhu Experimental Catchments were established in the Lammerlaw Ranges (Figure 3.2) in 1979 by the New Zealand Forest Service to assess the impacts of converting native Otago tussock grassland to *Pinus radiata* plantation forestry. These catchments have been the focus of numerous studies on the effects of land use change on hydrology (e.g., O'Loughlin *et al.,* 1984; Pearce *et al.,* 1984; Fahey & Watson, 1991; Fahey & Jackson, 1997). The experimental catchment design retained one catchment in indigenous tussock grassland (*Chionochloa rigida*) covering 2.1 km^2, and another was planted in *Pinus radiata* (3.1 km^2). The paired catchments are located 60 km due west of Dunedin City in the headwaters of the upper Waipori catchment (Figure 3.2), both facing north and ranging in elevation from 460 to 680 m above sea level. Clearance of the *Pinus radiata* catchment began in late 2014, with approximately 50% of the 3.1 km^2 catchment cleared by March 2016; earth works in preparation for further harvest were conducted in May 2016 and all activity paused over winter until harvest operations resumed in October 2016.

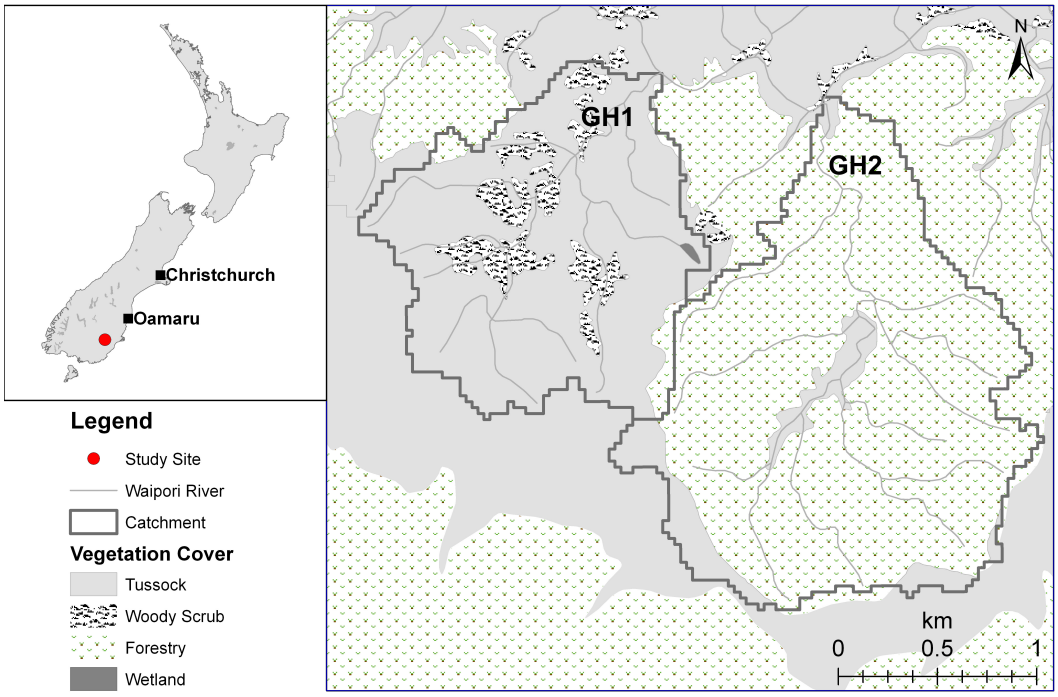

Figure 3.2 Location of the Glendhu Experimental Catchments in the Lammerlaw Ranges in Otago. The smaller catchment (GH1) is tussock grassland with mānuka scrub, and the larger catchment (GH2) is plantation forestry (Pinus radiata).

Discrete 500 mL samples were collected daily using ISCO automatic water samplers, and 1 L grab samples were manually collected every two to four weeks, between January and October 2016. Water samples were collected upstream of the gauging weir at the bottom of each catchment. Turbidity was measured using a HACH portable nephelometer using a white-light tungsten bulb following US-EPA (1993) (method EPA 180.1) nephelometer specifications. Each subsample was measured five times and the results averaged. Water samples were weighed on a two decimal point balance to determine water volume (adjusted for water temperature) and filtered through pre-washed and dried 0.7 μm glass fibre filters and oven dried at 105°C for 24 hours to determine TSM in mg L^{-1}. Filters were weighed on a four decimal point balance and re-dried three times. Subsequently, the glass fibre filters were then dried in a muffle furnace at 500°C for 30 minutes to determine the loss on ignition of the organic portion of the TSM. Organic matter is oxidised to CO_2 and ash between temperatures of 500ºC and 550ºC, so that the loss of mass is equivalent to the loss of organic matter. The muffle furnace was set to the lower end of that temperature range because delicate felsic minerals (e.g., biotite mica) appeared singed at higher temperatures during preliminary analysis. A burn time of 30 minutes was sufficient for such small samples (<0.2 g), but larger samples require longer burn times (Heiri *et al*., 2001). To convert the loss on ignition mass from POM to POC requires some knowledge about the ratio of organic carbon to organic matter (Grove & Bilotta, 2014). The standard approach is to apply a van Bemmelen factor, which ranges from 1.4 – 2.5, with a value of 2 typical of most organic matter; that is, approximately half of the organic matter mass is comprised of carbon (Pribyl, 2010). In this study, values are reported as POM since the specific van Bemmelen factor for this catchment is unknown (see Grove and Bilotta (2014) for the limitations of the loss on ignition method for estimation of POC). Where POC has been stated for this case study it has been estimated by using a van Bemmelen factor of 2 following the recommendation of Pribyl (2010).

The filters were reweighed to determine the mass loss, equivalent to the organic portion, which was assumed to be 50% carbon. The difference in mass by the loss on ignition method was recorded as POM in mg L^{-1}. In total, 91 samples were analysed from the tussock catchment (GH1) and 124 samples from the forested catchment (GH2). Samples that had a SSC below the method detection limit (0.3 mg L^{-1}, due to the analytical errors associated with the precision of the balance) were excluded from the data set.

3.4 Results

Water samples from the Glendhu Experimental Catchments show that on average 45% of the TSM was present as POM in the tussock catchment and 60% in the forested catchment. Under base flow conditions there was high variability in POM, both as a percentage of TSM and as a portion of overall flux. For example, in the tussock catchment POM ranged from 0.6–20.3 mg L^{-1} (equivalent to 10 – 86% of TSM), and 0.7 – 39.7 mg L^{-1} (23–95% of TSM) in the forested catchment (Table 3.2). Turbidity, POM, TSM, and percentage of TSM as POM (POM %wt) differed significantly between the two Glendhu study catchments (using the Mann-Whitney U-Test). However, there was no significant difference in SSC between the catchments (Table 3.2), indicating that differences in turbidity and TSM between the two catchments are likely attributable to the organic portion of suspended material. A wide range of POM as a percentage of TSM values existed (15 – 95%) for samples collected at median stream flow (Figure 3.3), highlighting the variability of POC in the Glendhu catchments; the results also show that POM is usually a higher proportion of TSM in the forested catchment than in the tussock catchment.

Table 3.2 Concentration (in mg L^{-1}) of the organic and inorganic portions of water samples in the Glendhu Experimental Catchments, turbidity as measured on a portable nephelometer, suspended sediment concentration and portion of particulate organic matter (POM) as a percentage of total suspended material (TSM) dry weight (POM %).

	Mean	Median	Max	Min	Count
Tussock GH1					
Turbidity (NTU)	1.2	1.0	5.6	0.3	77
POM	5.8	4.7	20.3	0.6	60
POC	2.9	2.4	10.2	0.3	60
SSC	6.3	3.8	32.8	0.5	91
TSM	10.2	6.5	37.3	0.5	91
POM %	46.0	45.0	86.0	10.0	60
Forest GH2					
Turbidity (NTU)	5.5	3.0	47.3	0.8	94
POM	8.9	6.4	39.7	0.7	124
POC	4.5	3.2	19.8	0.4	124
SSC	7.8	4.3	52.8	0.2	124
TSM	16.8	11.2	74.5	1.5	124
POM %	60.0	60.0	95.0	23.0	124

No correlation was evident between POC concentration and rainfall. Time series analysis of the rainfall record and the POM concentration showed no strong seasonal trends, or any consistent response to large rainfall events (Figure 3.3 and 3.4). For example, the largest three rainfall events during the study period occurred on 22 May 2016 (50 mm over 19 hours), 18 February 2016 (46 mm over 8 hours), and 28 May 2016 (45 mm over two days). During the two storm events in May, the concentration of POM was higher in the forested catchment than the tussock. For example, on 28 May 2016, POM concentration was 26.5 mg L^{-1} in the forested catchment and 1.1 mg L^{-1} in the tussock catchment. The storm in February 2016, when 39 mm fell over 8 hours on 17 February followed by 46 mm the next day, represents an intense rainfall event but POM remained less than 2.7 mg L^{-1} in the forested catchment (no data for the tussock catchment). Smaller events (e.g., 10–20 mm d^{-1}) similarly showed inconsistent changes in POM concentration relative to rainfall (Figure 3.4). The data suggest that intense storms do not necessarily lead to high POM concentrations, and therefore POM in these streams likely reflects the availability of the material, rather than storm characteristics.

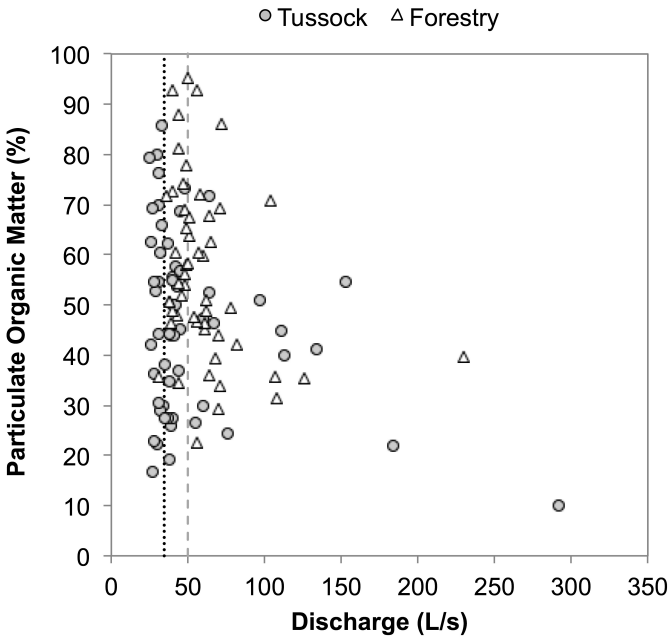

Figure 3.3 Portion of total suspended material as particulate organic matter (POM) (as a percentage of dry weight) plotted relative to stream flow at time of sample collection. Median daily stream flow over the 18-month study period is indicated by the dotted line (tussock catchment, GH1) and the dashed line (forested catchment, GH2).

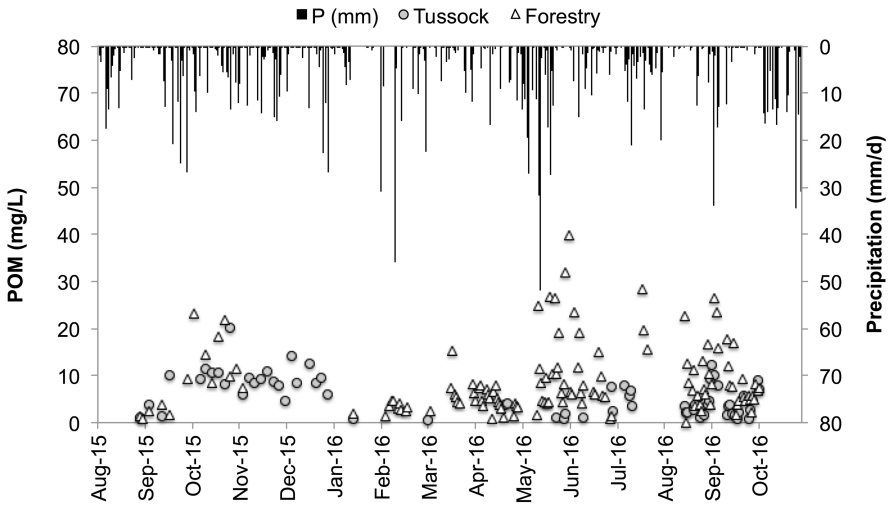

Figure 3.4 Particulate organic matter concentration (POM as mg L^{-1}) relative to daily precipitation (mm/d) for the tussock (circles) and forestry (triangles) Glendhu Experimental Catchments.

To evaluate the impact of rainfall on POM, three storm events between August and October 2016 (transition to spring) were examined in closer detail. Daily rainfall totals for an event between 5 and 8 October 2016 were 12.4 mm, 16.6 mm, 0 mm and 14.0 mm, resulting in a small hydrographic response with a peak discharge of ~100 L s^{-1}. In the two-week period prior to this event, both rivers were at base flow (~ 50 L s^{-1}); however, POM ranged between 1–10%, and did not appear to respond to the increase in flow. Furthermore, the highest POM value (7% on 22 September 2016 in the forestry catchment) did not correspond to any rain or change in discharge. A similar lack of POM response to rainfall and increase in discharge was observed on 25–27 August 2016, when 16 mm of rain fell over two days and stream flow increased to ~150 L s^{-1} (Figure 3.5). In this instance, POM for the tussock catchment never exceeded 5%, and POM for the forested catchment ranged between 5–15%, a decrease from 22% on 21 August 2016 (which was also not associated with any hydrographic response). A significant rainfall event occurred on 4–6 September 2016, with 35 mm falling over 13 hours late on the evening of 4 September 2016, and a further 11 mm falling on 6 September 2016 over 8 hours. Both catchments responded rapidly, peaking at 1,300 L s^{-1} in the tussock catchment and 700 L s^{-1} in the forested catchment. During this larger event, there appeared to be a distinct increase in POM in the tussock catchment, peaking two days after peak discharge at 12 mg L^{-1}; whereas the forested catchment showed no clear response with POM ranging from 5–15% over the period and peaking on 11 September 2016 (Figure 3.6).

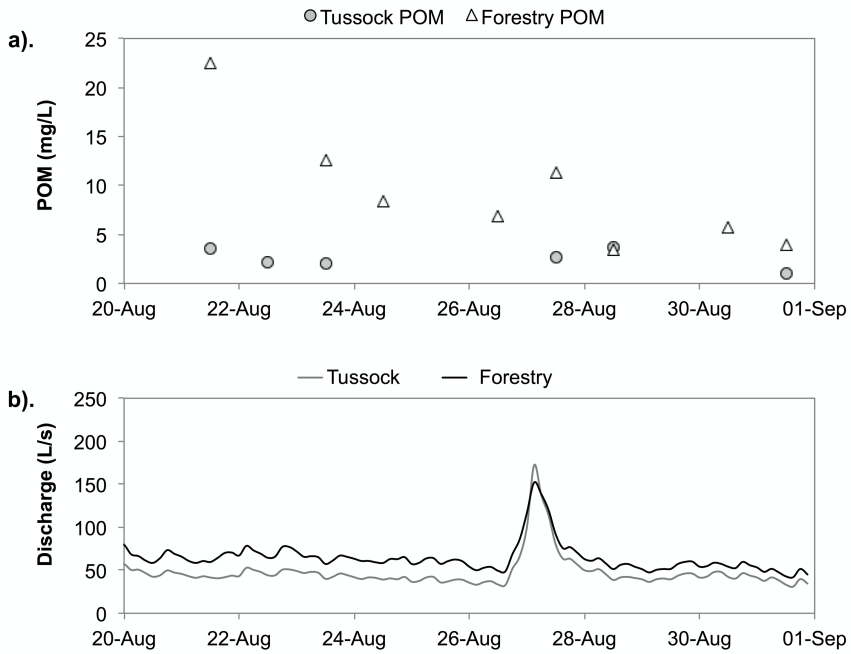

Figure 3.5 Variations in particulate organic matter (POM) concentration (mg L^{-1}) prior to, and during, a small rainfall event in August 2016, where: a) shows the POM concentration in the tussock (circles) and forestry (triangles catchment) and b) shows the discharge for this period (L s^{-1}).

3.4.1 Assessing the Relationship Between Suspended Material and Turbidity

For each catchment TSM, SSC and POM were plotted against turbidity and tested with linear regression to assess whether there was a statistically significant relationship (Figure 3.7). The presence of outliers and clustering of values suggests that there is no predictive pattern to the data; that is, turbidity cannot be used to predict the concentration of POM, SSC or TSM in the forestry catchment under base flow conditions (Figure 3.7a–c). There was a weak relationship between TSM, SSC and turbidity in the tussock catchment, and no relationship between POM and turbidity in the tussock catchment (Figure 3.7a–c). The turbidity, SSC and POM data from the tussock and forestry catchments are highly variable suggesting that there may be different factors influencing concentrations of SS and POM (although the relationships of SS and POM to turbidity are not statistically significant). Clearly under base flow conditions a predictive model of suspended material from turbidity cannot be established in these study catchments. Interestingly, the POM concentration is significantly related to TSM (Figure 3.8).

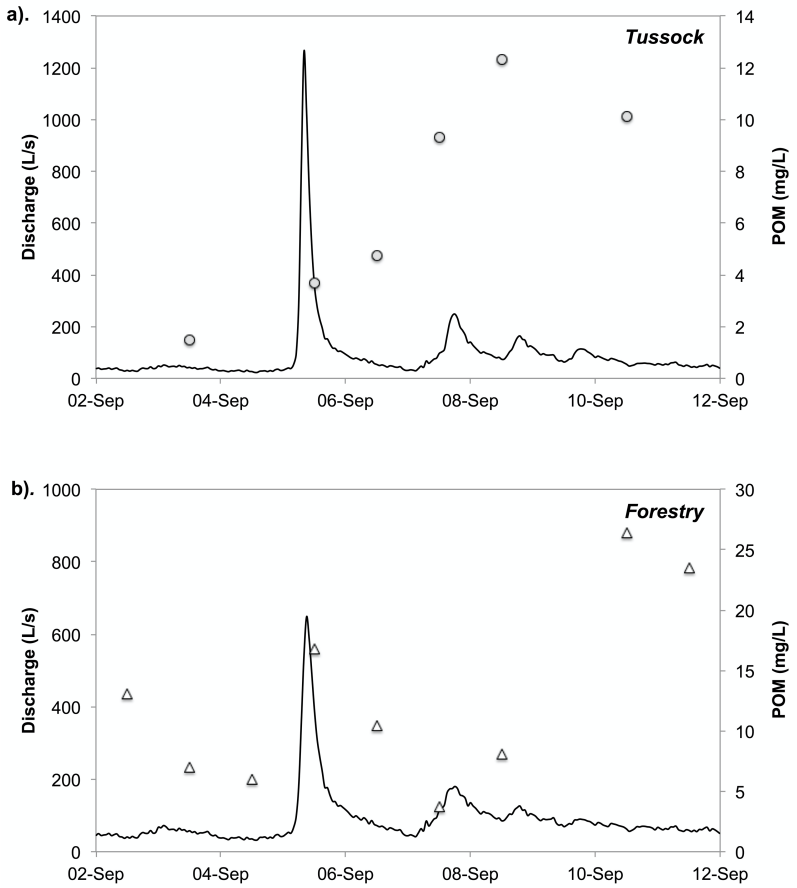

Figure 3.6 Variations in particulate organic matter (POM as mg L^{-1}) prior to, and during, a rainfall event in September 2016, where: a) shows the POM concentration in the tussock catchment (circles) and b) shows the POM concentration in the forested catchment (triangles), both relative to stream discharge (L s^{-1}).

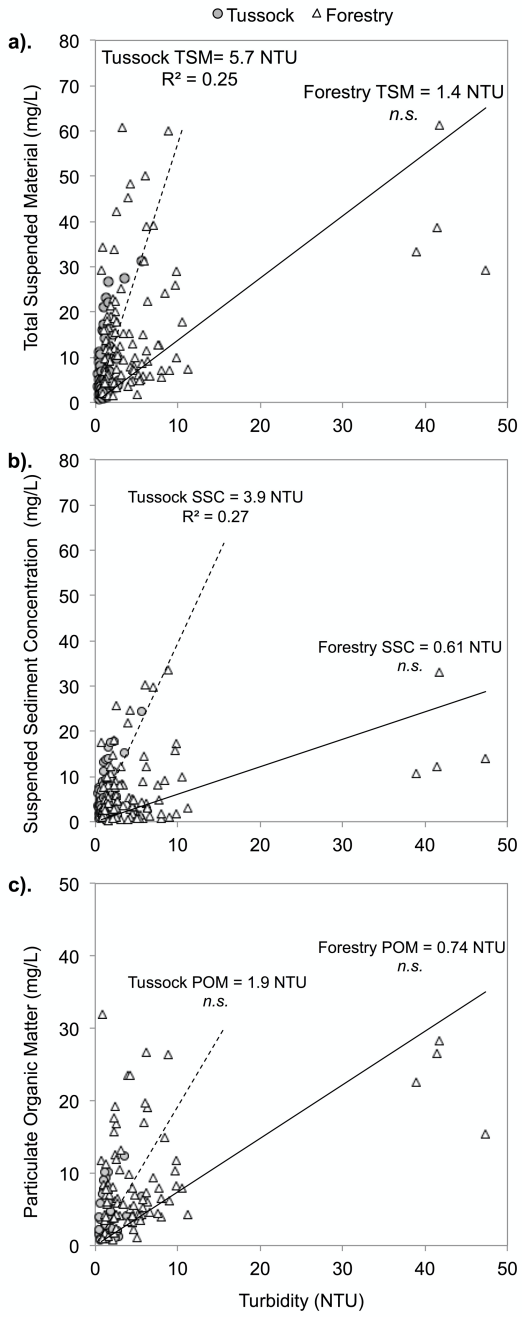

Figure 3.7 Variability in: a) total suspended material; b) suspended sediment; and c) particulate organic matter concentrations (mg L^{-1}) relative to turbidity in the tussock and forestry catchments. Fitted lines indicate the predicted regression relationships between the variables, and n.s. indicates no statistically significant regression relationship.

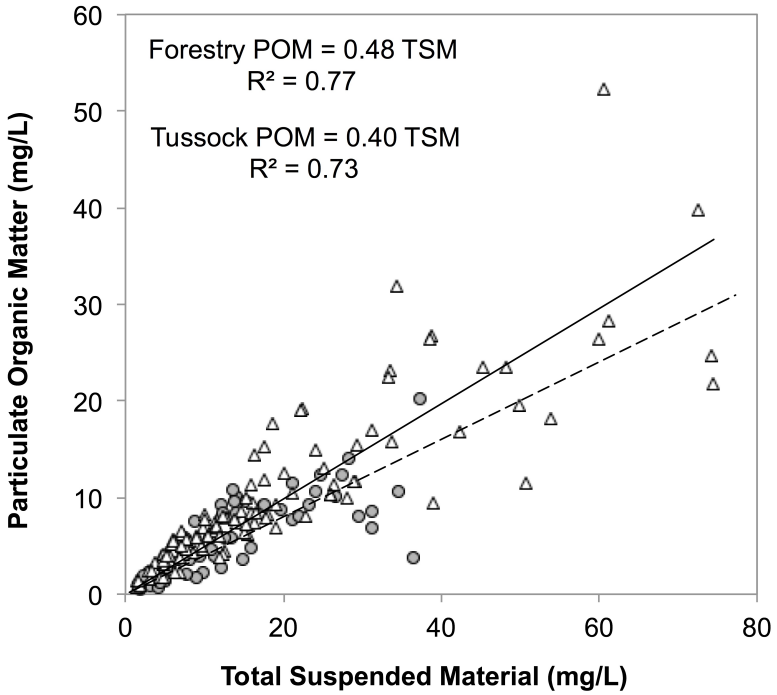

Figure 3.8 Particulate organic matter relative to total suspended material, indicating a strong linear relationship (e.g., as total suspended material increases so too does the concentration of organic matter) in the tussock (circles) and forested (triangles) catchments.

To assess whether the lack of any linear relationships between turbidity and suspended material was a function of temporal changes in the land system related to changes in soil moisture and plant growth, a simple seasonal analysis was undertaken. Data were aggregated into meteorological seasons, and then analysed using Spearman's Correlation. Correlation analysis revealed that TSM and turbidity are strongly correlated at the seasonal level (Table 3.3). In spring, in the forested catchment there was a moderate correlation of all variables, whereas in the tussock catchment, POM and SSC did not correlate with turbidity. On the basis of this analysis it suggests that not only is land cover a controlling variable, but also time of year; for example, the variables are more strongly correlated during winter in the tussock catchment than in the forested catchment.

Table 3.3 Spearman's correlation coefficient of the association between turbidity (NTU) and concentration of particulate material, as particulate organic matter (POM), suspended sediment (inorganic, SSC), and total suspended material (TSM). All reported correlation coefficients were statistically significant at the 95% confidence level, and n.s. indicates no significant correlation was observed. No seasonal data for summer is available due to insufficient data points.

	POM : NTU	SSC : NTU	TSM : NTU	POM : TSM	Count
Forestry (all data)	0.24	*n.s.*	0.21	0.94	94
Autumn	0.34	*n.s.*	*n.s.*	0.91	35
Winter	0.44	0.68	0.53	0.98	29
Spring	0.59	0.45	0.58	0.91	30
Tussock (all data)	*n.s.*	*n.s.*	0.33	0.85	61
Autumn	*n.s.*	*n.s.*	*n.s.*	*n.s.*	*5*
Winter	0.46	0.35	0.42	0.79	33
Spring	*n.s.*	*n.s.*	0.57	0.91	26

3.5 Discussion

The data presented above illustrate that POM can contribute a large portion of the TSM in runoff from both tussock and forested catchments, comprising on average 45% and 60%, respectively. These data indicate that the organic portion of TSM is significant, but also highly variable under base flow conditions. Such an observation is not unique to the Glendhu catchments; for example, a pilot study conducted over 2002 to 2003 by Madej (2015) suggested that the organic content of sediment loads in streams draining old-growth redwood forests could be as high as 65%, but is highly variable. The high POM content is likely a contributor to the absence of any statistically significant relationships between turbidity and SSC under baseflow, in conjunction with the potential confounding effects that water discoloration may have on turbidity readings.

3.5.1 Particle properties and water colour

The use of turbidity as a surrogate for determining SSC relies on the assumption that suspended particles do not alter in physical properties as concentration varies (Gippel, 1989). A similar study of five small forested catchments also found that turbidity and suspended sediment relationships were weak, but improved somewhat when consideration of particle characteristics (e.g., size, shape) and water colour were taken into account (Gippel, 1989). Although in Gippel (1995) that furthered earlier work of Gippel (1989), correction factors for water colour and particle size did not improve significantly the variance of SSC-turbidity and concluded that variance was due to other factors. This aligns with the assumption that the physical properties of suspended material must remain consistent for a linear relationship to be produced. The presence (or otherwise) of organic debris along with inorganic suspended sediment complicates this assumption, as organic and inorganic particles have vastly different hydrodynamic properties, particularly in shape and density (Omar & MatJafri, 2009). Furthermore, water discoloration also affects turbidity causing a potential interference in establishing SSC from turbidity measurements (US-EPA, 1993). When flowing water contains organic and inorganic suspended material, the scattering (attenuation effect) of light in a turbidimeter's response is different between the materials. Inorganic material causes hard scattering, compared to organic particles that have a lower specific gravity and a larger scattering surface area for a given mass (Gippel, 1995; USGS, 2005; Jastram *et al.*, 2010). These responses of turbidity to particle properties help validate the need to understand the proportions of POM and SSC of TSM in streams, as turbidity does not accurately reflect the concentrations of each suspended material type.

Water colour indicates the presence (or not) of dissolved organic carbon (DOC), which absorbs the blue part of the visible spectrum and shifts the perceived colour of water towards longer wavelengths of light, giving a yellow-brown colouration (Gippel, 1995). The DOC from dissolved organic matter includes organic acids such as fluvic or humic acid, and tannins derived from organic decay, described most commonly as coloured dissolved organic matter (CDOM). Gippel (1995) suggests altered water colour from DOC is not a problem for the measurement of just turbidity, but is problematic when using turbidity as a surrogate for determining SSC. When water appears a yellow-brown colour there is a reduction in turbidity and scattered light is partly absorbed when using white-light tungsten-type nephelometer lamps (US-EPA, 1993; Omar & MatJafri, 2009). The Glendhu catchments episodically show a yellow-brown water colour (Figure 3.9), which is attributed

to organic acids leaching from peat-rich wetland soils. This may be an important confounding factor for why turbidity was not related to changes in POM and SSC. In the extreme case, it may be that when significant portions of both CDOM and POM are present, it may produce an SSC-turbidity relationship with a much steeper slope, than when low portions of organic matter are present. Thus, it is possible for multiple regression slopes to occur depending on the nature of the particulate material in suspension. Relationships established between SSC and turbidity over events may show a strong relationship between the two variables but are unlikely to be the same under base flow conditions. In situations where there may be interference from organic acids and water coloration (i.e., CDOM), turbidity may need to be measured by alternative methods, such as infrared LED lamps, which are not affected by coloration but have less sensitivity at lower ranges and poor detection of fine particles (Omar & MatJafir, 2009).

Figure 3.9 Streamflow through the v-notch weir draining the Glendhu experimental tussock catchment (GH1). The water shows a distinct yellow hue that is frequently observed in both GH1 and GH2 catchments.

3.5.2 POC in New Zealand Rivers

In the wider Waipori Catchment, of which the Glendhu Experimental Catchments are in the headwaters, there are two previous studies that have included measurements of SSC.

Suspended material concentration and turbidity data for the Waipori River at its inflow into the Lake Waihola-Waipori Wetland Complex was measured by Schallenberg and Burns (2003). Their study reported a high percentage of POC relative to SSC, with an average value of 54% and a range of 34–100%, and POC concentrations varied from 2 – 28.7 mg L^{-1}, which is similar to our values (range of 0.4–19.8 mg L^{-1}). Turbidity ranged 2 – 7 NTU with an average of 4 NTU, which is also consistent with the range of values observed in the Glendhu catchments under baseflow conditions. The alignment of the results between Schallenberg and Burns (2003) and this study suggests that high POC extends beyond the Glendhu catchments and is typical of the wider Waipori Catchment.

The lack of a relationship between turbidity and SSC was also observed by Lovett (2009), whose investigation in the lower Waipori Catchment similarly failed to develop any significant relationship between SSC and turbidity ($r^2 = 0.044$). Numerous turbidity values were observed for single values of SSC, and it appeared as though two different relationships existed within the dataset. By comparing the two apparently different relationships, Lovett (2009) determined there was no difference between SSC of the two subgroups, but that turbidity varied significantly, and was likely a contributing factor to the inability of turbidity to predict SSC. In the Glendhu catchments, similar issues were apparent in the turbidity dataset, although variability in SSC measurements for the same turbidity was observed. This 'stacking' of values suggests that for any given turbidity there is a range of SSC values that may be potentially detected, and vice versa. The presence of this problem identified by Lovett (2009) further downstream indicates that the observed non-significant turbidity and SSC relationships are not confined to the headwaters, and that potentially SSC and turbidity behaviour is inconsistent catchment wide.

Compared to other New Zealand studies of POC in surface water, the results from the Glendhu catchments appear high. Lyons *et al.* (2002) established a value of <0.5% of TSM as POC, and Carey *et al.* (2005) identifying a value of <1%. Gomez *et al.* (2003) is the only study to report slightly higher values, with POC being 0.4-4% of TSM. Additionally, in a review of organic carbon inputs to the ocean, Ludwig and Probst (1996) synthesised data from some of the world's largest rivers, and reported POC portions of TSM ranging from 0.3%–10.1%. These values are much lower than observed in the Glendhu catchments (23% and 30% of TSM). This raises the question of why the POC portion of TSM is much higher in the Glendhu catchments and wider Waipori Catchment compared to these other studies.

The three previous New Zealand studies focused on steep catchments with catchment areas >350 km^2, and the international studies were larger still, with catchment areas > 9,000 km^2. Larger catchments have much lower portions of suspended material as POC (Madej 2015). Smaller catchments have a lower competency for transporting material, so that under base flow conditions POC can be easily transported compared to the entrainment of inorganic sediment, and thus POC represents a higher overall portion of load. Larger catchments mobilise inorganic sediment from bedload, bank collapse and deep landslides, whereas smaller headwater catchments are dominated by shallow sheet flow and other shallow pathways that are typically responsible for transport of organic debris (Gomez *et al.,* 2003). Furthermore, the stability created by established vegetation cover reduces the occurrence of deep erosion from gullies, landslides, and deep regolith limiting the mobilisation of inorganic mineral material, favouring erosion from organic rich top soil layers (Madej, 2015). The inconsistent response of POM in the Glendhu catchments to both precipitation and discharge can be at least partially explained by the small catchment size. In small catchments, turbidity and organic content depend partly on processes independent of discharge, with litter fall, entrainment and transport of surface soil organic matter more important; whereas in larger catchments discharge is the controlling variable of suspended material (Coynel *et al.,* 2005b; Madej, 2015). In addition, the source of organic material can change over a hydrograph, and may differ between base flow and event flow (Gomez *et al.,* 2003; Coynel *et al.,* 2005b; Wheatcroft *et al.,* 2010), potentially explaining the lack of any systematic response of POM to event discharge and the observed variability of POM over low flows in the Glendhu catchments. Further work is required to resolve what other processes are the controlling variables of POM concentration and proportions, particularly in relation to identifying the sources of POM and how these sources are attenuated during storm events.

3.5.3 Source of particulate organic matter

One objective of this study was to assess whether POM was a significant contributor to suspended material in headwater catchments, which it was in the two Glendhu catchments. However, the research has not established the source of POM, and how that differs in small headwater catchments. POC in the Waipaoa Catchment was identified using $\delta^{13}C$ as being sourced from gully erosion (Gomez *et al.*, 2003). The POC was identified to be allochthonous carbon, which is consistent with the observation that mountain streams export

allochthonous POC, mostly derived from the erosion of surface soils and poorly weathered regolith (Komada *et al*., 2004). However, seasonal variations in the source of POC to rivers may occur, with an increase in autochthonous carbon during spring and summer from diatoms and phytoplankton blooms, as well as detritus from periphyton and macrophyte growth, which has been attributed to changes in POC to TSM ratios in the Columbia River, North America (Sullivan *et al*., 2001). From a river management perspective allochthonous POC is indicative of landscape disturbance, principally as surficial soils are lost from the terrestrial domain, and are of limited biological availability. However, autochthonous POC is readily available for biological uptake and is an important food source for aquatic species. Further work is needed to ascertain the source of the POC in the Glendhu catchments and whether it is a sensitive measure of soil disturbance. In the Glendhu catchments, it is apparent that the portion of suspended material exported as POM is higher in the forested catchment, which was undergoing clearance during this study, and is likely a more sensitive indicator of the effects of forest clearance compared to the (inorganic) SSC, which was not statistically different to the concentration measured in the tussock control catchment.

3.6 Conclusion

In the headwaters of the Waipori Catchment, Otago, a significant portion of TSM comprises organic material (45% in a tussock catchment and 60% in a forested catchment). Although these values are much higher than previously reported for other New Zealand river systems, they are consistent with other studies undertaken in the Waipori Catchment. The inability to produce any statistically robust relationship between turbidity and SSC in both the tussock and forested catchments has implications for monitoring strategies in this catchment. The high POM component of TSM contributes to the poor relationships between turbidity and suspended material. However, even when the organic component is subtracted from the suspended material component to determine the (inorganic) SSC, there is no improvement in the relationship between turbidity and SSC. It is likely that regular discoloration of the water by CDOM alters the light-attenuating properties of the water column when tested using tungsten-type white light turbidimeters. This results in a range of turbidity values when there is no significant concomitant change in the concentration of suspended (inorganic) material. In catchments where organic material contributes to both the dissolved and particulate load of the water column this potentially interferes with the standard method of

determining SSC from turbidity records, particularly under base flow conditions. During higher flow events the data show the portion of organic material tends to decline, meaning the effect of low goodness of fit measures between turbidity and SSC are particularly acute under base flow conditions. These results indicate that turbidity is a poor indicator of SSC in some catchments. Even when the POM component is accounted for in SSC calculations, the presence of dissolved organic acids may still contribute to inaccurate records of turbidity. In such instances, it may be worth assessing alternatives to tungsten-type nephelometers for measuring turbidity. It must be considered that these instruments are subject to other limitations.

Sediment in streams and rivers is recognised in New Zealand's NPS-FM (2014) as an important attribute in terms of monitoring and managing stream quality and ecosystem health. At a local level, regional authorities are tasked with monitoring water clarity, and turbidity is an effective way to monitor water clarity. The current research demonstrates, however, that the measurement of suspended material and its impact on water quality is confounded by the presence of organic material, both in terms of impacts on calculating suspended load and interference with turbidity measurement. A number of potential factors contribute to the variability in POM concentrations under base flow. Under some circumstances there may be flushing and dilution effects associated with hydrographic responses, and seasonality may affect what particulate (either organic or inorganic) dominates TSM. Further work is needed in the Glendhu Experimental Catchments to determine the sources of POC, whether it is allochthonous or autochthonous, and whether POC is a sensitive indicator of soil and land disturbance.

4 Catchment-Scale Influences on Riverine Organic Matter in Southern New Zealand

Research article published in *Geomorphology* in December 2019[2]. See Appendix 11.2.

4.1 Abstract

Riverine particulate organic matter (POM) is a critical vector for nutrient cycling of carbon at both regional and global scales. POM and suspended sediment (SS) are transported concomitantly through rivers, and their concentrations change in association with landscape transformations and natural fluctuations. The proportion of POM to SS mobilised in rivers under baseflow is an important component of carbon flux to oceans, and is a useful metric for understanding hillslope–river coupling and hydraulic connectivity. POM was quantified during baseflow conditions in southern New Zealand to assess the role of different catchment characteristics that control the spatial variability of organic matter in the fluvial environment. The proportion of POM to total suspended material (TSM) can be <5%, or much higher at 50 – 80% across southern New Zealand, with the highest concentrations associated with lowland agricultural catchments. Particulate organic carbon yields were estimated to be between 0.04 – 2.7 t km^{-2} a^{-1} discharged into the Pacific Ocean. The POM% responds to both intrinsic and extrinsic catchment characteristics, affecting the availability of organic material and mechanisms for transport including vegetation cover, topographic controls, and hydrological controls. Across southern New Zealand it is evident that riverine organic matter is spatially organised and connected to broader hillslope processes, albeit difficult to predict at the catchment scale.

[2] Minor changes to the narration of this research article have been made to improve coherency between chapters.

4.2 Introduction

Riverine particulate organic material (POM) sequesters 90 – 240 Mt a^{-1} of carbon globally and is a small, but significant, component of the global carbon budget (Hope, 1997; Lyons *et al.,* 2002). It is estimated that POM accounts for up to 20% of total carbon export, 60% of total nitrogen export, and 90% of total phosphorus export (Meybeck, 1982; Sanchez-Vidal *et al.,* 2013). Thus, riverine POM is a critical vector for nutrient cycling at both regional and global scales, particularly in carbon cycle studies with an emphasis on determining particulate organic carbon (POC) fluxes (e.g., Meybeck, 1993; Ludwig & Probst, 1996; Robertson *et al.,* 1999; Lyons *et al.,* 2002; Wu *et al.,* 2007). POC is a subset of total organic carbon (TOC), with the other component being dissolved organic carbon (DOC). POM flux is connected to hillslope processes, denudation, and suspended sediment (SS) flux; so that understanding the flux of POC (as a subset of POM) requires consideration of extrinsic (external to the catchment, e.g., rainfall) and intrinsic (within catchment, e.g., landcover and hydrology) catchment characteristics to inform source land uses and pathways.

Discharge is a critical intrinsic catchment variable driven by rainfall in catchments, although the observed behaviour of organic matter with discharge is complex, often confounded by antecedent conditions and storm fluctuations (Hope *et al.,* 1994; Coynel *et al.,* 2005; Sabater *et al.,* 2006). Catchment hydrology, including runoff generation and hydrological flow pathways affect the quantity and quality of organic matter by controlling the contribution of allochthonous or autochthonous sources (Hope *et al.,* 1994; Robertson *et al.,* 1999; Sanchez-Vidal *et al.,* 2013). POM concentration typically increases with discharge, although the relationship is often weak as organic matter can be delivered to, or become, temporarily diluted as flow changes (e.g., Zhang *et al.,* 2009). Consequently, base flow and event flow POM responses are typically observed separately (Meybeck, 1982; Coynel *et al.,* 2005; Zhang *et al.,* 2009; Sanchez-Vidal *et al.,* 2013; Madej, 2015), although focus is primarily on event flow behaviour. Discharge typically explains less than 30% of the variation in concentration and ratio of POM to suspended material, and unit stream power explains less than 20%; suggesting that there are other more significant controls (Naiman, 1982; Madej, 2015).

Carbon supply is affected by season, influencing sediment and organic matter storage and their release into the fluvial environment (Hope *et al.,* 1994). Season controls the timing of organic matter availability, and the input to streams depends on biological demand. The release of carbon from catchments is strongly controlled by the effects temperature and rainfall impart on biological production (Meybeck, 1982; Hope *et al.,* 1994; Robertson et al., 1999; Wu *et al.,* 2007); therefore, global variability in the regulation of these controls on organic matter is observed between hemispheres (Hope *et al.,* 1994). Thus, differences exist between the Northern Hemisphere where there are large changes in carbon pools between seasons relative to the Southern Hemisphere, which is dominated by evergreen forest, and as a result seasonal shifts in carbon cycling are not as strong (Keeling & Whorf, 2004).

Additional intrinsic catchment controls on carbon (and organic matter) flux are related to the type of land cover, disturbance patterns, soil type, catchment size, and topography. For example, anthropogenic disturbances increase organic matter concentrations in fluvial environments (e.g., Zhang *et al.,* 2009) and engineered structures (e.g., dams and reservoirs) may reduce organic matter concentrations (e.g., Ittekkot & Arain, 1996; Wu *et al.,* 2007). Similarly, disturbances in forested catchments cause increased riverine concentrations of organic matter, in both particulate and dissolved forms (e.g., Bormann *et al.,* 1974; Hedges *et al.,* 2000; Zhang *et al.,* 2009). Catchment size and topography, including slope, control stream flow generation and stream response to storm flow. Smaller catchments, for example, have higher proportions and concentrations of organic matter due to shorter residence times and direct coupling of hillslopes with streams (e.g., Schlesinger & Melack, 1981; Hope *et al.,* 1994; Robertson *et al.,* 1999; Coynel *et al.,* 2005; Madej, 2015).

The proportion of POM to total suspended material (TSM) is a function of organic matter migration (e.g., organic litter and leaf debris) that occurs simultaneously with the erosion of inorganic mineral material (e.g., mineral soil and regolith), resulting in the delivery of both organic and inorganic particulate materials to the fluvial environment (Sanchez-Vidal *et al.,* 2013). Consequently, fluvial TSM contains both particulate organic and inorganic material, of variable proportions, over space and time. Spatio-temporal drivers inherently affect the composition of stream flow particulates, although the connections between the two are rarely explained (Sanchez-Vidal *et al.,* 2013). The proportion of POM to the total suspended flux globally is highly variable, and has been reported to be as low as 1 – 2.5% (e.g., Ittekkot & Arain, 1996; Ittekkot, 1988; Lyons *et al.,* 2002; Gomez *et al.,* 2003; Wu *et al.,* 2007; Zhang

et al., 2009), or much higher at 45 – 70% (e.g., Naiman, 1982; Hasholt & Madeyski, 1998; Golladay, 1997; Schallenberg & Burns, 2003; Madej, 2015). Those studies showing higher proportions of organic matter are typically observed in forested catchments with a higher availability of organic material (e.g., Golladay, 1997; Madej, 2015), or in waterways draining organic-rich wetlands (e.g., Schallenberg & Burns, 2003). Low proportions of POM to total suspended material, however, are more likely observed in inorganic sediment-rich environments, like alpine regions (e.g., Carey *et al.,* 2005; Lyons *et al.,* 2005; Bright *et al.,* 2018 (see: Chapter Five)) where information pertaining to POM is sourced primarily from organic carbon assessments (e.g., Gomez *et al.,* 2003).

The objective of this paper is to determine the contribution of POM to suspended material across spatial scales at base flow and explore the dependence on certain catchment characteristics that control the variability in the ratio of POM to SS in the Southern Hemisphere, by using southern New Zealand catchments as a case study. Our paper seeks to establish:

1. How much POM is fluxed by southern New Zealand rivers, and the association of this POM to suspended sediment and carbon flux;
2. How much POC is discharged through rivers in southern New Zealand in association to POM, and the estimated POC yields for 84 southern New Zealand catchments;
3. If known extrinsic and intrinsic controls associated with POM concentration differ to the independent controls that affect POM proportions.

Our approach quantifies suspended sediment, POM, total organic carbon (TOC) and the dissolved organic carbon (DOC) portion of TOC, and turbidity across seven high order catchments in southern New Zealand with a total coverage of 67,800 km^2. Such research is important to elucidate the linkage between the terrestrial environment and rivers, and the influence of catchment scale characteristics on organic fluxes. Examining these processes at the catchment scale provides the opportunity to assess the role of source-to-sink principles across different scales that often define and constrain the management of environmental issues.

4.3 Methods

Discrete grab samples (in 1 – 5 L HDPE containers) were collected under base flow conditions from 134 sampling points across 7 high order catchments in southern New Zealand (Aparima, Clutha/Mata-Au, Mataura, Oreti, Taieri, Waiau, and Waitaki) (Figure 4.1). Samples were analysed for SSC (mg L^{-1}), POM (mg L^{-1} and as a percentage of total suspended material, i.e., POM%), and turbidity (FNU, NTU). Suspended sediment and POM concentrations were calculated by filtering water samples through pre-washed and dried 0.7 µm glass fibre filters following standard methods (see: ATSM, 2002). Filters were oven-dried at 105°C for 24 hours, then weighed and re-dried at least three times, or until filter weights converged to determine the total suspended sediment concentration. The glass fibre filters were burned in a muffle furnace at 500°C for 30 minutes, to incinerate the organic portion, then reweighed to determine the loss on ignition, which is an index of POM (see: Grove & Bilotta, 2014). Samples below the method detection limit of 0.3 mg L^{-1} were excluded from the data set.

DOC and TOC (in mg C L^{-1}) were collected in 20 mL amber glass vials and measured using a Shimadzu Total Carbon Analyser with an analytical precision of 0.2 mg C L^{-1}. These measurements were used to derive the POC concentration (where POC = TOC – DOC). If POC and POM are known from measurements, these data can be used to calculate the van Bemmelen factor (VB_f) (see: Pribyl, 2010); where VB_f = POM/POC, and was used to convert all POM concentrations where POC was not directly measured. For southern New Zealand, the mean VB_f was 1.3 (n = 84). Dissolved and total recoverable metals were measured on a Spectro-Blue ICP-OES. Ten mL sub-samples for dissolved metals were filtered using 0.22 µm nylon filters and pre-treated with 100 µL of ultra pure HNO_3 used as a carrier solution. Total recoverable metals used 20 mL subsamples treated with 200 µL ultrapure HNO_3 and 200 µL ultrapure HCl then digested at 95°C for 2 hours following method EPA 200.8. Particle loading coefficients were calculated using the method outlined by Nasrabadi *et al.* (2018).

Grab samples were collected from a small unnamed headwater stream in the Taieri Catchment and sampled fortnightly to monthly, from August 2015 to February 2018 (Glendhu GH1) (see: Chapter Three, Bright & Mager, 2016). The longer record of sample collection provided the opportunity to examine variations in organic matter between events

and seasons and complement the seasonal samplings in the Taieri, Clutha/Mata-Au, and Waitaki catchments (Table 4.1). Twenty-eight sub-catchments that drain the eastern margin of the axial Southern Alps into the Clutha/Mata-Au and Waitaki catchments were sampled 15 times from 2012 – 2017 to assess seasonal changes in POM under base flow. Twelve sites in the Taieri catchment were sampled monthly from July 2017 to October 2018. The remaining 56 sampling sites from the Waiau, Aparima, Oreti, and Mataura catchments were collected during the austral summer of 2017 – 2018 to provide a geographical expansion of the temporal datasets.

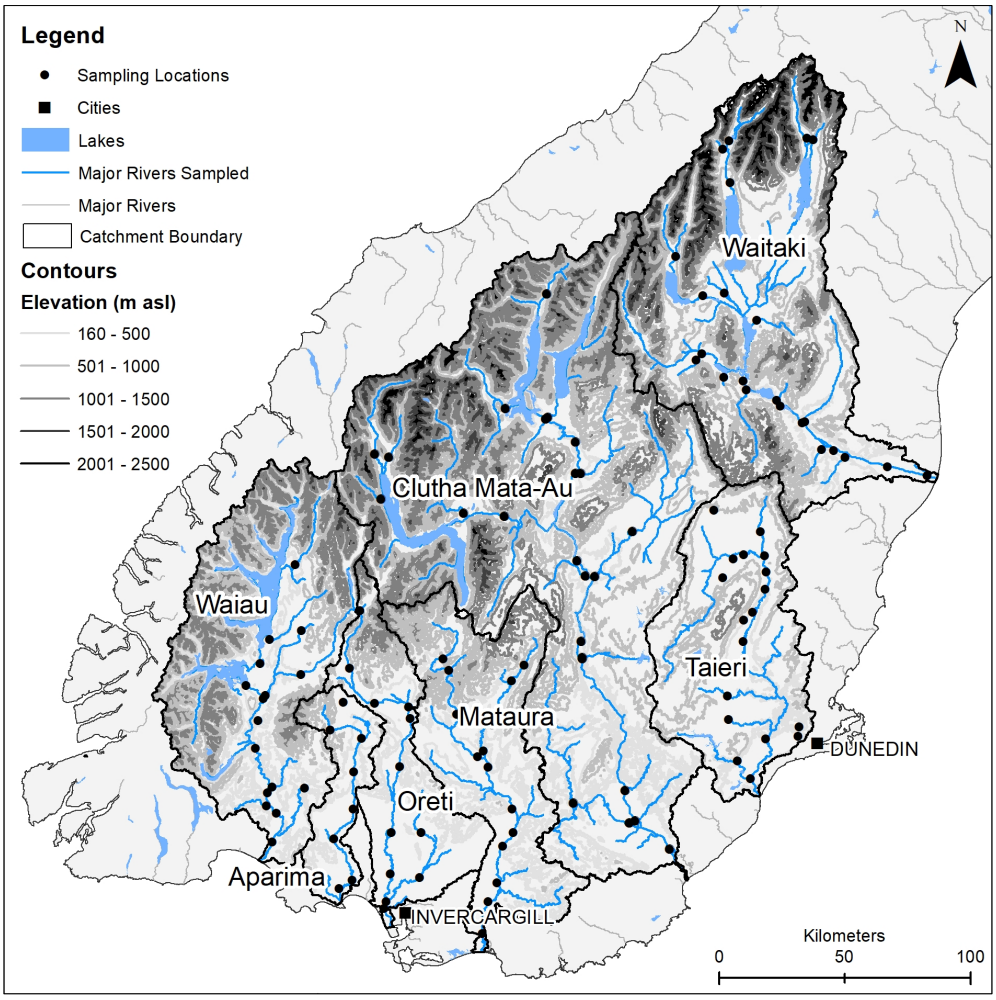

Figure 4.1 Map of southern New Zealand showing the 134 locations within 84 sub-catchments of seven high order catchments that are the focus for this study.

Table 4.1 Catchment characteristics for the seven high order catchments sampled for suspended sediment, particulate organic matter, and turbidity across southern New Zealand.

Catchment	No. Sites	Area (km^2)	Stream Order	Mean Annual Discharge ($m^3\ s^{-1}$)	Rainfall (mm/a)	Land cover
Aparima	9	806	6	17.3	1,081	Pasture (55%), indigenous (19%) and exotic forest (16%)
Clutha/Mata-Au	41	5,343	8	1,327	1,168	Pasture (35%) tall tussock (20%) and low producing grassland (17%).
Mataura	15	2,694	7	76.7	1,084	Pasture (80%), and indigenous (6%) and exotic (4%) forest.
Oreti	10	1,390	7	51.5	1,116	Pasture (80%), exotic forest (8%), low producing grassland (4%).
Taieri	22	5,706	6	35.6	2,018	Pasture (47%), tussock (22%) and grazed tussock (14%). Pockets of exotic forestry (5%).
Waiau	9	2,557	7	564	1,451	Pasture (33%), indigenous forest (33%), tall tussock (10%). Pockets of exotic forestry (7%).
Waitaki	26	6,262	8	621	805	Low producing grassland (24%) and tall tussock grassland (21%). Depleted grassland (15%) and pasture (15%).

Existing geospatial datasets (Table 4.2) were used to extract metrics of catchment land use, lithology, soil order, climate conditions, and topography for all catchment areas above each sampling location (Table 4.1) and used as independent input variables for multiple linear regression using SPSS (v22). The parameters (Table 4.2) were selected as predictors based on previous research that has broadly identified these types of landscape characteristics that predispose catchments to losses of soil, sediment, and organic matter (e.g., Naiman, 1982; Hope *et al.,* 1994; Robertson *et al.,* 1999; Madej, 2015), since the flux of POM was likely linked to terrestrial denudation processes. Spatial patterns in observed variables (POC, POM) were mapped using ArcGIS (v15) and grouped using Hierarchical Cluster Analysis (HCA) using Ward's linkage and squared Euclidean distance in SPSS (v22). Ward's method and squared Euclidean distance was selected as the most suitable linkage method as it defines clusters by minimising difference in variance and constrains the number of defined clusters using in-built SPSS agglomeration coefficient thresholds (Blashfield, 1976). Cluster membership was validated by differences in median particulate organic matter concentration with a Kruskall-Wallis z-score.

Table 4.2 Basin, lithological, soil, and land cover catchment variables used in multiple regression modelling.

Type	Predictor	Units	Source
Basin	Catchment Size	km^2	Catchment polygons, mean flow, stream order, and FRE3 sourced from NZ River Environment Classification.[1]
	Mean Flow	m^3s^{-1}	
	Stream Order		
	FRE3		
	Mean annual rainfall	mm a^{-1}	Rainfall calculated from MfE average rainfall 1972-2013, based on NIWA virtual climate station network.[2]
	Suspended sediment yield (SSY)	t^{-1} km^{-2}	SSY from NIWA SSY estimator.[3]
	Slope	a^{-1}	
		%	Slope defined from LRIS NZLRI database (v3). [4]
Lithology	Lithology (NZLRI ED1)	%	Lithology extracted from NZLRI database data (v3). [4]
Soil	Soil Type (NZSC)	%	Soil type from LRIS FSL defined in NZLRI database (v3). [4]
	Carbon Content		Carbon content (% estimate) from LRIS FSL defined in NZLRI (v3). [4]
	Erosion		Erosion categories defined by LRIS NZLRI database (v3). [4]
Landcover	Alpine vegetation, crop, exotic forest, indigenous forest, grassland, pasture, scrub, shrub, snow and ice, tall tussock grassland, urban, gravel rock and landslide, lake river and pond.	%	Landcovers defined by LRIS Land Cover Database (v4.1). [5]

Note: All variables with % are calculated as % of catchment area.
[1] New Zealand River (MfE) Environment Classification (2016). Ministry for the Environment Online Data Portal. See also Booker (2015).
[2] Average Annual Rainfall, 1972 – 2013 (2015). Ministry for the Environment Online Data Portal.
[3] Suspended Sediment Yield Estimator (Hicks *et al.,* 2011).
[4] NZLRI New Zealand Soil Classification (v3) (2010). Landcare Research NZ LRIS Online Portal.
[5] Landcover Database (v4.1) (2015). Landcare Research NZ LRIS Online Portal.

4.4 Results and Discussion

4.4.1 How Much POM is cycled through southern New Zealand Rivers?

POM and SSC were highly variable across Southern New Zealand (median POM ranges BDL – 58.4 mg L^{-1}; median SSC ranges BDL – 513 mg L^{-1}) (Figure 4.2a – b). Median concentrations of POM are moderate to low (< 5 mg L^{-1}) through most of southern New Zealand, with the exception of the Otautau Stream (9.5 mg L^{-1}) and the Hopkins River (58.4 mg L^{-1}). Areas of high median SSC were observed in alpine headwater catchments that drain the Southern Alps (e.g., Shotover Kimi-ākau, Dart/Te Awa Whakatipu, Tasman, Hooker, Godley), and the Mataura, which was in spate at the time of sampling. POM as a percentage of total suspended material (POM%) was highly variable (Figure 4.2c), with percentages generally low in alpine areas (<5%), and highest in small non-alpine headwater catchments (e.g., Glendhu, Upper Waipori, Lowburn, Bannockburn and Fraser) or larger catchments on

the central plains of Southland (e.g., the lower Waiau and Oreti that are dominated by agricultural farming).

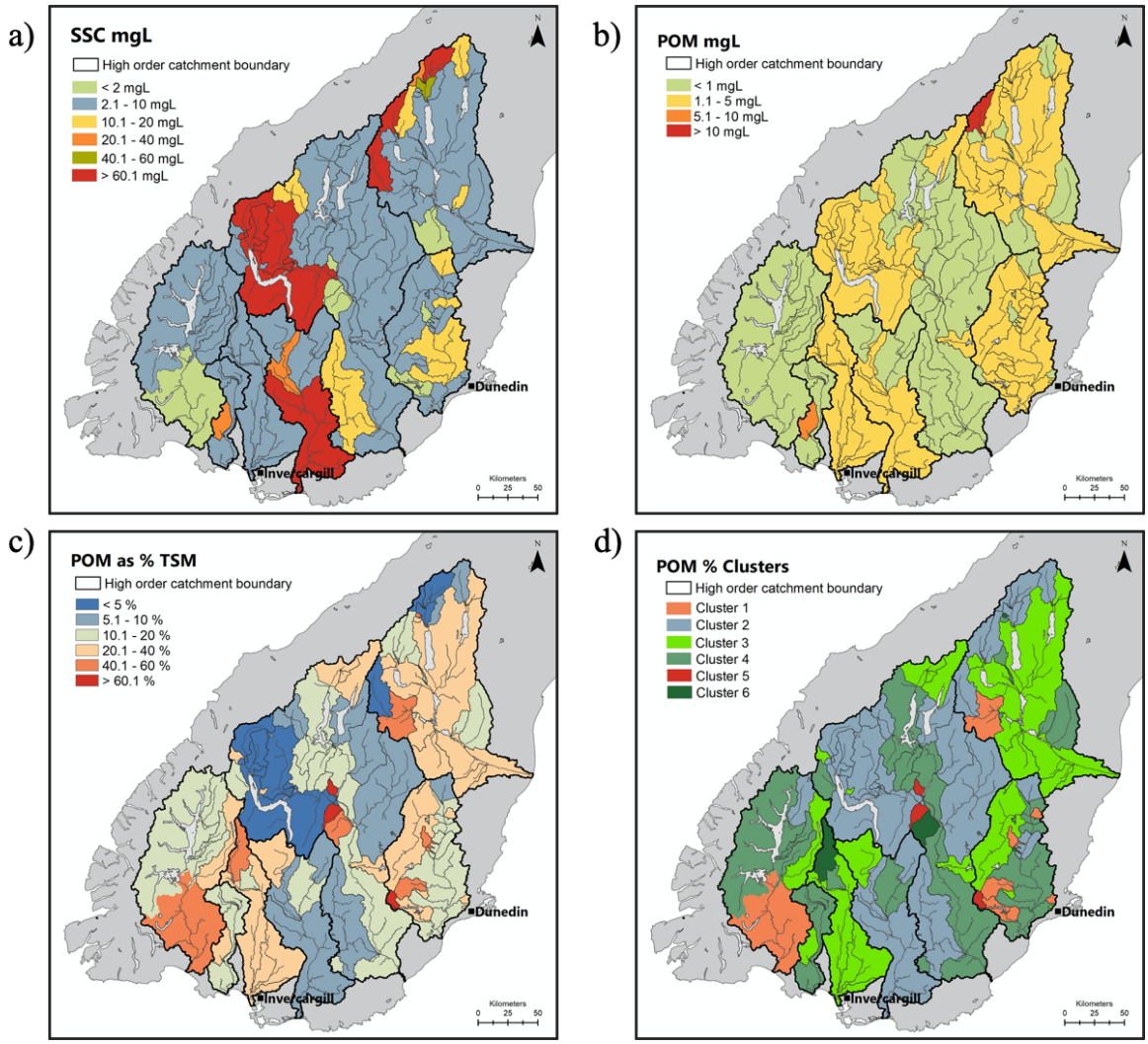

Figure 4.2 a) Suspended sediment concentration (SSC); b) particulate organic matter (POM) concentration; c) POM as a percentage of total suspended material (TSM); d) hierarchical clusters for POM%; for 84 sub-catchments across southern New Zealand catchments.

The spatial distribution of POM% is complex and higher POM% is unrelated to high concentrations of POM, but is concomitant with areas of low SSC under baseflow (Figure 4.2c). POM concentrations are mediated by the regulatory role of in-stream biological processes that are determined by catchment characteristics (e.g., soil and land cover) and temporal controls (e.g., temperature) (e.g., Robertson *et al.,* 1999). The river continuum concept suggests the mechanisms that control biological equilibrium through loading,

transport, use, and storage of organic matter occurs longitudinally through river channels (Vannote *et al.,* 1990; Battin *et al.,* 2008). Downstream organic matter is dependent on an upstream supply and therefore is supply limited (Robertson *et al.,* 1999; Battin *et al.,* 2008). However, under baseflow conditions no systematic changes in POM concentration downstream in southern New Zealand could be detected. Winterbourn *et al.* (1981) outlined a number of cases in New Zealand and elsewhere where the river continuum concept was not applicable. Organic matter fluctuated throughout the catchments, downstream, and was typically higher in the headwaters and smaller tributaries, but these rivers do not appear to be organically limited. In organic-rich environments, like southern New Zealand, where there is a dense network of small headwater river catchments, the typical conditions on organic matter limits may not apply, as there is continued supply of organic material throughout the stream network and validates the assumptions of Winterbourn *et al.* (1981).

For catchments draining the Southern Alps there were seasonal shifts in median POM concentration or POM% (Figure 4.3). Variations in POM concentration were often lower in winter and highest in autumn, although did not vary significantly across land use types, except for alpine and agricultural land uses. The observed autumnal increase in POM (mg L^{-1}) is likely attributable to increased transport of organic material due to a reduction in biological demand and seasonal litter fall (Robertson *et al.,* 1999). The observed variations in POM concentration were also likely related to changes in flow; when sampled in spate, for example, POM concentrations increase, but the POM% reduces to <10% (Bright *et al.,* 2020a (see: Chapter Six)). Non-alpine catchments also displayed stronger seasonal shifts, for example, the Taieri (an agriculture dominated catchment) had a median spring and summer concentration of 1.4 mg L^{-1}, compared to 2.6 mg L^{-1} for autumn and winter, and contributed 13 – 22 POM%. The Taieri is an organic-rich catchment, so the observed POM increase during winter may also be due to a seasonal reduction in biological demand for carbon (e.g., Robertson *et al.,* 1999). POM concentrations had a median absolute deviation (MAD) of 0.4 mg L^{-1} (Taieri), and 1.0 mg L^{-1} (for Clutha/Mata-Au and Waitaki). Similarly, the MAD for the POM% was 4.8 (Clutha/Mata-Au), 9.8 (Taieri), and 12.5 (Waitaki). Therefore, the uncertainty (as 2 deviations) associated with the POM concentrations approximates ± 2 mg L^{-1}, and POM% of TSM ±25%. These uncertainties are of a similar magnitude as the modelled suspended sediment yields, and modelled discharges, which are in the order of ±20 – 25% (Hicks *et al.,* 2011). Where seasonal shifts were not observed, for example, the Dart/Te Awa Whakatipu (an alpine-dominated catchment) (seasonal POM

ranged from 3.1 – 3.8 mg L^{-1}) POM% was only a small portion of total suspended material (1 – 3 %).

POM as a percentage of total suspended material (POM%) was classified into 6 discrete clusters using HCA (Table 4.3). These data showed that POM concentrations are statistically different between small headwater catchments, which had very low POM and SSC concentrations, but that most of the particulate load was as POM (Clusters 1, 5 and 6). Alpine headwater catchments (Cluster 2) and higher stream ordered catchments (Clusters 3 and 4) had lower POM% (<30%), and higher concentrations of POM (~1.5 mg L^{-1}), suggestive of combined processes of organic material availability and increased stream competence for inorganic particulate transport. The spatial distribution of POM% clusters were aggregated spatially (Figure 4.2d) and likely responding to underlying lithological, topographical, and land use catchment characteristics related to geographical location.

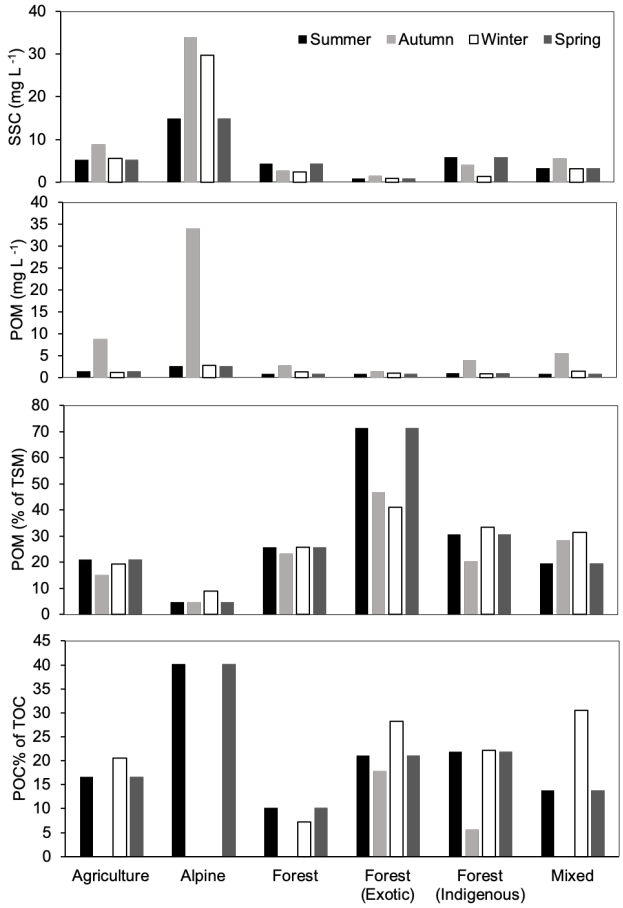

Figure 4.3: Seasonal median suspended sediment concentration (SSC), particulate organic matter (POM) and POM as a percentage of total suspended material (POM%) and particulate organic carbon (POC) as a percentage of total organic carbon (TOC) (POC% of TOC) for six dominant land use types across 84 southern New Zealand sub-catchments.

Table 4.3 Hierarchical cluster analysis of particulate organic matter (POM) as a proportion of total suspended material (POM%) for southern New Zealand. Suspended sediment concentration (SSC as mg L^{-1}), POM (as mg L^{-1}) and POM% across the 6 clusters with statistical difference determined by Kruskall-Wallace z-test (p-value <0.05 at 95%). Mean catchment modelled mean flow (Q, m^3 s^{-1}), and modelled suspended sediment yield (SSY as t km^{-2} a^{-1}) for each cluster are also summarised.

POM% Cluster	Count	*Q*	SSY	SSC	POM	POM%	Description
Cluster 1 Low SSC Low POM High POM%	9	69	55	1.9	0.7	42.0	**Low Order Catchments** + Brown and pallic soils; steep catchments; indigenous grassland cover and schist basement lithology. + Lower Waiau Exception e.g., Lug Creek, Silver Stream
Cluster 2 High SSC Low POM%	26	46	326	15.3	1.5	6.4	**Alpine Headwater Catchments** Brown, pallic and recent soil types; very steep catchments; glacial landforms, alpine headwaters with hill country agriculture; schist and semi-schist lithology. e.g., Upper Ahuriri, Dart/Te Awa Whakatipu, Manuherikia
Cluster 3 Moderate SSC, POM and POM%	20	44	103	4.1	1.4	27.6	**Mixed higher order and alpine catchments** Brown, pallic and raw soil types; rolling hills; mostly grassland agricultural catchments with forest, some alpine areas; schist and greywacke lithology. e.g., Waiau, Oreti, Routeburn
Cluster 4 Moderate SSC, POM and POM%	20	107	72	5.4	1.2	17.7	**High order catchments** Brown, pallic and recent soil types; flat undulating catchments with steeper headwaters; mostly agriculture; schist and greywacke lithology. e.g., Taieri, Clutha/Mata-Au, Aparima
Cluster 5 Low SSC Low POM Very High POM%	3	1	77	0.2	0.6	88.5	**Small headwater Otago catchments** Brown soil type; rolling to steep topography of thrust-block morphology; some agriculture; Caples schist. e.g., Lowburn, Bannockburn, Upper Waipori
Cluster 6 Low SSC Low POM High POM%	6	5	59	1.6	0.9	53.9	**Small headwater catchments** Brown soil type; steep fluvially bisected headwater catchments; agricultural land use with indigenous grassland and forest; schist and greywacke lithology. e.g., Birch Hill, Glendhu

In alpine catchments (e.g., Tasman, Hooker, Dart/Te Awa Whakatipu, Shotover Kimi-ākau, upper Ahuriri – Cluster 2 Figure 4.2d) mineral material was dominant (POM <10%) due to intense physical weathering through high rainfall, freeze-thaw, landsliding, and glaciation; as well as a plentiful supply of alluvium associated with intense fluvial dissection of Quaternary landforms including relict moraines, alluvial fans, and scree slopes. The thin alpine soils, plentiful sources of fine-grained inorganic sediment, and steep cascading and braided river forms lead to higher sediment transport competence and higher SSC under base

flow conditions. The alpine regions were also areas of the highest POM concentrations; even though POM is only a small percentage of TSM. New Zealand alpine soils are thin and exhibit a profile indicative of frequent rejuvenation (Larson *et al.,* 2014) as soil material is displaced readily from the hillslopes and transported to stream channels. In this way, POM is transferred regularly from the terrestrial surface to stream channels and drives the higher POM concentrations observed in alpine environments.

Clusters 1 and 6 were clusters that specifically exclude alpine catchments; these clusters comprise low and high intensity pastoral agriculture. For example, Cluster 1 contains catchments within eastern Otago (i.e., Deep Stream, Last Creek, Sow Burn) and the Waiau in Southland; whereas Cluster 6 contains central Otago dryland catchments (i.e., Bannock Burn, upper Waipori River, and Low Burn). These non-alpine catchments generally have low SSC mg L^{-1}, low POM mg L^{-1}, but a higher POM% (>40%), relative to the alpine catchments. The catchments within clusters 1 and 6 are notable in that they are covered in indigenous snow tussock (*Chionochloa rigida*), a resilient tall grass distinctive to the lower part of the South Island, New Zealand, and the low-intensity agriculture it sustains, and therefore represent a landscape unit conducive to low in-stream concentration of particulates, but higher overall proportions of POM relative to inorganic suspended sediment. Previous work has shown that small headwater catchments in the upper Waipori with significant tussock grassland cover have unusually high POM% (see: Chapter Three, Bright & Mager, 2016), likely attributable to the ability of tussock grasslands to retain large proportions of carbon and produce a rich source of organic material (Tate *et al.,* 2000; Mark *et al.,* 2013). The seasonal changes in biomass mean that tussock litter is a readily available source of POM, particularly in early spring. Similarly, agricultural grasslands, particularly those under year-round grazing accumulate organic nutrients, namely carbon in the soil organic matter that is ploughed, cultivated and cropped, maintaining a high level of soil organic material that is available throughout the year (Jackman, 1964). Under intensive pastoralism, for example, ovine and bovine farming systems that are extensive in southern New Zealand, effluent from free range grazed animals allows for soil organic matter and organic carbon to be mobilised through soil chemical changes (Schipper *et al.,* 2010), providing a mechanism for higher organic matter inputs to fluvial environment.

4.4.2 How much Organic Carbon is fluxed through southern New Zealand Rivers?

POC yields ranged from < 1 – 100 t km^{-2} a^{-1} across southern New Zealand, with higher yields along the arch of Southern Alps, and lower yields in the lowlands and near the coast (Figure 4.4). For the higher ordered catchments POC yields were: Aparima (0.04 t km^{-2} a^{-1}), Waiau (0.18 t km^{-2} a^{-1}), Oreti (0.37 t km^{-2} a^{-1}), Waitaki (0.42 t km^{-2} a^{-1}), Mataura (0.44 t km^{-2} a^{-1}), Taieri (1.61 t km^{-2} a^{-1}), and Clutha/Mata-Au (2.72 t km^{-2} a^{-1}). These data suggest that POC yields exported to the coast were typically < 1 t km^{-2} a^{-1} into Fouveaux Strait, and between 0.4 – 2.7 t km^{-2} a^{-1} into the south-east Pacific Ocean. Substantially more organic carbon was delivered to the ocean as DOC, ranging from 1.3 – 16.2 t km^{-2} a^{-1} for Fouveaux Strait, and 1.7 – 16.9 t km^{-2} a^{-1} for the south-east Pacific Ocean, with the greatest fluxes from the Waiau and Clutha/Mata-Au. It should be noted, however, that these data are derived from baseflow organic carbon concentrations, weighted to mean annual stream flow, with a conservative uncertainty of ±25% and do not account for the fluxes of carbon that may be mobilised during event flows.

The proportion contribution of DOC to TOC (DOC% of TOC) showed that across southern New Zealand DOC was the main flux of organic carbon. It was only in alpine catchments with indigenous vegetation cover that the export of organic carbon was higher as POC (Table 4.4). The POC% of TOC was weakly associated with SSC since POC may be sourced from recently deposited organic debris on the terrestrial surface, and not older, deep-seated organic carbon pools that are only shifted during periods of deeper mass movements (Gomez *et al.,* 2010). Shallower erosion processes acting on hillslopes direct organic debris to stream channels that contain modern plant derived carbon (e.g., allochthonous POM) (Gomez *et al.,* 2010). Turbidity (as NTU) and POC% of TOC were positively correlated, suggesting that turbidity may be a useful metric for the estimation of POC in catchments (Figure 4.4).

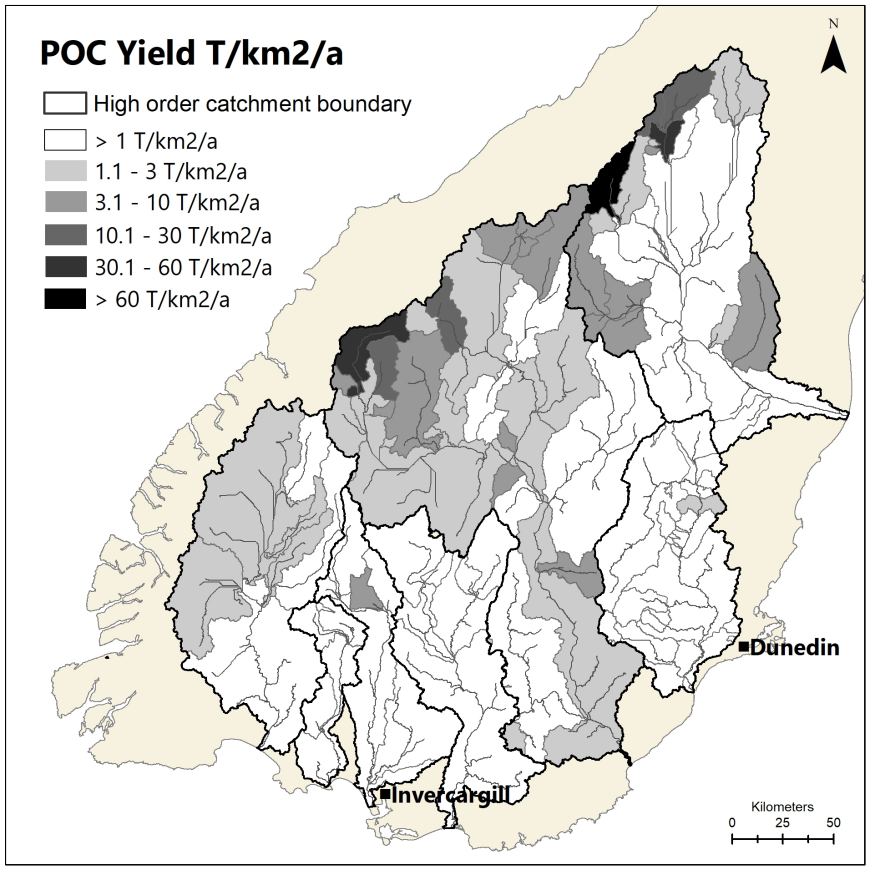

Figure 4.4 Particulate organic carbon (POC) yields for 84 catchments across southern New Zealand.

Table 4.4 Median turbidity (as NTU), suspended sediment concentration (SSC mg L^{-1}), particulate organic matter (POM as mg L^{-1} and as a percentage POM%), and dissolved organic carbon (DOC mg L^{-1}) and particulate organic carbon (POC mg L^{-1}), with van Bemmelen factor (VB_f). DOC as percentage of total organic carbon (TOC) and POC as percentage of TOC, and yields for DOC and POC (as t km^{-2} a^{-1}) across dominant vegetation classes for southern New Zealand.

	NTU	SSC	POM	POM %	DOC	POC	VB_f	DOC % of TOC	POC % of TOC	DOC Yield	POC Yield
Indigenous Vegetation Class											
Alpine	6.8	11.6	1.9	9.6	1.1	1.2	1.4	40.7	59.3	5.8	15.7
Forests	1.5	4.1	0.8	18.9	1.7	0.5	2.0	81.0	19.0	5.1	2.5
Grassland	2.3	6.1	1.2	18.8	2.3	0.7	1.1	64.3	35.7	2.1	2.2
Anthropogenic Vegetation Class											
Agriculture	3.4	6.1	1.5	18.2	3.7	0.7	1.4	80.6	19.4	1.9	0.7
Forests (plantation)	1.8	1.6	1.0	52.5	2.6	0.7	1.0	76.3	23.7	1.1	0.3
Mixed	2.7	2.9	0.8	27.5	2.3	0.4	1.1	85.7	14.3	6.6	0.6

Higher POC yields occurred along the Southern Alps, and lower yields were observed across the lowlands, near the coast, and where anthropogenic activity was most concentrated (Figure 4.4). These observations concur with the observed behaviour of alpine catchments across global high relief islands (e.g., Lyons *et al.,* 2002; Gomez *et al.,* 2003), like the South Island of New Zealand. High gradient alpine catchments with high annual rainfall enable rapid transport of sediment, whereas floodplains store sediments and act to minimise the flux of POC even when there is high erosion rates within the catchment, so that longitudinally, there is a general decrease in POC yield (Robertson *et al.,* 1999; Lyons *et al.,* 2002; Carey *et al.,* 2005). No systematic downstream decline in POC in southern New Zealand rivers was observed, rather changes in POC concentration reflected a general decrease in POM% downstream and a switch between POC to DOC associated to changes in land cover from indigenous vegetation in headwater catchments to anthropogenic modification on the lowlands (Figure 4.5). Previous assessments of POC yields in New Zealand (e.g., Gomez *et al.,* 2003; Carey *et al.,* 2005; Lyons *et al.,* 2005) have focused on high denudation and low anthropogenic disturbance areas; Carey *et al.* (2005), for example, reported POC yields of 1.3 – 168 t km^{-2} a^{-1} from 13 alpine catchments. Of the southern New Zealand catchments measured in this study, 90% had a POC yield of < 10 t km^2 a^{-1}. Catchments with yields > 10 t km^2 a^{-1} were only typical of high denudation catchments subject to frequent stochastic slope failure, and high rainfall that leads to higher POC yields (e.g., Lyons *et al.,* 2002). Overall the POC yields of southern New Zealand are relatively modest compared to assessments of other high relief islands (see: Lyons *et al.,* 2002).

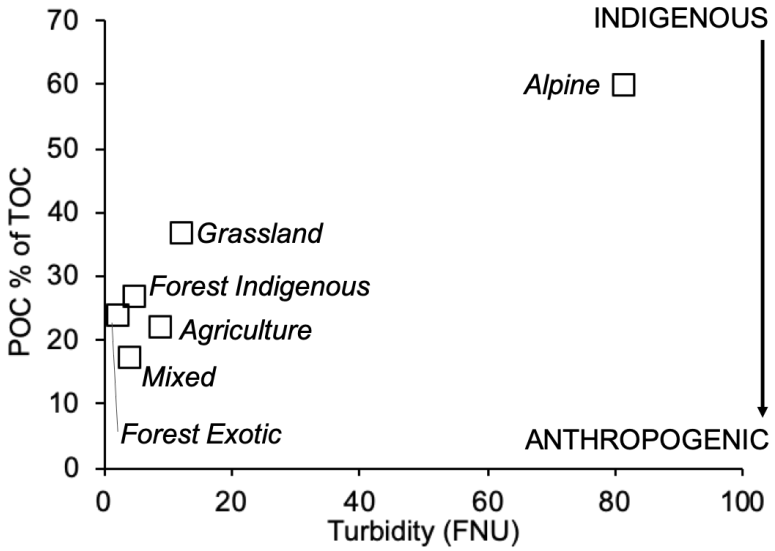

Figure 4.5 Particulate organic carbon (POC) as percentage of total organic carbon (TOC) (POC% of TOC) for 84 southern New Zealand catchments classified by dominant vegetation class versus turbidity measured in units FNU.

Of the 555 global rivers in the GEMS-GLORI database 54 had POC concentrations, these varied from 0.3 – 13.0 mg L^{-1}; and equivalent yields of 0.0 – 6.2 t km^{-2} a^{-1}, and 68% were <1 t km^{-2} a^{-1}. DOC yields ranged from 0 – 16.1 t km^{-2} a^{-1}, with a median of 1.4 t km^{-2} a^{-1}, and POC contributed on average 37% of TOC (see: Meybeck & Ragu, 2012). By comparison to the major rivers discharging to oceans globally, southern New Zealand POC yields are similar to the global median of 0.4 t km^{-2} a^{-1}. This distinctly Southern Hemisphere example illustrates that our POC yields are consistent with those of the Northern Hemisphere (e.g., Naiman & Sedell, 1979; Naiman & Sibert, 1978; Coynel *et al.,* 2005; Wu *et al.,* 2007; Zhang *et al.,* 2009; Madej, 2015).

4.4.3 Intrinsic and extrinsic catchment characteristics influence on POM

Twelve independent variables (Table 4.2) were used as independent predictors in stepwise multiple regression modelling to build a predictive model for riverine particulate concentrations and carbon under baseflow (Table 4.5). POM concentration and SSC were predicted by a model that included lithology type, with schist lithology and mean annual rainfall explaining 26% of the variation in POM concentration and 22% of the variation in SSC. The weak model response observed here is due to the emphasis on baseflow generation

of material and is decoupled from SSC and suspended sediment yields (SSY) that are almost exclusively entrained during event flow (e.g., Mager *et al.,* 2018). Even under baseflow, lithology influences SS and POM, but explains very little of the variation in the concentration of these particulates. Initial model outputs suggested that lithology confounded the results by priming the model output for dependence on lithological type. Geology across most of southern New Zealand is geographically constrained by the Southern Alps and tectonic metamorphism of silt and mudstones, and as such promotes a highly erodible environment which is a primary control on suspended sediment yield (Bloomberg *et al.,* 2011; Hicks *et al.,* 2011; Basher, 2013). Lithology in these initial runs is likely acting as a proxy indicator of autocorrelated landform elements i.e., terrain steepness, soil type, preservation and availability of unconsolidated alluvium and colluvium landforms, that contribute to sediment delivery (Hicks *et al.,* 2004). To account for this, lithological categories were removed from subsequent model runs to explore the relevance of other controlling variables exclusive of the concomitant transport effect that lithology has on SS and POM.

Rainfall was a common predictor for all particulate concentrations and POC yield (Table 4.5; Figure 4.6) and confirms that like SS, POM is associated with reduced shear stress in wet conditions. Rainfall drives physical weathering of (inorganic) sediment and annual SSY across New Zealand (see: Hicks *et al.,* 2011); and suggests co-dependence of organic matter concentrations on SS for transport under baseflow. Also plausible however, is a dependence on the same processes that control transport ability, for example, rainfall splash and overland hydrological pathways that lead to surface erosion (Gomez *et al.,* 2003). Rainfall determines the level of field saturation, soil water contact time, and detachment potential, that prime hillslopes for erosion via surface and sub-surface processes (Hope *et al.,* 1994; Hope *et al.,* 1997; Dawson *et al.,* 2002; Aiken, 2014). In locations where high POM concentrations were observed without high SS, the dependence on rainfall is likely a representation of wetter catchments having a higher organic pool, for example, cool temperate forests or pastoral catchments at lower elevations on a catchment rainfall gradient (e.g., Gomez *et al.,* 2010).

Table 4.5 Independent catchment characterises listed in hierarchal order of importance in linear model (determined by stepwise linear multivariate regression), with slope coefficients (β), model fit (r^2) and D-W (Durbin-Watson statistic) used to determine statistical significance (*). Showing turbidity (as NTU and FNU), suspended sediment concentration (SSC), total suspended material (TSM), POM as a percentage of TSM (POM%), particulate organic carbon (as mg L^{-1} and as a yield t km^{-1} a^{-1}, and as a percentage of total organic carbon).

	Model Parameter	β	r^2	D-W
Turbidity (NTU)	Severe Erosion	2.88	0.10	1.97
Turbidity (FNU)	Soil Type: Podzol	5.44	0.38	2.20
	Carbon Content: High	-4.73		
SSC (mg L^{-1})	Rain (mm a^{-1})	0.02	0.09	2.19
TSM	Soil Type: Podzol	24.02	0.70	2.12
(mg L^{-1}) *	Carbon Content: High	-13.50		
	Rain (mm a^{-1})	-0.15		
	Snow and Ice (% cover)	22.6		
	Soil Type: Raw	4.96		
POM% *	Stream Order	-7.49	0.46	2.03
	Slope: Rolling 10-20°	0.31		
	Grassland (% cover)	0.41		
	FRE3	2.86		
	Rain (mm a^{-1})	-0.01		
POC	SSY	0.001	0.27	1.47
(mg L^{-1})	FRE3	-0.08		
POC Yield	Rain (mm a^{-1})	0.003	0.15	2.09
(t km^2 a^{-1})				
POC % of TOC *	Gravel, Rock, Landslide (% cover)	0.57	0.54	0.93
	SSY (t km^2 a^{-1})	0.01		
	Erosion Moderate (% cover)	0.24		
	Catchment Area (km^2)	-0003		

Soil characteristics were important variables for predicting TSM in southern New Zealand, in particular the presence of podzol and raw soil types, and high soil carbon. Podzol soils in New Zealand occur in high rainfall areas and, in combination with forest cover, leach organic acids releasing aluminium and iron complexes from soil organic matter (Hewitt, 2010). Podzols across southern New Zealand also have a thick humus layer with plentiful organic material that protects lower mineral horizons, although are susceptible to sheet erosion, and likely explains relevancy of high soil organic carbon soils (NZ Soil Bureau, 1968; Hewitt, 2010). To assess the connection between TSM and podzol type soils, Particle Loading Coefficients (PLC) for SS and POM were calculated for aluminium (Al^{2+}) and total iron (Fe^T). The PLC is a metric used to quantify particulate-bound nutrients and pollutants transported within the suspended load of rivers (Rügner *et al.,* 2013). Metals are commonly particulate bound during transport due to charge affinity to the surface of suspended

particulates, especially clay-sized material, but also to organic materials like humic acids and organic coatings (Balkis et al., 2009; Citeau *et al.,* 2003). Al and Fe are dominant in podzol soils but also relevant to most common soils types that have high background levels of Al^{2+} and Fe^{T} due to their affinity with organic humic complexes (Juo *et al.,* 1974; Drever & Stillings, 1997; Steffen *et al.,* 2002; Hewitt, 2010; Buurman & Jongmans, 2005), and therefore provide opportunity to assess role of soil in transport of inorganic suspended sediment and POM. Median PLC of Al^{2+} and Fe^{T} for POM (0.06 and 0.19 respectively) were greater than the PLC of SS (0.02 and 0.08 respectively). Al^{2+} and Fe^{T} are associated closely to clays or organic matter by forming metal oxides (Buurman & Jongmans, 2005). The co-migration of Al^{2+} and Fe^{T} complexes with POM suggests that the riverine POM may be associated to organic soil complexes at baseflow; but as PLC for SS were also significant, it cannot be discounted that Al and Fe may also have a mineral contribution from amorphous and crystalline inorganic oxides (Juo *et al.,* 1974).

Land cover types also influenced model ability to predict particulate concentrations, although it was only a modest contributor; snow and ice coverage, grasslands, and gravels/bare ground were the only land covers detected as being significant. The coverage of snow and ice was a strong predictor of TSM, due to intense physical weathering processes associated with alpine areas (Hales & Roering, 2005), and the ready supply of fine-grained material from glacial abrasion and rejuvenation of raw soils common in alpine environments (Larson *et al.,* 2014). Similarly, the positive relationship between catchment coverage of unconsolidated gravels, rock, and landslides to POC% of TOC suggests in areas of high denudation, the amount of organic carbon displaced from hillslopes is coupled to physical weathering processes.

Slope of 10 – 20°, and grassland coverage both positively predicted POM% and although not statistically autocorrelated in the model, pastoral activity is common across rolling hill country with grassland cover that is less suited for more intensified land uses. Grassland types included low production (that is, non-irrigated) with short growing seasons and often managed for sheep and beef grazing, and depleted grasslands that are further limited by over grazing or burning (Thompson *et al.,* 2003). These depleted grasslands often have bare soils, which can be easily mobilised and detached in storms, and the fluvially dissected rolling slope provides a short transport pathway for material delivery to streams. The lack of other land covers being associated as factors contributing to particulate concentrations in southern

New Zealand is likely a factor of the complex land use mosaic, where land cover elements like forest cover, or indigenous tussock grasslands are highly fragmented across sub-catchments.

Hydrological variables of stream order and flushing event frequency (FRE3) were predictors of POM%. Stream order had an inverse effect on the prediction of POM%: so that POM% was greatest in lower stream ordered catchments. Small tributaries have a higher degree of connection between hillslopes and stream channels, with higher potential for direct lateral contributions of organic material from riparian vegetation (Naiman, 1982; Robertson *et al.,* 1999; Madej, 2015). As stream order increases, the stream channel widens and reduces direct input from vegetation (Robertson *et al.,* 1999; Wu *et al.,* 2007). Wider lowland alluvial channels with significant portions of exposed riverbed material typically store fine sediments and provide readily available source of mineral material (Wohl *et al.,* 2015), so that the effect is of increased storage potential, and a reduction in organic matter through biological uptake and reduced organic matter delivery.

The other significant hydrological variable was the frequency of flushing flows (FRE3) that was positively related to POM%. The relationship between FRE3 and POM% suggests that POM transport is sensitive to the number of flow events in a catchment. The FRE3 is used as an index of flow-driven disturbance of ecological processes (Booker, 2015) and suggests POM% may rely on the frequent disturbance of the terrestrial surface to accumulate allochthonous organic material for transport between storms. Thus POM% to some degree may be hydrologically driven (e.g., weak response to rainfall). POM concentrations typically positively respond to discharge, that is increase under event flow (e.g., Hope *et al.,* 1994; Coynel *et al.,* 2005; Sabater *et al.,* 2006; Hatten *et al.,* 2012). Similarly, POM% increases as mean annual rainfall decreases because as catchments get drier POM becomes an increasingly dominant component of suspended load as inorganic denudation is reduced.

The above analysis has illustrated that riverine organic matter is organised spatially and connected to broader hillslope processes, albeit difficult to predict at the catchment scale. Median POM concentrations across southern New Zealand demonstrate that organic matter in particulate form is persistently present under baseflow conditions and is a sustained flux of carbon to the ocean, at concentrations similar to the large global rivers. Organic matter is more conservative than SS (Naiman, 1982) and several factors determine the level that POM

accrues within a system; the type and amount of organic inputs, stream form, retention functions, and the frequency of events (Naiman & Sedell, 1979). TSM can be predicted by catchment characteristics at base flow, but the individual components of TSM (e.g., SSC and POM) are not as well predicted, and reflects the different sources, hillslope connectivity, and transport pathways of each particulate type relative to the other (Figure 4.6).

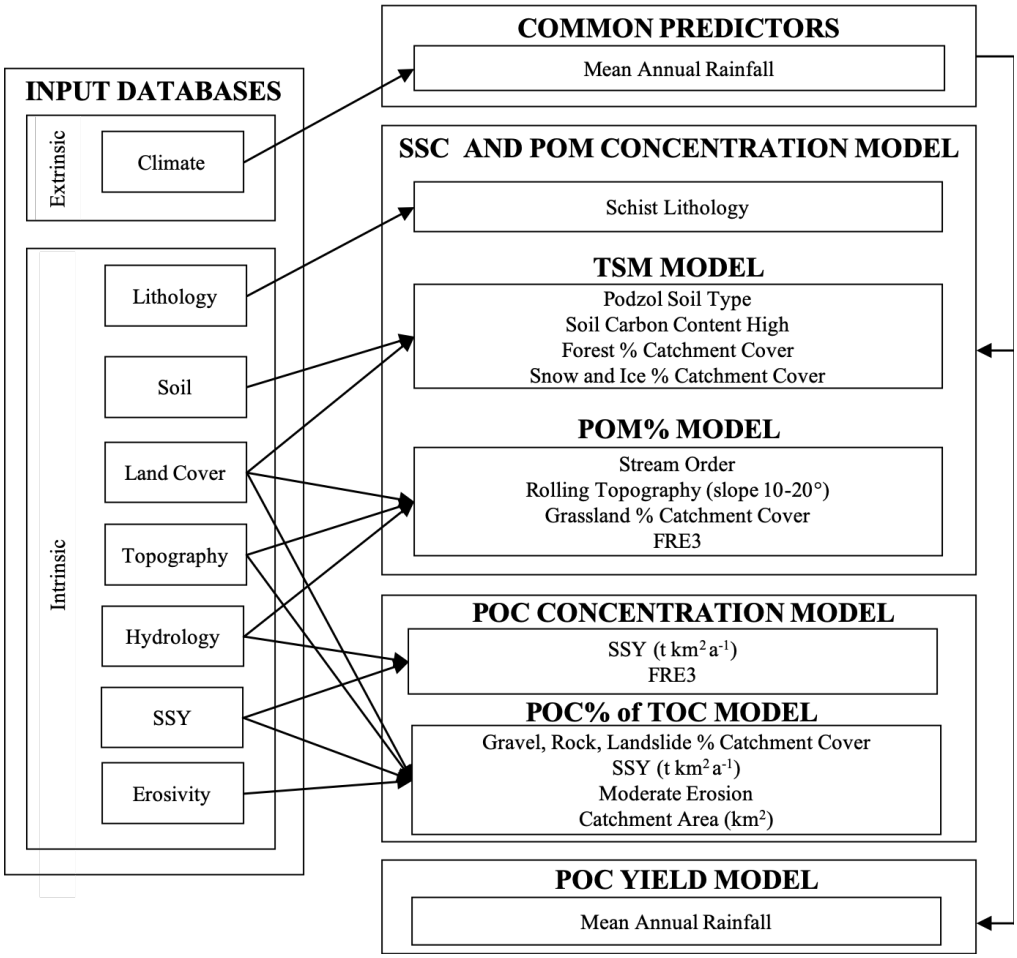

Figure 4.6 Predictive models for suspended sediment concentration (SSC) and particulate organic matter (POM), total suspended material (TSM) as concentration, the proportion that is POM of TSM (POM%), and particulate organic carbon (POC) concentration, POC as a percentage of total organic carbon (TOC) (POC % of TOC), and POC Yield, for 84 catchments across southern New Zealand.

4.4.4 Uncertainties of the stepwise method for model prediction

The main uncertainties and potential sources of Type I errors in analysis are: 1) the number of predictors used in the stepwise regressions; 2) potentially inflated r^2 values due to autocorrelations; and 3) the statistical inference processes of the stepwise procedure, whereby the algorithms operate by successive addition or removal of significant and non-significant variables (see: Anderson & Burnham, 2002; Whittingham *et al.,* 2006). Testing multiple predictors increases the risk of a spurious correlation (Type I error) as there is no error-level adjustment across the stepwise procedures (Mundry & Nunn, 2009). Furthermore, autocorrelation can inflate the r^2 value and overestimate the fit of the model leading to misrepresented conclusions (Whittingham *et al.,* 2006). Similarly, confidence in the final model can be affected by other models with similar r^2 that were excluded by the stepwise produce (Whittingham *et al.,* 2006). Some of these tendencies for stepwise regression to fit unusual predictors when a large number of predictors are input was reduced by running subsets of the data, that is, limiting to just lithological factors, or limiting to just land use factors, as to reduce the number of potential variables to less than the number of observations. The outputs were carefully examined for measures of correlation and multicollinearity coefficients, and rejected models that indicated high measures of autocorrelation. The authors recognise these limitations, and that these uncertainties are propagated through the potential selection of landscape controls on organic matter fluxes. The adopted approach remains broadly applied in similar research despite the limitations of the stepwise method (e.g., Williams *et al.,* 2008; Wilson & Xenopoulos, 2008). Rather, the use of the stepwise method has been used here as an exploratory tool to identify potentially relevant landscape elements that influence particulate concentrations and organic flux, and that these landscape elements should be considered when directing future research into the controls on organic fluxes at regional and local scales.

4.5 Conclusion

Riverine organic matter concentrations across southern New Zealand are highly variable under baseflow, ranging from < 0.3 – 58.4 mg L^{-1}, and are a small, but persistent component of total suspended material. The riverine organic flux contributes POC yields exported to the coast of 0.04 – 0.4 t km^{-2} a^{-1} into Fouveaux Strait, and between 0.4 – 2.7 t km^{-2} a^{-1} into the south-east Pacific Ocean. Under base flow, substantially more organic carbon was fluxed to

the ocean as DOC compared to POC. A a van Bemmelen factor of 1.3 is derived for southern New Zealand and determined that baseflow POC yields are largely consistent with previously reported global observations. Regression modelling revealed that under baseflow conditions the concentration of SS and POM is associated, albeit weakly, to lithology, rainfall, and transport competence that is typically controlled by event hydrology. Spatial variation in baseflow TSM was influenced by soil characteristics (especially the presence of podzol and raw soils types), mean annual rainfall, the presence of permanent snow and/or glacial ice. POM as a percentage of total suspended material is highly variable across southern New Zealand, ranging from <10%, or much higher at 50 – 80%, and controlled by both intrinsic and extrinsic catchment characteristics. POM as a percentage of TSM was controlled by stream order, rolling topography, grassland land cover, flooding frequency and mean annual rainfall.

In southern New Zealand POM and SS are transported concomitantly within the fluvial system and at baseflow the concentration of each particulate is influenced by the same catchment characteristics. Organic carbon fluxes are associated strongly with denudation, so that areas of high physical weathering are also associated with higher particulate organic carbon fluxes. However, land cover type influences the type of organic carbon flux, with a switch to higher losses as dissolved carbon in anthropogenic-modified land covers (e.g., pastoral grasslands, compared to indigenous forests or grasslands).

5 Predicting suspended sediment concentration from nephelometric turbidity in organic-rich waters

Research article published in *River Research and Applications* in 2018[3]. See Appendix 11.2.

5.1 Abstract

Turbidity is an optical measure of water clarity, combining the net optical affect from the materials suspended and dissolved in a body of water. When a mixed composition of suspended inorganic and organic materials, and dissolved substances are present in a stream or river, turbidity measurements can be influenced by the interferences caused by the different organic and inorganic materials present; different turbidimeters are more or less sensitive to these interferences. Two different methods of turbidity measurement were assessed (EPA 180.1 and ISO 7027), and examined the effect of particulate organic matter, and dissolved colour from organic acids on the measurement of turbidity, and the ability to produce predictive relationships between turbidity and the suspended sediment concentration for a variety of Otago catchments, in the South Island of New Zealand. Results suggest that the presence of organic matter and dissolved colour causes interference with turbidity measurement, however turbidity measurement following ISO 7027 methods are less susceptible to interference for environmental monitoring purposes; but will yield significantly different rating equations between suspended sediment and turbidity compared to EPA 180.1 methods.

[3] Minor changes to the narration of this research article have been made to improve coherency between chapters. The use of 'proxy' has been replaced with 'surrogate', for where turbidity is described in the use of estimating suspended sediment concentration.

5.2 Introduction

Turbidity, quantified in nephelometric units, is a widely used surrogate indicator of suspended particles in water bodies employed by researchers and environmental monitoring agencies (Kitchener *et al*., 2017). In the broadest sense water turbidity is inversely related to water clarity, in terms of light penetration and visual clarity, because the presence of suspended particles within a water column act to decrease light penetration and visual clarity, and cause light scattering, of which turbidity is a relative index of the side scattering of light (Davies-Colley & Smith, 2001). Poor water clarity diminishes light penetration through the water column and causes reduced photosynthesis and aquatic habitat quality. Whereas reduced visual clarity has a deleterious impact on recreational water use, aesthetic values and human health (Davies-Colley & Close, 1990; Smith *et al.,* 1997; Davies-Colley & Smith, 2001; Sadar, 2004; Hughes *et al.,* 2015). From an environmental monitoring perspective, turbidity is an inexpensive and convenient surrogate measure of the 'cloudiness' of water and provides an inexpensive relative index of the amount of particulate contaminants from land use disturbance, principally as suspended sediment concentration (SSC) (Ankcorn, 2003; Gray & Gartner, 2009). However, turbidity is not a physical quantity, rather, it is a convenient relative index, used to predict the quantity of suspended particulates in a water column (Davies-Colley & Smith, 2001; Kitchener *et al*., 2017). Its use is problematic, however, because particles have different light scattering properties, and these particulate properties (e.g., size, shape, and composition) contribute different amounts of light scatter that result in noisy or poor relationships between the physical quantity of suspended sediment (SS) and observed turbidity.

Turbidimeters come in many different forms, but in principle operate by using a light-emitting source that interacts with water and the materials suspended in the sample, with photons being absorbed or scattered (see: Omar & MatJafri, 2009). Typically, particulate material causes light scattering, whereas dissolved substances absorb light (Gippel, 1989). For example, organic particles and organic-coatings on inorganic sediments are strongly light absorbing, and this absorption is strongest on the shortwave length (blue) spectrum (Davies-Colley *et al*., 2014) resulting in a yellow-hue of the water body. However, the amount of light absorption from POM and dissolved substances depends on the light wavelengths used in the turbidimeters, so that not all instruments account for attenuation by POM and dissolved substances in the same way. Light attenuation may be especially

problematic when dealing with stream water that contains a variety of particulate and dissolved substances, which vary with catchment characteristics and hydrology (Gippel, 1989). As a result, there may be variability in turbidity response observed in natural water samples as result of changing sample composition, and is a long-recognised limitation of some turbidimeters (e.g., McCarthy *et al*., 1974; McCluney, 1975; USGS, 2005; Sadar, 2004); however, such limitations and suitability of application are generally overlooked by users (Gippel, 1989). A comparison of twelve different nephelometric turbidimeters under laboratory conditions, for example, showed turbidity measurements varied five-fold between instruments (Rymszewicz *et al*., 2017). Such limitations of turbidimeter suitability and vulnerability to dissolved optical properties are not an issue if turbidity is being used to assess suitability for drinking water; but this may be an issue when monitoring for environmental standards in natural river systems. For example, cool temperate rainforests leach organic acids and the resultant absorption of light in the blue spectrum, and resultant yellow hue may be inaccurately determined as elevated turbidity. Thus, turbidity is a complex indicator that is a function of light absorption and scatter and responds to both natural and disturbed elements in the water column, so collection of turbidity data needs to be carefully matched to the purpose of monitoring.

Light absorption or scattering is a function of light transmittance through a fluid, the reflectivity of the material, and the particule size (Gippel, 1995; Ankcorn, 2003; Omar & MatJafri, 2009). Light is either absorbed or scattered through Rayleigh or Mie scattering, or geometric optics. These models of optical theory assume a spherical particle, where Rayleigh scattering is limited to small non-absorbing spherical particles (usually in the range of 2–75 nm). More typical of the refraction that occurs in suspension in water is Mie scattering, where light is absorbed or scattered from non-absorbing spherical particles of unlimited sizes, but are usually in the size range of 20 nm – 765 μm (Kitchener *et al*., 2017). For particles > 200 μm light refraction, reflection, and absorption is explained through geometric optics theories, which are most applicable when the wave length of the light source is less than the particle size of the incipient surface (Kitchener *et al*., 2017). When translated to measurements of turbidity, these optical properties strongly influence the type and direction of light scattering, and are contingent on the light wavelength and detectors used in turbidimeters to measure the light scattering.

The relationship between turbidity and suspended particles, or the suspended sediment concentration (SSC), depends on the particle size distribution and other sediment characteristics of the suspended material (Lewis *et al.,* 2007). If suspended particles do not differ in their physical properties, as their concentration varies, a linear relationship between turbidity and SSC should exist, as an increase in turbidity usually relates to a predictable increase in SSC (Gippel, 1989). In practice, however, non-linearity occurs between turbidity and SSC as a result of high scatter in turbidity data due to differing amounts of light side-scattering from suspended particles. Such substances that are optically different to mineral/inorganic particulates include: organic matter and other floating debris, algae, air bubbles and coloured dissolved organic matter (CDOM) (Davies-Colley & Nagels, 2008; Omar & MatJafri, 2009). Thus, turbidity measurements combine the net optical effect of particulates (both organic and inorganic) as well as any dissolved material; resulting in interferences with the desired use of turbidity measurements is to predict the (inorganic) SSC.

Clay, silt, organic and inorganic matter, soluble coloured organic compounds (i.e., CDOM), and plankton are all components present within natural flowing waters that contribute to turbidity, and each has distinctive optical properties that may influence turbidity measurements (Table 5.1) (Gippel, 1995; Sadar, 1999; Ankcorn, 2003). Dissolved organic acids and CDOM are particularly problematic to turbidity measurements. The presence of CDOM in terrestrial water bodies causes a yellow-tinted colour in the river waters, which has a negative influence on some turbidity measurements, although results vary depending on the CDOM concentration (Gippel, 1989; Gippel, 1995; Pavelich *et al.,* 2002). Thus, if the amount of inorganic SS in a water sample is being predicted, it is contingent on turbidity data not being vulnerable to influences introduced by the presence of other light refracting or absorbing properties in the water. When the optical characteristics of particles vary, the result is high scatter in plots between turbidity and SS, causing weak relationships and reducing the ability for turbidity to predict SSC (Gippel, 1989). These effects may be further influenced by the presence of particulate organic matter (POM), which have a different shape and density compared to inorganic minerals, and thus scatter light differently. Organic matter includes plant fragments, organic soils, colloids, faunal casings and a variety of other organically-derived components, that may be either allochthonous (e.g., in floods) or autochthonous (e.g., under base flow) in source. Inorganic particles scatter light, whereas organic particles tend to absorb light, particularly in the short-wave portion of the light

spectrum (Davies-Colley & Smith, 2001). Thus, when rivers contain high levels of organic matter, particularly under event flow conditions, the result is for an opaque, brown, or 'muddy' appearance. The amount of organic matter, as CDOM or POM, in rivers is highly specific to catchment characteristics, and may reflect land use disturbance associated with pastoralism or forest clearance, or natural processes of carbon cycling through wetlands, soil leaching, or high sources of particulate organic matter within the catchment (see Chapter 4).

Table 5.1 Summary of the effects from different influences on accurate turbidity readings and the potential bias (positive or negative) effects. (Sources: Sadar, 1999: 2004).

Influence	Details	Effect on turbidity
Light absorption	Matrix of light absorbing particles prevent light reaching the detection system	Negative bias
Particle Size	Larger particles scatter longer waves length of light more effectively	Positive/negative bias
	Smaller particles scatter short wavelengths of light more effectively	Positive/negative bias
Bubbles	Bubbles affect the measurement accuracy	Positive bias
Sample cell variation	Scratches and imperfections on sample cells can cause light to be refractions and reflections	Positive/negative bias
Stray light	Light that is measured by the detection because of sample cell imperfections, internal reflection, and contamination from dust or electronic noise	Positive bias
Particle settling	Bias results from rapid settling and depends on the length of time to perform a measurement	Positive/negative bias
Instrument	Degradation of instrument optical performance	Positive/negative bias
Contamination	Introduction of stray matter from bed disturbance or other sources.	Positive bias

The objective of this study is to examine the effects of two turbidimeters on the ability to predict SSC from natural river samples with regards to differences in POM that occur in differently vegetated catchments. Previous studies have examined the variability between turbidimeters (e.g., Hongve & Akesson, 1998; Barter & Deas, 2003; Lewis *et al.,* 2007; Rymszewicz *et al*., 2017); however, the effects of such interferences on predictive

relationships between SSC and turbidity have not been considered with regard to the influence of organic-rich riverine suspended loads. The study compares the response of two different turbidimeters and the predictive relationships between turbidity and SSC, for natural river samples that includes rivers under base flow and event flow conditions, as well as variable POM concentrations as a way to examine the effect of organic particulates on turbidity.

5.3 Methods

Seventy-eight samples were collected from a headwater catchment undergoing plantation forestry clearance in Otago, New Zealand (45.83°S 169.72°E). The Glendhu (GH2) catchment is part of a long-term paired catchment study established to understand the effects of plantation forest development on ground formerly occupied by indigenous snow tussock (*Chionochloa rigida*) (see: Fahey & Payne, 2017). An ISCO automatic water sampler collected daily 500 mL water samples between April–September 2017, as a part of a high-resolution study into SS and POM. A further eight catchments (Table 5.2) in Otago were also sampled that included a range of vegetation and land use covers, from relatively pristine alpine catchments (e.g., Dart/Te Awa Whakatipu, Rees/Pua Hiri, and Shotover/Kimi-ākau) to pastoral agricultural and native grassland catchments (e.g., Deep, Lee and Taieri catchments). The catchments range in area from a small headwater tussock catchment (2.1 km^2) in the Glendhu (GH1) catchment, up to the moderately-sized Taieri Catchment (5,706 km^2). Grab samples (1.5 L) were collected from Deep Stream, Lee Stream, Taieri River, and the GH1 catchment during the austral winter and spring of 2017, whereas the four rivers that drain the Southern Alps of New Zealand were sampled (1–1.5 L) episodically between October 2012 and September 2017 over a range of flow conditions between October 2012 and September 2017.

The lithology of all catchments is comprised of Permian to Triassic aged schist (TZIII or TZIV) from the Caples and Rakaia terranes, except the Taieri, which has Miocene-Eocene terrestrial siltstones and sandstones in the north from the Hawkdun formation, and isolated Miocene extrusive volcanics from the Dunedin Volcanics Group (Edbrooke *et al.,* 2014). The catchments were selected on the basis of their percentage cover of indigenous grassland (tall snow tussock), so that there was a selection of tussock dominated, mixed indigenous

vegetation, and exotic pasture catchments. A tussock land cover was selected specifically because previous work has observed frequent organic stained runoff, with a distinct yellow hue in GH1 (see: Chapter Three, Bright & Mager, 2016).

Table 5.2 Catchment characteristics for the rivers that were sampled for suspended sediment, particulate organic matter and turbidity. Land cover classifications from the Land Cover Database (v4.1) (Landcare, 2015).

River	Area (km^2)	Stream Order	Discharge ($m^3\ s^{-1}$)	Rainfall ($mm\ a^{-1}$)	Land Cover
Dart/Te Awa Whakatipu	586	5	76.7	4,065	Indigenous forest (30%), tussock (24%), herbfield (16%), bare ground (16%) and 12% ice.
Deep	412	5	4.5	725	Pasture (53%) with tussock (36%) and grazed tussock (7%).
Glendhu (GH1)	2	2	0.06	1,300	Tussock (80%) with pockets of indigenous scrub.
Glendhu (GH2)	3	2	0.04	1,300	Cleared ground (75%) and plantation forest.
Lee	314	5	2.6	786	Pasture (89%) with pockets of scrub, tussock and forestry.
Rees/Pua Hiri	285	5	25.8	2,488	Tussock (57%) with indigenous forest (10%), herbfield and indigenous scrub. 20% bare ground or alluvium.
Routeburn	82	4	13.5	3,562	Tussock (32%), indigenous forest (30%) and herbfield (21%), bare ground/alluvium (11%).
Shotover/Kimi-ākau	1099	6	49.6	2,018	Tussock (72%) with pockets of herbfield and indigenous forest. Bare ground/alluvium (8%).
Taieri	5706	6	35.6	751	Pasture (47%) tussock (22%) and grazed tussock (14%). Pockets of exotic forestry (5%).

Suspended sediment and POM concentrations were calculated following standard methods (see: ATSM, 2002), of filtering water samples through pre-washed and dried 0.7 µm glass fibre filters. These filters were oven-dried at 105°C for 24 hours, and weighed and re-dried three times. The glass fibre filters were dried in a muffle furnace at 500°C for 30 minutes, and reweighed to determine the loss on ignition, which is an index of POM (see: Grove & Bilotta, 2014). Samples below the method detection limit of 0.3 mg L^{-1} were excluded from the data set.

Two nephelometric methods were used to determine turbidity following EPA 180.1, and ISO 7027 methods. EPA Method 180.1 uses a tungsten lamp light source, with a wavelength

of spectral peak response between 400–600 nm, whereas ISO 7027 uses a near infrared light source with a wavelength of 860 nm (Gippel, 1989; Hongve & Akesson, 1998; Ankcorn, 2003; Sadar, 2004). The tungsten light source produces a number of light wavelengths that improves detection of smaller sized particles, but is susceptible to the effects of CDOM (Omar & MatJafri, 2009). The ISO 7027, however, uses a monochromatic light (e.g., a light emitting diode (LED)) that produces a narrow band of light and is less susceptible to inference from CDOM (Gippel, 1995; Sadar, 1999; Omar & MatJafri, 2009; Khairi *et al.,* 2015), however, the narrower light wavelengths of the ISO 7027 method is less sensitive to smaller particle sizes (Gippel 1989; Omar & MatJafri, 2009).

Two turbidimeters are compared, HACH 2100P and HACH 2100Q-is, both calibrated to the manufacturers specifications with formazin standards. Calibration was determined by the arithmetic mean of 5 measurements of the 10, 20, 100, 800 NTU formazin standards, and repeated three times. Equipment accuracy and precision were determined using distilled deionized water (DDW) and a series of natural water samples ranging from low to high turbidity. Samples were agitated between readings to prevent particle settling. The reported units for the Hach 2100P is NTU, and FNU for the Hach 2100Q-is. Samples from the Dart/Te Awa Whakatipu, Rees/Pua Hiri, and Shotover/Kimi-ākau rivers collected during storm flow required dilution to accurately determine turbidity, and were diluted with ultrapure water through a series of 10 dilutions following the standard USGS (2005) method, so that turbidity was able to be determined in the range of < 40 NTU as recommended by the EPA 180.1 method.

Three of the alpine catchments (Dart/Te Awa Whakatipu, Rees/Pua Hiri, and Shotover/Kimi-ākau) were sampled under storm flow conditions. Forty litres of water were collected into a plastic container at each site, and a subsample retained for turbidity and SSC concentration measurements. The remainder of the storm flow samples were used for a settling experiment to assess the influence of fine particulate on turbidity. The settling velocity (w) was determined using a modified Stokes' Law (from Ferguson & Church, 2004) (eq. 1).

$$w = \frac{RgD^2}{C_1 v + (0.75 C_2 RgD^3)^{0.5}} \qquad (eq.\ 1)$$

where: R = 1.65 (ratio of fluid to particle densities)
g = acceleration of gravity (9.8 m s^{-2})
D = particle diameter (in m)
C_1 = dimensionless constant of 18
C_2 = dimensionless constant of 1 for natural grains
v = kinematic viscosity of water (1.235 x 10^{-6} m s^{-2} at 12ºC)
w in units of m s^{-1}

Storm samples were left for 134 hours, which is the time required for an equidimensional quartz density particle of 1 µm particle to settle 0.35 m in a standing water column, as determined using equation 1. Once settled, a 100 mL sample was decanted from the top of the standing water and used as a naturally-settled sample for turbidity comparison with the filtrate water sample. The filtrate water samples are derived from the residual water retained from filtering sub-samples of river water through a 0.7 µm glass fibre filter. The turbidity of filtrates was determined using the HACH 2100P and HACH 2100Q-is turbidimeters and compared to the naturally-settled unfiltered samples. The percentage that fine particulates (FP) (e.g., < 0.7 µm filters, or < 1 µm for naturally settled water) contributed to the overall turbidity of the sample was determined using equation 2 from Gippel (1989):

$$FP\ contribution = \frac{Turbidity\ Filtrate}{Turbidity\ Total\ Sample} \times 100 \qquad (eq. 2)$$

5.4 Results

5.4.1 Turbidity and suspended sediment

The turbidity and SSC relationship at Glendhu (GH2) showed a poor statistical fit (see: Chapter Three, Bright & Mager, 2016) (Figure 5.1a). Under a range of flow conditions, there was a good relationship between total suspended material (TSM) and turbidity (NTU and FNU), (r^2 = 73% and 75% respectively), however, there was a statistically significant difference in the slope coefficients of these regression relationships (2.73 for NTU compared to 0.49 FNU); signifying a different turbidity response dependent on nephelometric method

(Figure 5.1). The regression relationships determined in the GH2 catchment between the different fractions of suspended load and turbidity (as NTU and FNU) are statistically different with turbidity as NTU producing steeper regression equation slope coefficients compared to the FNU coefficients (p value < 0.001 of slope test). The relationships between turbidity and POM are the strongest (81% and 79%, Figure 5.1c), suggesting that POM relates better to turbidity than the inorganic SS (Figure 5.1a versus Figure 5.1c). The relationship between TSM and turbidity (as NTU and FNU) likely reflects the high proportion of POM that is included as a component of TSM, because in the Glendhu catchment POM dominates particulate flow (Table 5.3).

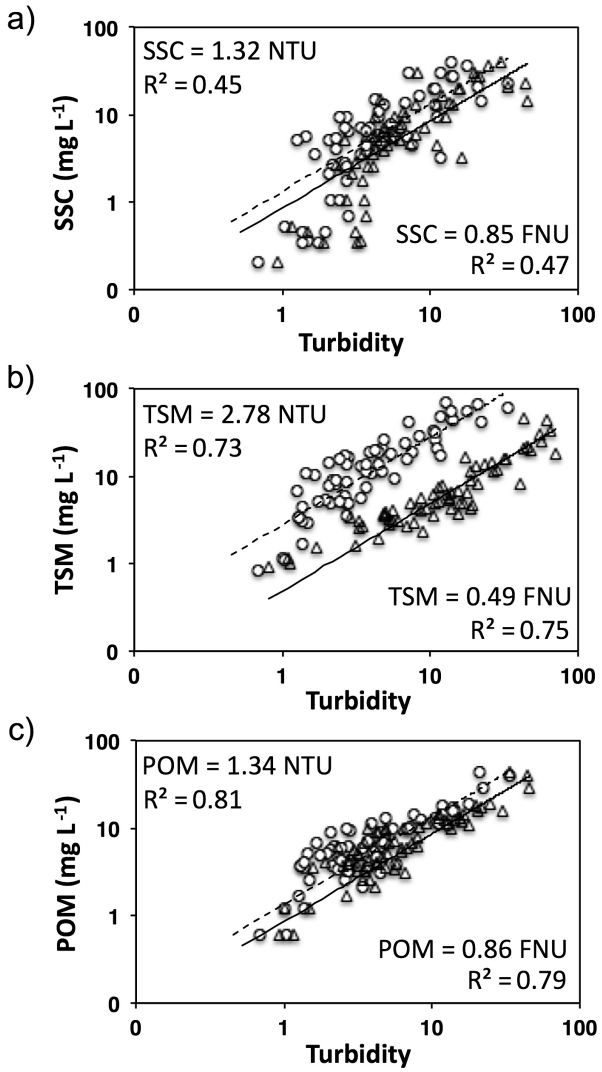

Figure 5.1 Relation of suspended matter metrics to turbidity for an organic-rich stream. Linear regression relationship between turbidity (in FNU (triangle) and NTU (circle) units) relative to a) suspended sediment concentration (SSC), b) total suspended material (TSM), and c) particulate organic matter (POM) for 78 samples from the Glendhu Experimental Catchment GH2, which is undergoing forest clearance.

The alpine rivers have a high suspended sediment load under base flow conditions (Table 5.3) and POM is usually <5% of the TSM under all flow conditions, with the exception of the forested Routeburn catchment, which has a low SSC (< 2 mg L^{-1}) that under base flow conditions is comprised of ~56% POM. For the large alpine rivers, there is a strong relationship (r^2 > 89%) between turbidity (as NTU) and SSC, with slope coefficients approximating 2 (Figure 5.2), a relationship typical of New Zealand rivers (see: Hicks *et al*., 2004). These relationships between turbidity (as NTU) and SSC for the Dart/Te Awa Whakatipu, Rees/Pua Hiri, and Shotover/Kimi-ākau rivers are strong relative to the SSC-turbidity relationship observed at GH2. The regression slope coefficients of the relationships between turbidity (as NTU and FNU) with SSC in GH2 are 1.1 and 0.7 respectively, suggesting that these do not follow what is typically observed in alpine New Zealand rivers. Furthermore, the regression coefficients between turbidity (as NTU) and SSC for GH1, Deep, Lee, and Taieri rivers are 1.87, 0.98, 1.58, and 1.33 respectively; like GH2 these rivers have high POM export as a portion of TSM, which likely affects the predictive ability of SSC-turbidity relationships, even when accounting for organic matter through the laboratory methods. Non-parametric statistical analysis of the time series data from the GH2 catchment shows that the turbidity values determined using the HACH 2100Q-is are statistically higher (p-value <0.05) than the HACH 2100P, with median values of 3.06 and 1.96 respectively. Of the 145 samples collected between April and September 2017 (in GH2 catchment), there are 126 occurrences where the HACH 2100Q-is produced a higher turbidity value than the HACH 2100P, by 10% or more.

Table 5.3 Median suspended material concentration (suspended sediment concentration SSC; particulate organic matter POM) and turbidity (NTU) reported for alpine rivers in Otago observed over all flow conditions, and median suspended material concentration and turbidity reported for organic rich rivers under all flow conditions for other selected Otago catchments.

River	SSC (mg L^{-1})	POM (mg L^{-1})	POM% of TSM	Turbidity (NTU)	Number of Samples
Alpine Rivers					
Dart/Te Awa Whakatipu	193.2	3.4	<2%	85.9	11
Rees/Pua Hiri	38.4	< 2.0	<5%	21.5	11
Shotover/Kimi-ākau	59.2	2.5	<5%	21.0	11
Routeburn	2.2	1.3	56	2.1	5
Organic Rivers					
Glendhu (GH1)	4.7	2.9	39	1.6	376
Glendhu (GH2)	7.2	6.0	56	3.6	445
Deep	1.8	1.0	34	2.8	3
Lee	7.7	2.3	24	6.8	4
Taieri	16.4	1.4	8	14.0	17

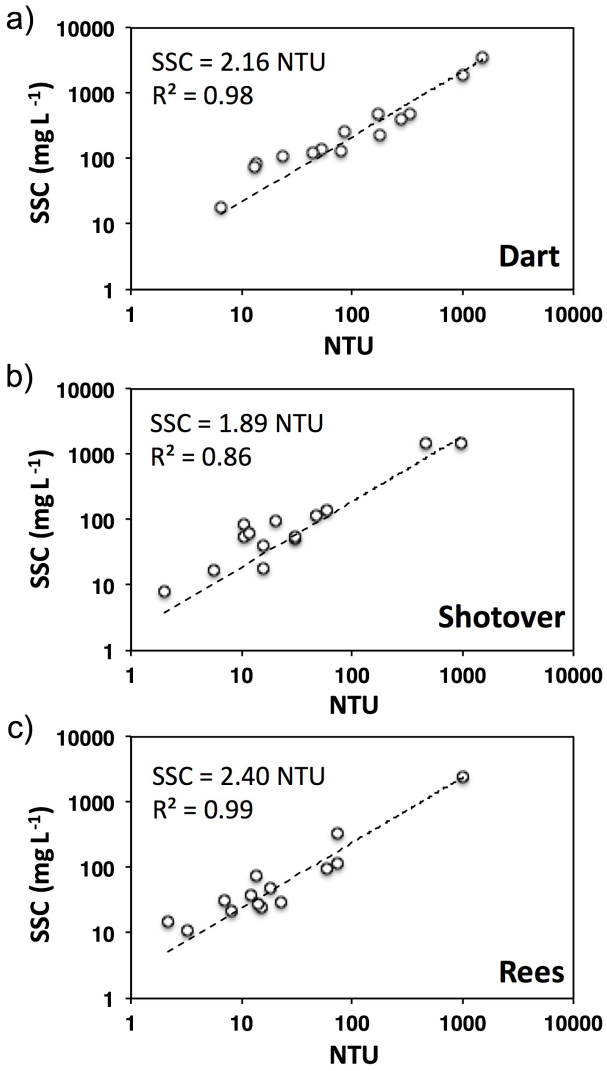

Figure 5.2 Suspended sediment concentration versus turbidity for three alpine rivers. Linear regression relationship for three alpine rivers in Otago, New Zealand showing a strong relationship between turbidity (as NTU) and suspended sediment concentration (SSC). Data taken from 15 discrete sampling times between 2012 and 2017 and includes storm flow events for a) Dart/Te Awa Whakatipu, b) Shotover/Kimi-ākau, and c) Rees/Pua Hiri.

5.4.2 Effect of fine particulates on turbidity

The two turbidimeters produced different turbidity values for natural waters, and showed different sensitivities to light scattering of colloidal-sized particles. A simple analysis was carried out to test the sensitivity of the two turbidimeters to sample filtrates where particulates > 0.7 µm had been removed by filtering through glass fibre filters. A series of samples from alpine rivers in Otago with high mineral components were compared to agricultural catchments within the Taieri Catchment, where POM was a significant source of TSM (Table 5.3). In these organic-rich environments, like the Deep Stream, POM

dominates the suspended load, and the effect of colloidal-sized particles on turbidity measurements was 7.5% for the HACH 2100P and 5.8% for the HACH 2100Q-is (Figure 5.3). Where POM is an insignificant component of TSM (e.g., Dart/Te Awa Whakatipu, Rees/Pua Hiri, and Shotover/Kimi-ākau), the effect of colloidal-sized particles was minimal, being < 0.8% (Figure 5.3). For the forested Routeburn catchment, the effect of colloidal-sized particles was 2.8% for the HACH 2100P and 2.1% for the HACH 2100Q-is. Thus, the effect of colloidal-sized particles on turbidity was lowest in alpine rivers, and increases in grassland-dominated catchments (Figure 5.3).

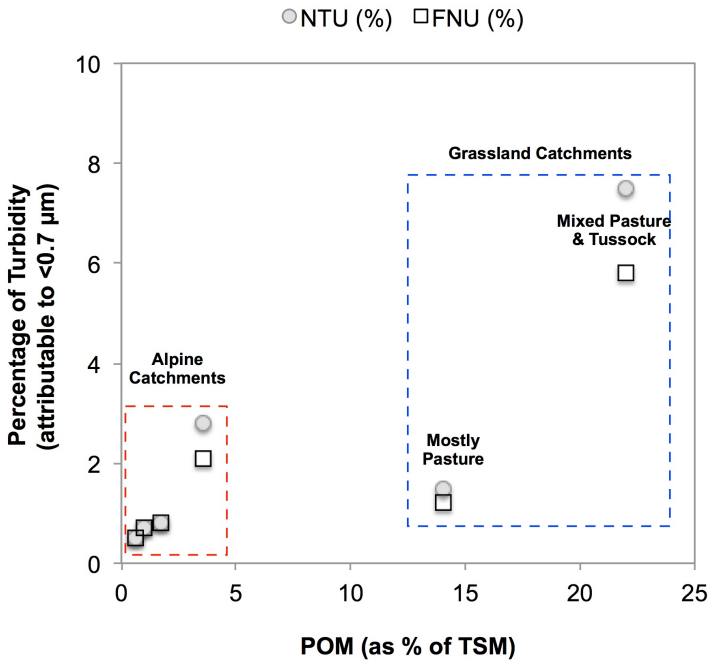

Figure 5.3 Influence of small particulates on turbidity measurements. Comparison of turbidity of natural river samples relative to the amount of particulate organic matter (POM% of total suspended material, TSM) and the residual effect of CDOM or small particulates (< 0.7 µm) on turbidity.

Rivers in flood are more turbid due to the entrainment of organic and inorganic particulates, and typically appear a 'muddy brown' colour. Suspended particles either absorb or reflect light proportional to their grain size and shape, and composition. A further experiment was undertaken to assess the impact of fine material that occurs at the (arbitrary) dissolved-particulate boundary (equivalent to 0.7 µm for filter pore size in this study) of flood-waters to assess the turbidity effect of non-settling particulates (i.e., < 1 µm for a spheroid quartz grain) on water turbidity, and the respective sensitivity of each turbidimeter to these suspensions. The flood samples from alpine rivers, when allowed to naturally settle, did not

exhibit the distinctive 'yellow hue' associated with CDOM, rather, a faint grey cloudiness was evident, suggesting that forward light scattering off mineral grains occurs systematically across all particulate sizes, even at the boundary between dissolved and particulate grains. The measured turbidity of the naturally settled samples (i.e., samples that were left for 134 hours) ranged from 29–42 NTU and 32–58 FNU, and illustrated that particulates between the range of dissolved (0.7 µm) and in suspension (here defined as 1 µm) are very effective at light attenuation, and produced turbidity 5–10 times higher than that attributable to colloidal-sized particulates (i.e., < 0.7 µm). The intense light scattering observed at < 1 µm is likely due to the high silicic mineral content of the clay particulates, being dominated by the mechanical disintegration of the indurated schist lithology, that is comprised of quartz and micaceous minerals.

5.4.3 Performance of different turbidimeters

Using a series of formazin standards, the turbidity values obtained from the two different meters showed reasonable between-meter numerical agreement, with higher uncertainty at the 800 turbidity standard (Table 5.4). The HACH 2100Q-is performed best over a series of replicates, compared to the HACH 2100P that showed some minor variation over all four formazin standards. In comparison to the manufacturers' specifications for the two turbidimeters (Table 5.4), the precision or repeatability of instruments, and the accuracy is identical, except for the accuracy of the HACH 2100P being slightly lower than reported by the manufacturer.

Table 5.4 Mean (± standard deviation (SD)) for turbidity measurements determined using the HACH 2100P and HACH 2100Q-is turbidimeters showing within-meter and between-meter coefficient of variations (CV) for a dilution series of four formazin standards.

	HACH 2100P n=15			Hach 2100Q-is n=15			Within-meter CV (%)		
Turbidity (NTU FNU) Class	Mean (±SD)	Accuracy	Precision	Mean (±SD)	Accuracy	Precision	HACH 2100P	HACH 2100Q-is	Between-meter CV (%)
10	10.3 ± 0.2	0.2	0.1	10.1 ± 0.1	0.2	0.1	2%	0%	1%
20	20.4 ± 0.2	0.4	0.2	19.9 ± 0.1	0.4	0.2	1%	0%	1%
100	99.9 ± 0.9	2	1	99.1 ± 0.3	2	1	1%	0%	1%
800	836.3 ± 5.6	17	8	794.2 ± 3.7	16	8	1%	0%	3%

The turbidity values of the samples collected from the Otago rivers, including distilled deionised water (DDW) as an example of particle free water, shows that the variation between the different turbidimeters is less for samples of moderate to high turbidity, and that greater variability between meters is observed for low turbidity samples (Table 5.5), where a large amount of variability exists at the lower turbidity values. The within-meter coefficient of variation suggests a similar pattern, with samples of moderate to high turbidity showing less variation between replicates of the same sample. The HACH 2100P performed worse on the samples of DDW compared to the HACH 2100Q-is, but for the other samples, both meters showed similar within-meter variation.

Table 5.5 Mean (± standard deviation (SD)) turbidity values, and minimum and maximum values for the combined turbidity data from both the HACH 2100P and HACH 2100Q-is turbidimeters for different environmental samples and distilled deionised water (DDW), showing the between-meter and within-meter coefficient of variation (CV).

						Within-meter CV (%)	
Sample	Turbidity Class	Mean Turbidity (± SD) n=150	Min.	Max.	Between-meter CV (%)	HACH 2100P	HACH 2100Q-is
DDW	Low	0.32 (0.2)	0.15	1.06	62%	49%	12%
Glendhu (GH1)	Low	0.44 (0.1)	0.24	0.85	22%	21%	22%
Glendhu (GH2)	Low	0.80 (0.17)	0.53	1.25	21%	12%	15%
Routeburn	Moderate	29.58 (5.4)	20.3	42.4	18%	10%	12%
Deep	Moderate	33.58 (3.7)	27.0	39.20	11%	4%	5%
Lee	High	176.63 (17.9)	140.0	208.0	10%	4%	5%
Taieri [1]	High	246.01 (24.9)	193.0	298.0	10%	6%	6%
Dart [1]	High	262.11 (21.3)	225.0	302.0	8%	3%	4%

[1]Storm flow samples

5.5 Discussion

5.5.1 Turbidity, suspended sediment, particulate organic matter

Given that turbidity is a commonly used surrogate for determining river SSC (e.g., Hughes *et al.,* 2012) it is important to minimise any analytical uncertainty through methods and nephelometric applications. The potential influences of particle characteristics, CDOM, and fine particulates to turbidity measurements are well documented (e.g., Gippel, 1995; Hongve & Akesson, 1998) but are generally not considered in relation to the effects on determining turbidity and SSC relationships. As illustrated in the GH2 case study, there is a significant difference in the regression equations between riverine particulate concentrations and the two turbidimeters. The HACH 2100Q-is with its near infrared light source is less susceptible to organic matter influences on turbidity because light absorbance at these wavelengths is

minimal (Gippel, 1995; Sadar, 1999; Omar & MatJafri, 2009; Davies-Colley *et al.*, 2014), whereas the HACH 2100P uses a wider range of visible wavelength light that is sensitive to the effects of organic matter, causing absorption and a potential negative bias influence on turbidity values (Omar & MatJafri, 2009). The steeper regression slope coefficients between the riverine particulates and turbidity (NTU) is likely a consequence of the disproportionally lower turbidity values, for the same particulate concentrations, compared to the turbidity (FNU) results, supporting the observation that the ISO 7027 method are less influenced by the absorption of light by CDOM. These results are consisted with previous field-based studies where different relationships between the SSC and turbidity in a variety of units have been observed (e.g., Hongve & Akesson, 1998; Barter & Deas, 2003; Lewis *et al.,* 2007; Rymszewicz *et al*., 2017), although hydrological controls and variable sources are also key considerations (Gippel, 1995; Walling, 2005; Hughes *et al.,* 2012). Instrument variability is also a key source of potential uncertainty in monitoring programmes that rely on turbidity, because turbidity values are not transferable between instruments of different manufacture, as evident from the inter-instrument study of Rymszewicz *et al*. (2017). From a monitoring perspective, however, such influences are a commonly overlooked limitation on the use of turbidity as a predictor variable for SS, and must be considered prior to examining patterns of hysteresis or other environmental processes.

5.5.2 Effect of fine particulates on turbidity

The effect of fine particulates that occur at the dissolved-particulate boundary were examined by comparing the turbidity of filtered and unfiltered samples using two methods; filtration through a 0.7µm glass fibre filter, and by applying a settling velocity derivative of Stokes' law. Results from this study showed that fine particulates contributed 1.2 – 7.5% of total turbidity and these were consistent with samples that contained a significant portion of POM. In samples where POM was < 5% of the suspended material, the effect of fine particulates to overall turbidity was <1%. Water (dis)colouration is primarily the result of dissolved CDOM and POM (e.g., humic substances and suspended organic debris) that absorbs blue light from the visible spectrum, shifting the perceived colour of the water to longer wavelengths, giving water a brown, yellow or red colour (Kirk, 1976; Timperley, 1985; Smith *et al.,* 1997; Davies-Colley & Close, 1990; Davies-Colley & Smith, 2001; Pavelich *et al.,* 2002). Such results are consistent with the work of Gippel (1989) who identified that CDOM contributed 20 – 60 % of sample turbidity at base flow, but during

events declined to < 10%. By accounting for the effects of CDOM, Gippel (1989) showed improvement in SSC–turbidity relationships when the turbidity of the filtrate was subtracted from the original turbidity value. Furthermore, Hogve and Akesson (1998) identified the reduction in turbidity values when using methods operating on light wavelengths 400–600 nm, when adding humic acid (a type of CDOM) to samples. Although the contribution of CDOM was not as high in this study relative to previously reported values, the significance of absorption of light by CDOM remains evident through the differences observed between turbidimeters with SSC and POM, and the residue turbidity of filtered samples from organic-rich rivers.

The difference observed between the filtrate and naturally-settled samples is a function of the arbitrary boundary definition between particulate and dissolved load. Filter pore sizes range between studies, where pore sizes between 0.45 µm - 1.5 µm are common. Based off these experimental observations, it is likely that material between the 0.7 – 1.0 µm size remained in suspension, and retained sufficient optical scattering to effect turbidity measurements. Material that comprises the fraction that passed through the 0.7 µm filter includes fluvic and humic acid, which comprise ~50 – 70% of the dissolved fraction, with other chemical compounds (e.g., fatty acids, amino acids, carbohydrates, and hydrocarbons (Hope *et al.,* 1994)). Material >1 µm is arbitrarily defined as the particulate fraction, however, particulate material exists on a continuous scale and the 0.7 – 1.0 µm fraction is likely to comprise of very fine clay-humic-metal complexes (Hope *et al.,* 1994), which are potentially responsible for the residual cloudiness of the naturally-settled samples. Further work is warranted to explore what grain sizes have the greatest light scattering effects, but based on the observations here even fine granular material at the dissolved boundary has the potential to influence turbidity measurement.

5.5.3 Turbidimeter performance

This study showed that two turbidimeters, conforming to two different standard methods, performed well with numerically similar outputs on diverse river waters. Similar results were observed by Barter and Deas (2003) who identified minor variability between five different turbidimeters that all operated on different optical designs. However, the natural water samples collected by this study showed far more variation, particularly for low turbidity values. The precision of the HACH 2100P and HACH2100Q-is were similar for the low

turbidity samples; but the HACH2100P had much higher uncertainties when determining the turbidity of particle-free water (DDW). Particle free water (like DDW) is estimated to have a turbidity of 0.01 – 0.012 NTU, which is a consequence of molecular scatter that occurs as light interacts with water (Sadar, 1999). The average value across both turbidimeters obtained by this study of 0.32 is much higher, and perhaps reflects the impurities that can exist on the surface of the sample cell curvets that may cause additional scattering of light, and a positive bias (Sadar, 1999; Omar & MatJafri, 2009), this may have been a particular issue for the HACH 2100P which has an optical system designed to be more sensitive to low turbidity samples (USGS, 2005). Barter and Deas (2003) also identified variation ranging 6.6 – 44.1% over low to high turbidity samples, with variation between meters generally decreasing with increasing turbidity. The decreasing variation with higher turbidity was observed in the current study, and is likely the result of the turbidimeters optimal performance in the middle range of the 0 – 1,000 NTU and FNU operating range.

5.5.4 Future research and conclusion

The current study has identified that different nephelometric methods do not produce consistent predictive relationships to SSC in natural water samples. In particular, some turbidimeters are much more sensitive to CDOM, particularly in the presence of significant portions of POM. Turbidity in catchments with a high organic matter content do not produce strong predictive relationships to SSC, highlighting that for mixed composition samples, turbidity cannot be reliably used as a predictor for inorganic SSC. The suspended material composition (mineral inorganic material vs. organic material) of stream flow is rarely constant, and changes in response to numerous variations including the availability and transport of sediment and organic material; short-lived exhaustion over hydrographs, as well as connectivity to variable source areas. Therefore, the measurement of turbidity must consider the effects of a mixed composition, with emphasis given to the proportion of organic material being exhumed from the catchment. In catchments where organic matter is a significant component of the suspended load, turbidity may not be an effective indicator of SS, although accounting for some of the effects of dissolved organic substances may be possible by filtering samples, and retrospectively adjusting turbidity measurements. It may also be necessary that alternative indicators are needed to determine the SSC, such as developing rating curves between discharge and SSC, especially in catchments where SS

and POM are controlled by different hydrological processes. In situations where traditional turbidity to SSC relationships are used, it is imperative that the effect of various interferences on turbidity be considered.

6 Response of Nephelometric Turbidity to Hydrodynamic Particle Size of Suspended Fine Sediments

Research article in published by *International Journal of Sediment Research*, 2019[4]. See Appendix 11.2.

6.1 Abstract

Turbidity is used as a surrogate for suspended sediment concentration (SSC), and as a regulatory tool for indicating land use disturbance and environmental protection. Turbidity relationships to suspended material, however, show non-linear responses to particulate organic matter (POM), concomitant with changes in particle size distribution (PSD). In this paper the influence of ultra-fine particulate matter (UFPM) on specific turbidity is shown, and its association with POM in suspended sediments from alpine rivers in the Southern Alps of New Zealand. The approach was two-fold: a field-based investigation of the relationships between SSC, POM, and turbidity sampled during event flow; and experimental work on hydrodynamic particle size effects on SSC, POM, PSD, and turbidity. Specific turbidity changes over event flow and are sensitive to increasing proportional amounts of sand, UFPM and POM in suspension. Furthermore, the UFPM is the size fraction (< 6 μm) where POM increases. The implications are that the slopes of SSC-turbidity relationships are fraught in locations that may be dominated by cyclic release of POM, or distinct pulses of fine-grained material. Locations where the SSC-turbidity slopes approximate 2, POM is usually < 10% of the total suspended load. However, when SSC-turbidity slopes are < 1 this is likely caused by high amounts of side-scatter from UFPM concomitant with higher proportions of POM. Thus, the use of turbidity as a surrogate for determining SSC may have serious consequences to the measurement of representative suspended sediment data, particularly in locations where POM may be a significant contributor to overall suspended load.

[4] Minor changes to the narration of this research article have been made to improve coherency between chapters.
The use of 'proxy' has been replaced with 'surrogate', for where turbidity is described in the use of estimating suspended sediment concentration.
Since submission as a research paper, specific turbidity has been written as K_N and K_F to denotate the unitless nature of the metric, and represents turbidity measured from unit NTU and FNU.

6.2 Introduction

Riverine suspended material is a mixture of mineral and biogenic material that are produced by catchment land disturbance and physical weathering. Understanding the sources and pathways of suspended sediment (SS) is one of the main approaches to determining physical weathering rates in geomorphology (e.g., Milliman & Meade, 1983; Walling & Fang, 2003; Turowski *et al.,* 2010), however, quantifying material in suspension is also an indicator for environmental degradation (e.g., Davies-Colley *et al.,* 2014). Thus, inquiry into suspended material in rivers operates principally in two ways: as a measure of erosion and mass wasting processes, and as an indicator of land disturbance, most often associated with the effects of land cover change (e.g., forest clearance) and ensuring aquatic ecosystem health (e.g., Davies-Colley & Smith, 2001). Quantifying SS is challenging, and standard methods require the collection of discrete grab samples and laboratory analysis; and so, its continuous measurement is laborious. Instead, researchers and environmental managers alike opt to quantify riverine SS using turbidity as a surrogate (e.g., Gippel, 1989; Foster *et al.,* 1992), by establishing ratings between in situ turbidity and suspended sediment concentration (SSC) measurements. However, the physical characteristics of suspended material that is, particle size, shape, colour, density, and refractive index behave differently and produce different optical outputs, which undermine the precision of measured SS to turbidity relationships (Sadar, 1999; Kitchener *et al.,* 2017). Despite the recognition of these different optical properties, nephelometric turbidity persists as a convenient measure in environmental monitoring programmes, as a surrogate indicator of land disturbance and SS.

Suspended particulate load is usually < 2 mm in size, comprised mostly of silt (2 – 63 μm) and clay (< 2 μm) sized material (Owens *et al.,* 2005; Omar & MatJafri, 2009). Of the material in suspension, it is the fine particulate material (< 63 μm) that is the major pollution concern, with fine particulates often produced by forest clearance, agriculture, construction, and mining (Wood & Armitage, 1997; Owens *et al.,* 2005; Gray *et al.,* 2010; Davies-Colley *et al.,* 2014; Hughes *et al.,* 2015). The fine particulate fraction, however, is a mixture of both inorganic (mineral) material (e.g., silt and clay), and colloidal organic matter composed of living organisms, organic waste, and degraded detrital organic material (Aiken, 2014; Slomber *et al.,* 2016). Therefore, homogenous suspended material samples likely never exist in natural environments, rather a range of organic and mineral materials are always present due to terrestrial and fluvial processes, climate, and catchment characteristics (Stone &

Saunderson, 1992; Lewis, 1996; Walling, 2005; Bright & Mager, 2016 (see: Chapter Three); Bright *et al.,* 2018 (see: Chapter Five)). Organic material has different optical properties compared to inorganic material, so optical measures, like turbidity, scatter light differently to organic particles, and introduce substantial uncertainties to the estimation of SSC.

Such uncertainty arises because the degree of scattering caused by suspended particulates is controlled by particle properties size, shape, refractive index and density (Sadar, 1998). When particle properties vary significantly interference with a turbidimeter light source occurs, reflected as a negative or positive bias in the observed turbidity value (Gippel, 1989; Ziegler, 2002). Particles smaller than the wavelength of incident light exhibit a symmetrical scattering pattern with approximately equal amounts of light scattered both forward and backward, whereas larger particles scatter long wavelengths of light more readily (Sadar, 1998; Sadar, 1999; Omar & MatJafri, 2009; Merten *et al.,* 2014). Additionally, particle shape defines the type of scatter, in that the scattering created by plate shaped two-dimensional silicate crystals (i.e., phyllosilicates) are substantially higher than that of spheres of equal volume (Gippel, 1995; Davies-Colley & Smith 2001; Omar & MatJafri, 2009; Davies-Colley *et al.,* 2014). Therefore, when there are extreme variations in the composition of particle properties, precise turbidity measurements are likely impossible (e.g., Foster *et al.,* 1992; Clifford *et al.,* 1995).

The objective of this paper is twofold: firstly, to examine the importance and contribution of fine particulates (6 – 63 μm) and ultra-fine particulates (< 6 μm) on turbidity and the effect these have on turbidity measurements derived from different nephelometric methods (EPA 180.1 and ISO 7027). Secondly, the study evaluates whether different size classes produce higher effective turbidity rating equations by examining specific turbidity over different particle size classes. Such work is needed to establish the effect of particle size and other interferences (e.g., organic material) on optical water quality and SS, which is acknowledged but rarely explained. Two approaches were employed; firstly, quantifying specific turbidity response over a hydrograph as a measure of natural changes in suspended load optical properties; and secondly, a laboratory-based settling experiment to examine specific particle size class effects on SSC-turbidity relationships. Actual riverine-derived SS collected under storm flow conditions were used in settling tube experiments, in contrast to previous studies that used deposited sediments (e.g., Gippel, 1995; Merten *et al.,* 2014), and followed a procedure similar to that of Foster *et al.* (1992) and Holliday *et al.* (2003).

6.3 Method and Materials

6.3.1 Field site

The Southern Alps / Kā Tiritiri o te Moana are a rapidly uplifting mountain range in Aotearoa New Zealand that have some of the highest suspended sediment yields recorded globally (Hicks *et al.,* 2011). These alpine catchments have a high instance of stochastic slope failures, which enhance the erosion potential of mineral-rich (inorganic) material. The lithology and metamorphism grade vary along the mountain range, but are principally composed of quartzo-feldspathic sandstone (greywacke), semi-schist, and schist of Permian to Triassic age (TZIII or TZIV) (Rattenbury *et al.,* 2010; Edbrooke *et al.,* 2014) (Table 6.1). All catchments in this region have been conditioned by past glaciation, but depositional glacial landforms are rare having been overprinted by mass movement and evacuation by subsequent fluvial processes.

Data were collected from five headwater catchments (Dart/Te Awa Whakatipu, Rees/Pua Hiri, Shotover/Kimi-ākau, Ahuriri, and Haast/Awarua) in the southern portion of the Southern Alps, of New Zealand (Figure 6.1). The Dart/Te Awa Whakatipu, Rees/Pua Hiri, and Haast/Awarua catchments have small hanging alpine glaciers in their headwaters, which are a potential source of fine particulates. Additionally, fine sediment from the Te Horo landslip (reactivated December 2013) surges sediment into the Dart/Te Awa Whakatipu during heavy rain events (Cox *et al.,* 2014). The Rees/Pua Hiri River sediments are also derived from slope failures, and pulses of sediment associated with creeping landslides (Cook *et al.,* 2014). The Shotover/Kimi-ākau is underlain by highly fissile, fine-grained schists, which are easily eroded (Hicks, 1999; McSaveney & Glassey, 2002); 40% of its suspended load is likely from slope erosion attributable to high incidence of slow-creeping landslides (Crozier, 2010).

Table 6.1 Catchment characteristics. Mean annual discharge (Q) in $m^3 s^{-1}$, mean annual area-weighted rainfall (P) in mm a^{-1} from modelled data (see: Tait et al., 2006). Suspended sediment yield (SSY) is from rated and modelled studies and reported in t $km^{-2} a^{-1}$.

River	Area (km^2)	Stream Order	*Q*	P	SSY	Main Lithology	Land cover
Dart/Te Awa Whakatipu	586	5	52	4,065	2,278[2]	Rakaia terrane schist (41%), Caples terrane semi-schist (39%), Quaternary sediments (10%). Caples terrane unfoliated (9%). Te Horo Slip	Indigenous forest (30%), tussock (24%), herb field (16%), bare ground (16%), snow and ice (8.9%). Main glaciers: Dart (7 km^2), Whitbourn (4 km^2), Hesse-Marshall (3 km^2), Curzon-Hamilton (3 km^2).
Rees/Pua Hiri	285	5	26[1]	2,488	1,158[2]	Rakaia terrane schist of Aspiring lithologic association (60%), Caples terrane semi-schist (21%), Caples terrane schist (14%), Quaternary sediments (5%).	Tussock (57%) with indigenous forest (10%), herb field, and indigenous scrub; 20% bare ground or alluvium, snow and ice (3%). Main glaciers: Grant (2 km^2), Jura (1 km^2).
Shotover / Kimi-ākau	1,099	6	40	2,018	1,019[3] 1,186[2]	Rakaia terrane schist of Aspiring lithologic association (90%), quaternary sediments (6%).	Tussock (72%) with pockets of herb field and indigenous forest. Bare ground/alluvium (8%), snow and ice (<1%). No glaciers.
Ahuriri	1,284	7	24	1162	98[3] 113[2]	Rakaia terrane semi-schist (40%), unfoliated (28%), Quaternary sediments (29%).	Tussock (65%) with scrub (4.7%), herb fields (5.2%) and forest (2.8%). Bare ground/alluvium (9.7%), snow and ice (<1%). No glaciers.
Haast/Awarua	1,063	6	191	7617	4,072[4] 4,285[2]	Rakaia terrane schist (63%), Rakaia terrane semi-schist (31%), Quaternary sediments (5%)	Forest cover (49%) with tussock (20.8%), herb fields (10%), and scrub (4%). Bare ground/alluvium (12.6%), snow and ice (4%, of which 90% are in the Landsborough tributary). Main glaciers: Dechen (5 km^2), Strachan (4 km^2), Hooker (4 km^2), McCullaugh (3 km^2), Brewster (3 km^2).

1 Rees/Pua Hiri is not gauged, this is an estimated mean annual flow.
2 Modelled suspended sediment yield from SSY estimator of Hicks et al. (2011)
3 Estimated suspended sediment yields from flow rating by Griffiths (1981)
4 Measured suspended sediment yields reported by Hicks et al. (2011)

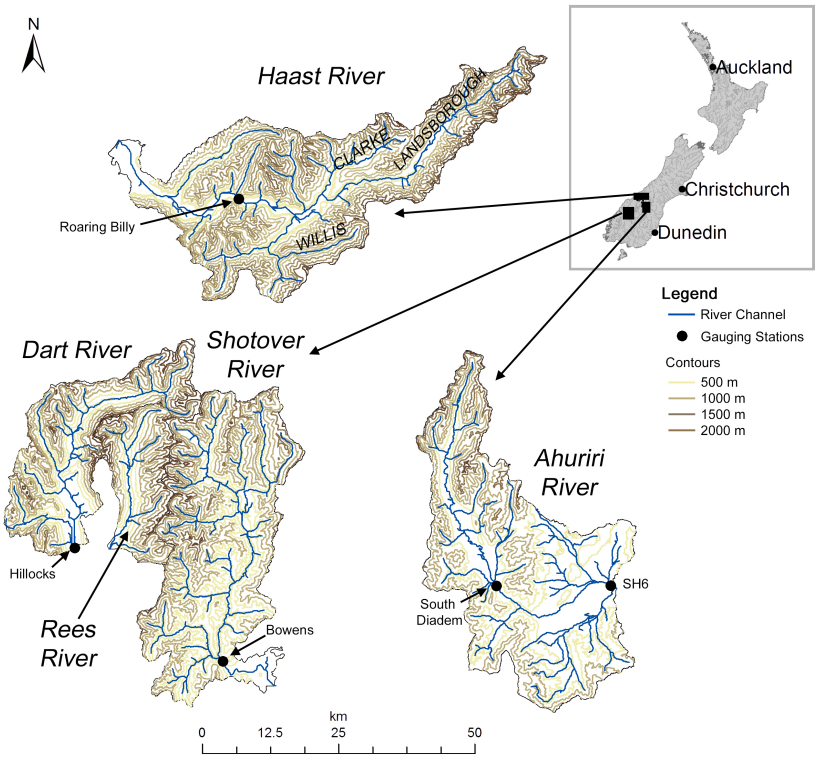

Figure 6.1 Location map for the Dart/Te Awa Whakatipu, Shotover/Kimi-ākau and Rees/Pua Hiri and the Haast/Awarua rivers.

6.3.2 Sediment collection and particle size analysis

A Sigma 900 automatic water sampler collected 0.5 L samples at 1-hourly intervals over three rainfall events: Ahuriri (Sep 2018 and March 2019) and Haast/Awarua (Feb 2019). Sample collection began prior to the onset of rainfall and sampled the ascending and descending limbs of the hydrograph. Samples were analysed for SSC, particulate organic matter (POM), and turbidity in units of NTU and FNU. Turbidity was determined using a HACH 2100P (method EPA 180.1) and HACH 2100Q-is (method ISO 7027) and reported in units of nephelometric turbidity units (NTU) and formazin nephelometric units (FNU), respectively, with an uncertainty of 1% (see: Chapter Five, Bright *et al.,* 2018). These two nephelometric turbidimeters were selected as the different operating light sources provides opportunity for turbidimeter comparison, and referred to herein as turbidity (NTU) and turbidity (FNU). SSCs were determined using standard filtration methods (see: ATSM, 2002) using prewashed and dried 0.7 µm glass fibre filters, dried at 105ºC, and weighed 3 times or until filter weights converged. POM was determined using a loss on ignition method where the glass fibre filters were furnaced at 500ºC for 30 minutes (see: Grove & Bilotta, 2014). All filter papers were weighed on a 4-point decimal balance, for a method

detection limit of 0.3 mg L^{-1} that represents the propagation of error through the consecutive weighing processes, due to the analytical errors associated with the precision of the balance.

Bulk suspended sediment was collected from five rivers during the ascending limb of a hydrograph prior to peak flow, when peak suspended sediment was expected to occur. Material in suspension was left to settle for a minimum of 5 days, apropos to the amount of time required for a 1 μm spherical quartz particle to settle in standing water (see: Chapter Five, Bright *et al.,* 2018). All collected sediment was dried at 40ºC, and a subset retained in river water. Particle size distribution (PSD) was measured using laser diffraction on a Malvern Panalytical Mastersizer 2000 and uptaken using a wet dispersion unit (Hydro2000) (see: Callesen *et al.,* 2018). PSDs were calculated from dried bulk SS, and wet suspensions held within the original river water. Analysis of the PSD were run in triplicate and reported as an average. There were no significant shifts in distribution or percentage of ultra-fine particulate matter (UFPM) between wet and dry samples. Comparisons of the cumulative frequency plots of the PSD of samples analysed with and without deflocculant showed no significant differences in overall PSD (as wt %), with a root mean square error <0.1.

A settling tube experiment was implemented to sub-sample fine particulates of uniform hydrodynamic sizes. Each bulk SS sample dose was poured into a 1 L plastic tube filled with distilled and deionised water. Sediment samples were not pre-treated as flocculation was not observed during particle size analysis, as samples comprised of < 1% organic matter. To extract sub-samples of specific size intervals, Stokes' Law (see: Ferguson & Church, 2004) was used to calculate the water depth and time needed to pipette a 20 mL sub-sample for each phi size (ϕ) (where $\phi = \log_2$ mm) from 4.0 ϕ (63 μm) to 10.0 ϕ (1 μm) in 0.5 ϕ intervals. Sub-samples were analysed to determine turbidity (NTU and FNU), SSC (in mg L^{-1}), and POM (in mg L^{-1}) and as a % of total suspended material (POM%), and specific turbidity (*K*) that the ratio of turbidity (measured as NTU and FNU) to SSC, and therefore denoted as K_N and K_F for specific turbidity measured from NTU and FNU respectively (see: Gippel *et al.,* 2015).

The dosage weight of sediment initially selected for the first experiment (15 – 20 g) was based on two requirements; firstly, a weight per volume of water that would return a SSC above the detection limit of the suspended sediment filtration method (0.3 mg L^{-1}), and a weight per volume of water that would produce a turbidity value within the operating range

of the turbidimeters and limit the number of dilutions, with dilutions required at > 1,000 NTU or FNU. The experiment was run five times at different dosage rates. The sand portion of the samples were not removed prior to the settling experiment to retain the natural PSD of the samples.

6.4 Results

6.4.1 General characteristics of event flow suspended sediment

Fine particulate matter (FPM, < 63 µm) comprised a minimum 75% of the PSD of the bulk suspended sediment collected during storm events (Figure 6.2). The proportion of sand transported during discrete events varied between catchment samples and ranged from 7 – 25%. The 10th percentile size fraction (D_{10}) is a measure of the size profile of the smallest 10% of particles; which ranged from 3 – 6 µm and suggests that UFPM constitute ~ 10% of the suspended load. Median particle sizes (D_{50}) varied from 13 – 29 µm (Table 6.2). However, assuming the fixed density of quartz at 2.7 g cm^{-3} for sediment volume, the mean particle size as the mass moment (De Brouckere mean, $D_{[4,3]}$) ranged from 25 – 56 µm and was larger than the D_{50}, due to volumetric skewness of the PSD coarse (sand) tail.

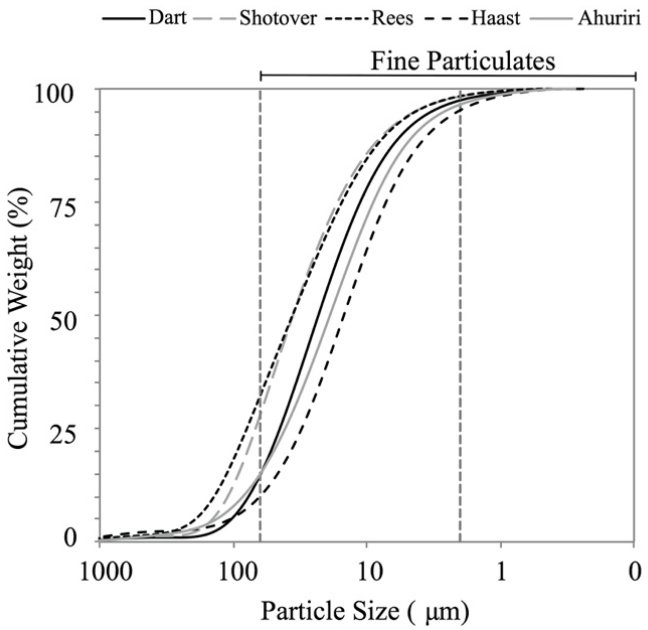

Figure 6.2 Cumulative particle size distribution for bulk suspended sediment samples collected from five New Zealand alpine rivers. Fine particulates (< 63 µm) comprised of at least 70% of the cumulative weight of suspended sediment, although the proportion of sand in suspension was highly variable between rivers (10–30%).

Table 6.2 Particle size distribution of bulk suspended sediment samples during storm events as determined by laser diffraction particle size analysis.

River	Sand (wt %)	Silt (wt %)	Clay (wt %)	D_{10}	D_{50}	D_{90}	$D_{[4,3]}$	$D_{[3,2]}$
Ahuriri [Sep-18]	13.3	76.8	10.0	3.8	16.5	73.9	38.1	7.8
Ahuriri [Mar-19]	14.3	76.9	8.8	4.3	19.8	78.2	42.1	8.4
Dart/Te Awa Whakatipu	12.4	80.2	7.4	4.7	20.1	67.1	36.2	9.4
Haast/Awarua (Feb-19)	7.4	78.9	13.7	3.0	12.7	50.2	25.5	6.3
Rees/Pua Hiri	24.4	70.6	5.0	6.2	28.9	103.5	55.7	12.9
Shotover/Kimi-ākau	11.6	81.7	6.7	5.2	22.5	64.3	42.4	10.4

6.4.2 Specific turbidity across hydrodynamic particle size classes

To test the efficiency of the two turbidimeters, the bulk SS collected during three event flows from the Dart/Te Awa Whakatipu, Rees/ Pua Hiri, and Shotover/ Kimi-ākau rivers was used in settling tube experiments. The data from all settling tube experiments for all suspension size classes were pooled, and the linear relationships compared. Both turbidimeters demonstrated a strong linear response ($r^2 > 0.6$ linear relationship) between SSC and turbidity (NTU and FNU) for the SS suspensions across the five different grain size categories (coarse silt to clay; 2 – 63 μm) (Table 6.3). The presence of fine particulates reduced the slope coefficient of the linear relationship for both turbidimeters (Table 6.3; Figure 6.3). The SSC-turbidity (as NTU and FNU) response for coarse silt (31 – 63 μm) and clay (< 3.9 μm) shows that turbidity as NTU and FNU behave similarly within particle size classes (Figure 6.3). However, there is a difference in SSC-turbidity (as NTU and FNU) slope coefficients for different particle size classes, where larger particle sizes produce greater SSC-turbidity coefficients.

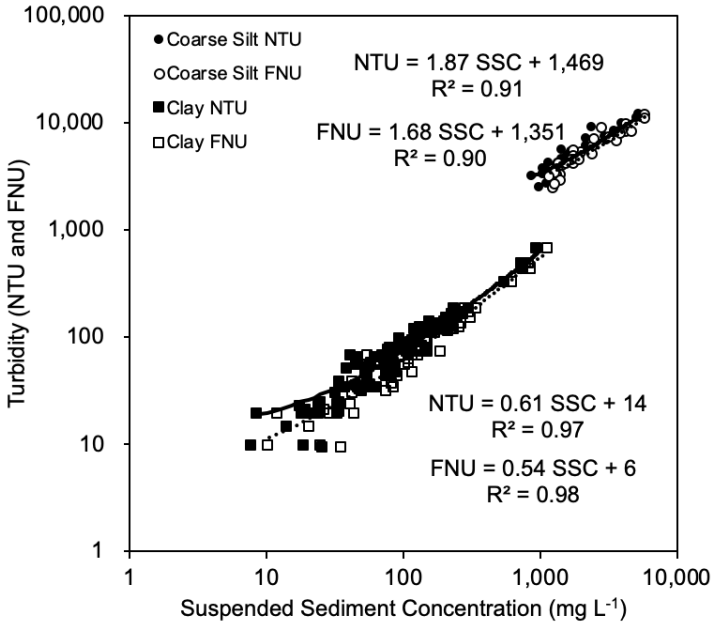

Figure 6.3 Suspended sediment concentration and turbidity relationships for coarse silts, and clay size particles derived from bulk suspended sediments collected from three alpine headwater catchments in southern New Zealand. Turbidity is reported in units of NTU and FNU.

The sensitivity of the two turbidimeters was calculated following the method of Merten *et al.* (2014) and calculated as the ratio of turbidity to the SSC. This ratio is more commonly referred to as specific turbidity (*K*), so that the greater *K*, the more sensitive the turbidity sensor is to changes in sediment concentration (Merten *et al.,* 2014). Specific turbidity is inversely proportional to the regression slope coefficient of an SSC–turbidity plot, when the slope coefficient is linear and passes through the origin. Thus, changes in the specific turbidity likely reflect differences in particle size, mineralogy, or composition of the suspended material indicating a change in sediment properties (e.g., Wass & Leeks, 1999). Both turbidimeters showed increasing sensitivity as grain size decreased, (i.e., an increase in K_N and K_F as grain size decreased) although across all grain size categories the HACH2100Q-is turbidimeter generally had a greater sensitivity to changes in SSC. The standard deviations for turbidity (as NTU and FNU) were calculated for both turbidimeters (Table 6.3) and highlights the heterogeneous nature of the sediment used. Therefore, some variation in sensitivity for the HACH2100P and HACH 2100Q-is is likely due to remaining variation of the PSD after sorting in the settling tube and shape within each particle size class sampled; or water colour which is relevant for the HACH2100P turbidimeter. The standard

deviation was greatest for larger particle size classes which comprise of a wider band of particle sizes because phi classes are a $\log_2$ scale within each class (see: Table 6.3), highlighting the compounding effect caused by non-homogenous samples.

Table 6.3 Suspended sediment-turbidity relationship for bulk suspended sediment subsamples determined for discrete hydrodynamic grain size classes using two different turbidimeters. The sensitivity (Specific Turbidity as K_N and K_F, for turbidity in NTU and FNU units respectively) is the ratio of turbidity to suspended sediment concertation (SSC), which is the inverse of the regression slope coefficient (β). Each class statistic is derived from 30 measurements, apart from clay, which has 75 measurements. The goodness of fit coefficient (r^2) is derived from the linear regression analysis of turbidity and SSC.

		Grain Size Class				
Sensor	Statistic	Coarse Silt	Medium Silt	Fine Silt	Very Fine Silt	Clay
HACH2100P	r^2	0.81	0.88	0.95	0.98	0.96
	β	2.38	1.85	1.28	0.86	0.65
	Specific Turbidity (K_N)	0.38	0.52	0.77	1.09	1.31
	Std Dev[1]	23.6	17.5	20.8	15.5	5.33
HACH2100Q-is	r^2	0.83	0.90	0.95	0.97	0.96
	β	2.17	1.7	1.19	0.80	0.59
	Specific Turbidity (K_F)	0.43	0.58	0.86	1.25	1.64
	Std Dev[1]	17.4	16.6	16.0	11.5	5.1

[1]Average standard deviation for each size class as determined as the variation over 5 replicate turbidity measurements per sample.

6.4.3 Composition effects on SSC – turbidity

Particle size affected K_N and K_F across the fine particle classes (6 – 63 μm), so that K_N and K_F were inversely correlated with particle size and maintained a relatively consistent linear relationship to particle size (μm). The response of K_N and K_F to particle size does, however, became unstable at the UFPM boundary (< 6 μm, 7.5 ϕ) (Figure 6.4). The UFPM boundary also corresponded to a notable increase in the POM% as particle size decreased. POM% was highest in the UFPM particle sizes (equivalent to fine silt and clay) and lowest for coarse silt (Table 6.4). This suggests that the high K that occurs at the smaller particle grain size classes may not be solely an increase in turbidimeter sensitivity to small-grain particles but also a response to increasing amounts of organic particulates, which likely have asymmetrical shapes and different optical properties. The amount of POM% that occurs in a sample was variable, and clearly depended on catchment characteristics, for example, the Dart/Te Awa Whakatipu had a lower POM content in the UFPM classes (10.7%) compared to the Rees/Pua Hiri and Shotover/Kimi-ākau (17%) (Table 6.4).

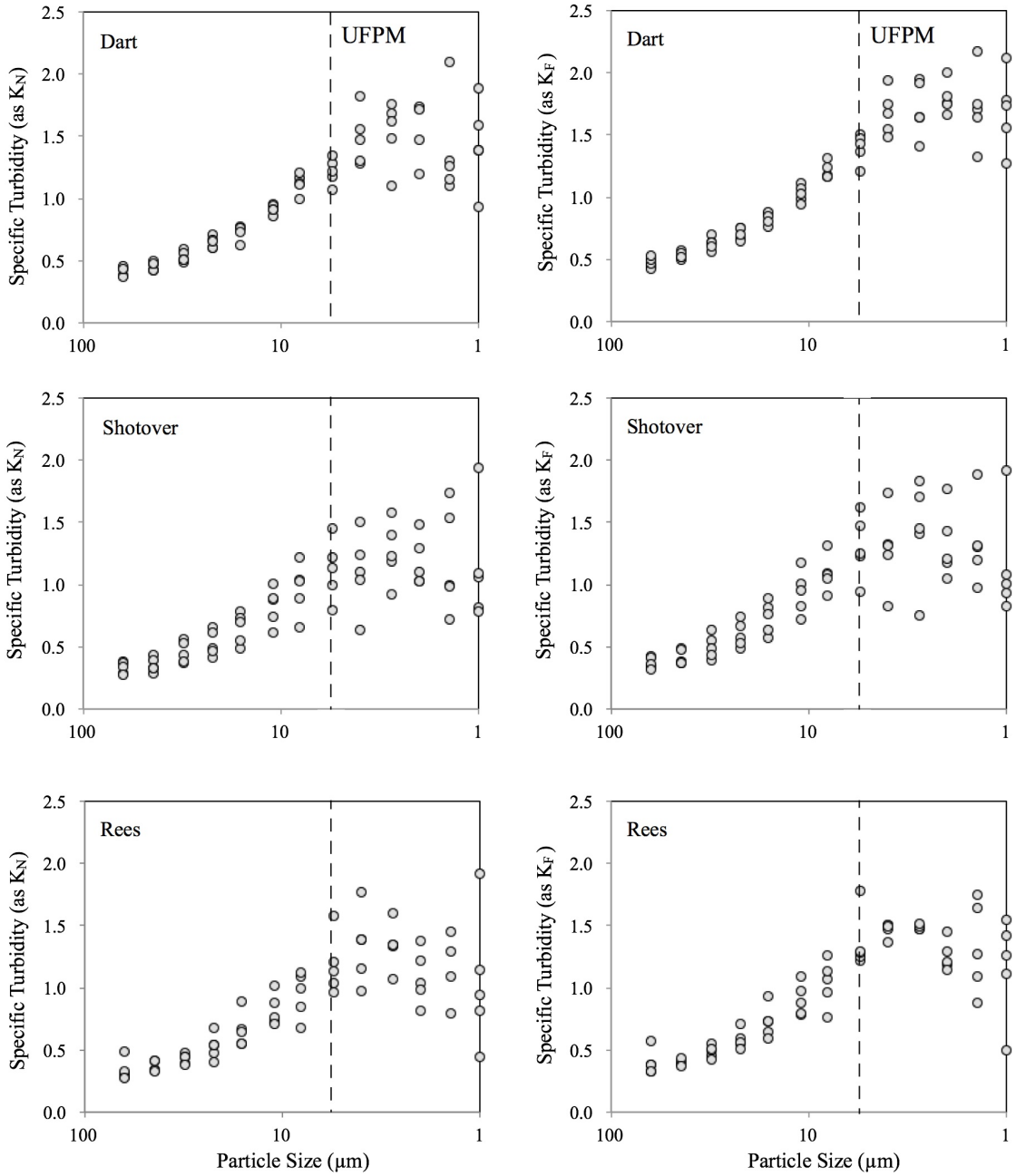

Figure 6.4 Specific turbidity (as K_N and K_F) follows a linear increasing trend with decreasing particle size, showing that the relationship between turbidity and suspended sediment when measured in either NTU or FNU is mostly linear for fine particulate matter (FPM). However, when particle size is < 6 µm (ultra-fine particulate matter, UFPM) there is no systematic relationship between turbidity and suspended sediment (as expressed as specific turbidity).

Table 6.4 Particulate organic matter (POM) as a percentage of total suspended material (i.e., POM%) for hydrodynamic particle size classes, Phi and µm, for three alpine rivers in southern New Zealand, and the division of fine particulate material (FPM, 6 – 63 µm) from ultra-fine particulate material (UFPM, <6µm).

Inorganic Size Class			POM (%)			
Size Class	Phi	µm	Dart/Te Awa Whakatipu	Rees/ Pua Hiri	Shotover/ Kimi-ākau	
Coarse silt	4	31.3–62.5	0.7	1.9	1.6	FPM
Medium silt	5	15.6–31.3	0.7	1.0	1.9	
Fine Silt	6	7.8–15.6	0.7	1.2	3.0	
Very Fine Silt	7	3.9–7.8	1.9	4.6	7.9	
Clay	> 8	< 3.9	10.9	17.8	17.0	UFPM

6.4.4 Specific turbidity during event flow

Turbidity and suspended sediment were measured over three hydrographic events. Two events from the Ahuriri River in September 2018 (peak Q = 52.6 m^3 s^{-1}; median annual Q = 18.7 m^3 s^{-1}) and March 2019 (peak Q = 49.9 m^3 s^{-1}); and one event from the Haast/Awarua River in February 2019 (peak Q = 788 m^3 s^{-1}; median annual Q = 126 m^3 s^{-1}) (Figure 5). These catchments are of similar catchment size (~1,000 km^2) but have distinctly different hydroclimatology and vegetation cover (Table 6.1).

POM as a percentage of total suspended material (POM%) was high under baseflow conditions, suggesting that organic material is diluted during storm flows (Figure 6.5d). During both Ahuriri events specific turbidity (as K_N and K_F) was highly variable prior to the onset of hydrographic response and concomitant with the trend in POM%, where it decreased initially on the ascending limb, and then increased with a slight decrease after peak discharge (Figure 6.5d). For both events there was no difference in antecedent conditions or the scale of the rain event (upper 5th percentile of daily flow); event 1 had 27.5 mm of rain (max intensity of 4.5 mm h^{-1}) and event 2 had 21.5 mm of rain (max intensity of 7.5 mm h^{-1}). Although the SSC, POM and K_N and K_F responded concordantly between events, the two events had a notably different SSC (event 1 maximum 193 SSC mg L^{-1}; event 2 maximum 618 SSC mg L^{-1}) (Figure 6.5b). The sediment sources between these two events was likely similar, given the consistent pattern in hysteretic relationships in SSC, POM, and K_N and K_F; and the difference in SSC was likely a function of differences in rainfall intensity. Similarly, in the Haast/Awarua River, POM% was higher under baseflow, being diluted during higher flow (Figure 6.5d). K_N and K_F initially dipped before increasing as peak

discharge occurs (Figure 6.5c), a trend observed with both peaks in discharge during the event, suggesting a link between event intensity and the mobilisation of factors controlling specific turbidity. However, by comparison the peak in SSC occurred after peak discharge in the Haast/Awarua catchment suggesting a delay in the delivery of sediment likely due to scale of the catchment and order of sub-catchments.

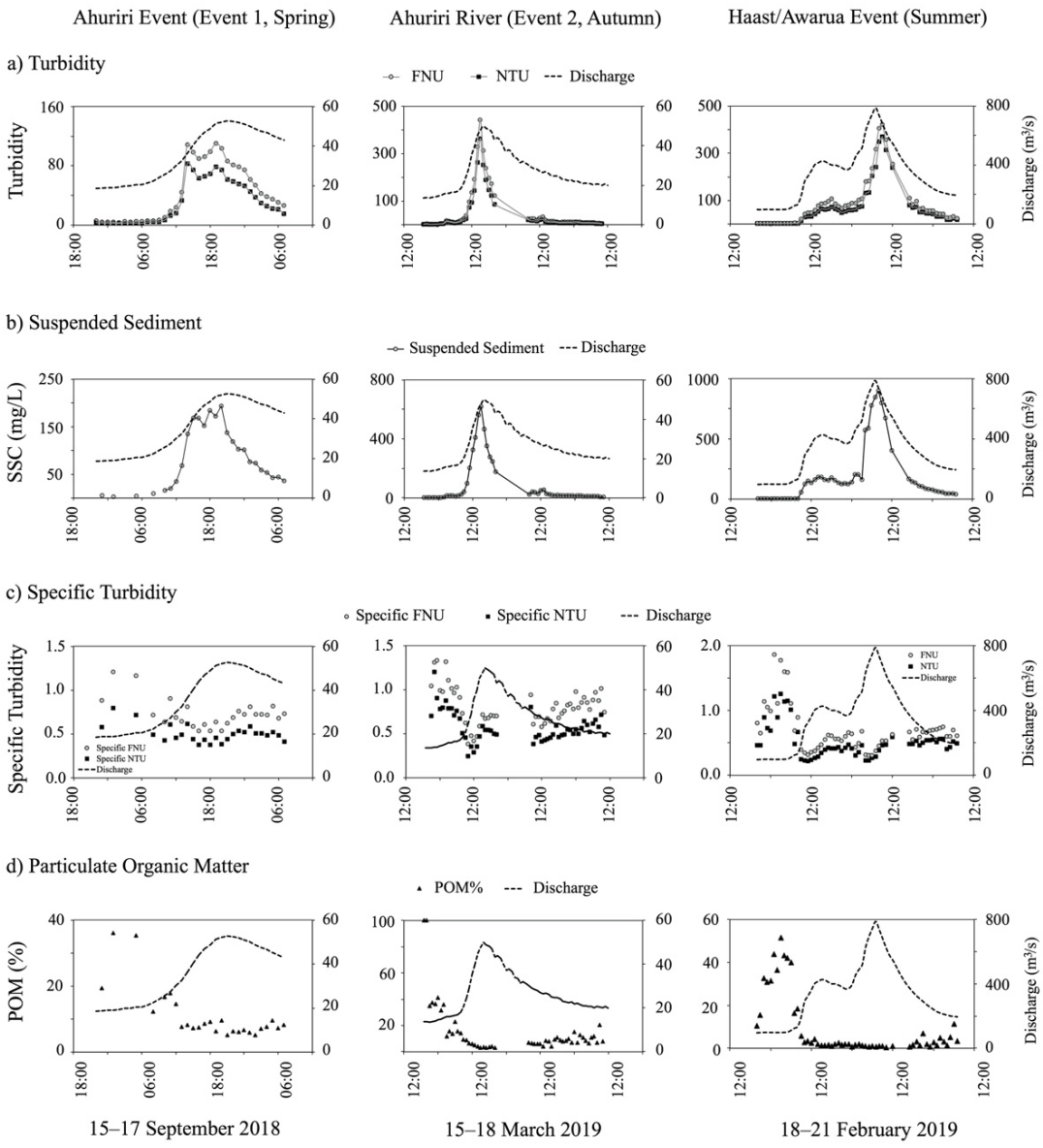

Figure 6.5 Plots of a) turbidity, b) suspended sediment, c) specific turbidity (as K_N and K_F), and d) particulate organic matter (POM) as a percentage of total suspended sediment for hydrographic events (September 2018 and March 2019) in the Ahuriri Catchment, and Haast/Awarua (February 2019) and the relation of these trends to discharge showing distinct hydrographic response of all variables.

The events observed in the Ahuriri exhibited typical clockwise hysteretic responses of SSC, POM%, and turbidity, and a clockwise-anticlockwise response for specific turbidity (as K_N) (Figure 6.6). The clockwise hysteresis suggests a ready supply of near-field material, either the mobilisation of in-channel sediment, or near-field supply of inorganic material; both of which are in plentiful supply within the multithreaded channel. Inorganic sediment is readily supplied from the highly erodible semi-schist lithology in the upland catchment, and remobilisation of Quaternary till and alluvium through the main stem; whereas organic material is plentiful within the river bed through the systemic incursion of invasive plant species Russell Lupin (*Lupinus polyphyllus*) and crack willow (*Salix fragilis*) onto the flood plain (Caruso *et al.,* 2013). An initial clockwise direction in K_N increased with discharge suggesting a change in sediment source or composition of the suspended flux with the onset of event flow. During the event, however, hysteresis direction switched to an anticlockwise loop, likely indicating temporary sediment exhaustion (Figure 6.6). By comparison, an anticlockwise hysteretic response was observed in the Haast/Awarua River for SSC and turbidity, and clockwise with an anticlockwise loop for POM% and K_N (Figure 6.6). The width of the Haast/Awarua turbidity hysteresis loop was wider than for SSC, suggesting turbidity was responding to more than sediment alone, unlike in the Ahuriri hysteresis where the loops appear similar. Specific turbidity hysteresis followed a clockwise–anticlockwise behaviour, as did POM%, suggesting that specific turbidity may be sensitive to POM concentration in the Haast/Awarua catchment. Lastly, the timing and phasing of SSC delivery in the Haast/Awarua displayed anticlockwise hysteresis (i.e., SSC peaks after peak discharge), likely due to the delay of sediment delivery down the Landsborough tributary, which is the main source of inorganic sediment in the Haast/Awarua catchment.

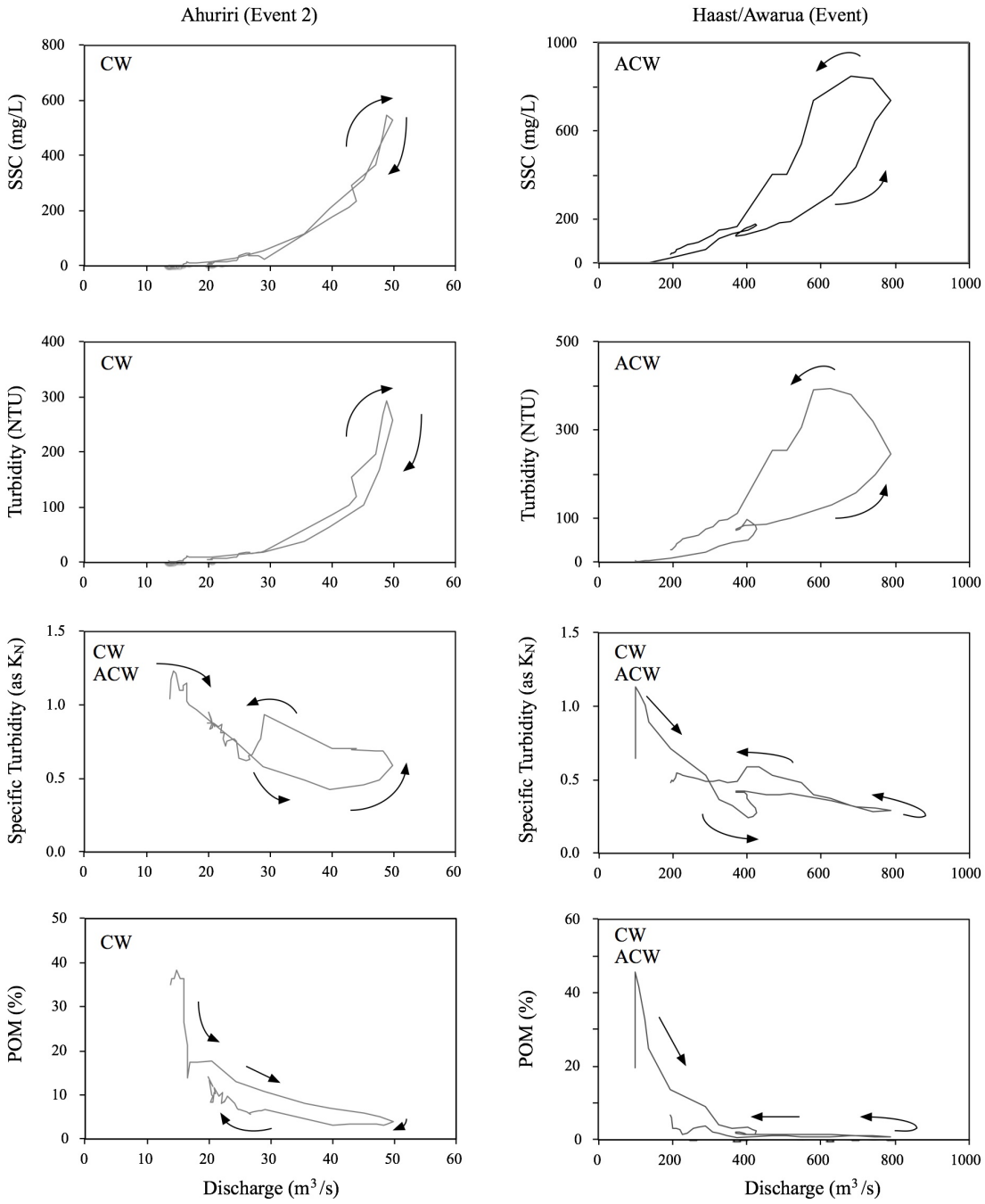

Figure 6.6 Hysteric response of suspended sediment concentration (SSC), turbidity (in NTU), specific turbidity (as K_N) and particulate organic matter (POM) as a percentage of total suspended material for an event in the Ahuriri in March 2019 (Ahuriri Event 2) and the Haast/Awarua in February 2019. Distinct hysteric response of the variables is clear with clockwise (CW) and anti-clockwise (ACW) behaviour representing changes in the parameters relative to discharge during hydrographic response.

6.5 Discussion

6.5.1 Specific turbidity during event flow

Specific turbidity is responsive to the heterogeneous nature of riverine suspended particulate load, which is a complex mixture of inorganic mineral and organic material with a distinct PSD and composition. The observed variability in specific turbidity over hydrographs illustrates the temporal-scale changes that occur between sediment concentration and turbidity, giving rise to specific turbidity values that differ between pre-event flow, and ascending and descending limbs. As demonstrated by the Ahuriri and Haast/Awarua event flows, an initial decrease in specific turbidity occurs on the rising limb suggesting that less efficient light attenuating material (e.g., sand) is entrained as flow increases and the entrainment threshold for coarser material is reached (Hughes *et al.,* 2015). Specific turbidity increases as discharge falls due to increased presence of fine particulates (or light absorbing organic material) that dominates flow as sand settles out of suspension (Lewis, 1996; Hatten *et al.,* 2012; Koiter *et al.,* 2015). The response to discharge underscores the temporal variability in suspended material and hydrographic response, and that particle size and composition have an acute influence on turbidity (Foster, 1992; Lewis, 1996; Jastram *et al.,* 2010; Navratil *et al.,* 2011). Therefore, the assumption that the PSD and composition remains stable at a specific location over time, or through the hydrograph, is not valid and is rarely explained in relation to SSC–turbidity behaviour (e.g., Gippel, 1995; Lewis, 1996; Wass & Leeks, 1999; Landers & Strum, 2013).

6.5.2 Specific turbidity response to particle size

The observed linear relationship between specific turbidity and particle size has been reported by previous studies (e.g., Foster *et al.,* 1992; Lewis, 1996; Wass & Leeks, 1999), although is rarely explained. It is hypothesised here that the linear effect of particle size on specific turbidity observed with both turbidity as NTU and FNU (i.e., K_N and K_F) is a function of the general principles of light scattering. For example, spherical particles of fine sand to clay (0.2 – 765 μm) produce a light attenuation effect consistent with regular scatter at 90° ±30° to the incident light source of a turbidimeter operating to a nephelometric method; at a wavelength (λ) 400 – 600 nm for EPA 180.1 method and λ 860 nm for method ISO 7027. Regular light scatter is produced by particles where the particle diameter is ten times greater than the incident λ source, when there is little difference in the x, y, z axial

length of particles (Kitchener *et al.,* 2017); and as such there will be a predictable relationship between specific turbidity and particle size. The results of the current study support this for the FPM range (63 – 6 µm), as observed for particles of medium-sized silts and larger, the response of specific turbidity to particle size was linear and reiterates the observation that particle size is a significant controlling variable that explains much of the variation in turbidity (NTU and FNU) across the FPM.

However, in this study also observed is a notable change in the relationship between K_N and K_F and particle size at the UFPM boundary, that is no longer linear for particles < 6 µm. It is proposed that for hydrodynamically-derived particle classes smaller than 6 µm, particle size is not the only factor that influences turbidity across the UFPM range. At these particle size classes (< 6 µm), the smaller particles scatter light irregularly and in all directions (Sadar, 1999; Omar & MatJafri, 2009; Merten *et al.,* 2014). Therefore, at the UFPM boundary the particle sizes that are < 6µm approach the boundary where particle diameter (D) is less than ten times the source λ, and therefore regular side scattering at 90° (± 30°) to the incident light source likely no longer describes the interaction between the light source and particle size. This, combined with the effects of irregular sized or shaped organic matter that occurs in the samples collected, increases the potential for multiple-scattering and forward-scattering light trajectories that are not at 90° to the incident source. For EPA Method 180.1 (λ 400–600 nm) particle D becomes > 10λ for particles between 4–6 µm, right at the boundary defined here as the UFPM. In comparison, for the ISO Method 7027 (λ 860 nm) particle D becomes > 10λ at 8 µm. Thus, as particle size decreases more irregular scatter occurs, at 4 – 6 µm for method EPA 180.1 and at 8 µm for ISO 7027; irregular scatter results in a higher specific turbidity and commensurate increase in sensitivity to small particles.

It should be noted, however, that K_N and K_F are not only a function of particle size but also particle shape (Gippel, 1989; Gray & Gartner, 2009; Omar & MatJafri, 2009). For instance, clay minerals (< 2 µm) are typically plate-shaped and scatter light more intensely than spheres of equal volume (Sadar, 1998; Davies-Colley & Smith 2001; Davies-Colley *et al.,* 2014). When the x-axis of the particle is much greater than y and z axis, the effect is for greater amounts of forward-scattering (Kitchener *et al.,* 2017), resulting in a different turbidity relative to incident volume of particles. It is this multiple light scattering effect that likely explains the change in specific turbidity for UFPM for both K_N and K_F.

6.5.3 Influence of composition on specific turbidity

The organic content of the suspended material of samples collected by present study (e.g., Table 6.4) increases as particle size decreases, commensurate with specific turbidity (as K_N and K_F) confirming that this organic material is strongly associated with the UFPM. Thus, different organic-to-inorganic composition affects specific turbidity, and contributes to the non-linearity across the UFPM fraction. The method used here did not explicitly measure the size of organic material, so the organic particles may be of variable shape and size based on the chosen inorganic particle size classes. These organic fragments will remain in suspension with fine (inorganic) material due to their density differences, and therefore behave like UFPM. The effect of organic matter on specific turbidity was not evident for the FPM sized material (i.e., 6 – 63 μm). POM interacts with light differently due to a lower refractive index relative to water meaning peak light attenuation occurs at larger particle sizes (Davies-Colley & Smith, 2001), and therefore the optical signal for a mixed composition sample is different to that of a homogenous sample of mineral material (e.g., Foster *et al.,* 1992; Gippel, 1995; Sadar, 1998; Ziegler, 2002; Lewis *et al.,* 2007; Gray & Gartner, 2009; Merten *et al.,* 2014). Natural waters have a diverse range of organic materials that can be associated with the mineral phase, and therefore the association of organic matter with inorganic colloids is inevitable (Wilkinson *et al.,* 1999; Owens *et al.,* 2005; Grabowski *et al.,* 2011). The UFPM size fraction (< 6 μm) traverses the particulate colloidal barrier (e.g., Aiken*,* 2014), so that organic matter in the UFPM likely includes organic coatings or mineral-organic colloids. The particulate size boundary selected by the method is constrained by the glass fibre filter pore dimension (0.7 μm) so most of the organic matter collected in the UFPM fraction is organic matter from clay–humic complexes, colloidal material or bacteria (Hope *et al.,* 1994; Wilkinson & Lead, 2007; Aiken, 2014).

The influence of POM on specific turbidity was most notable in the event flow analysis. During event flows of the Ahuriri and Haast/Awarua rivers, POM as a percentage of the total suspended material increased linearly with specific turbidity (as K_N) for samples with >10% POM. The effect of increasing amounts of POM in suspension was a doubling or tripling of specific turbidity (Figure 6.7). Thus, over any given event, the specific turbidity is unlikely to be constant, as it responds to changes in PSD as well as delivery of organic matter.

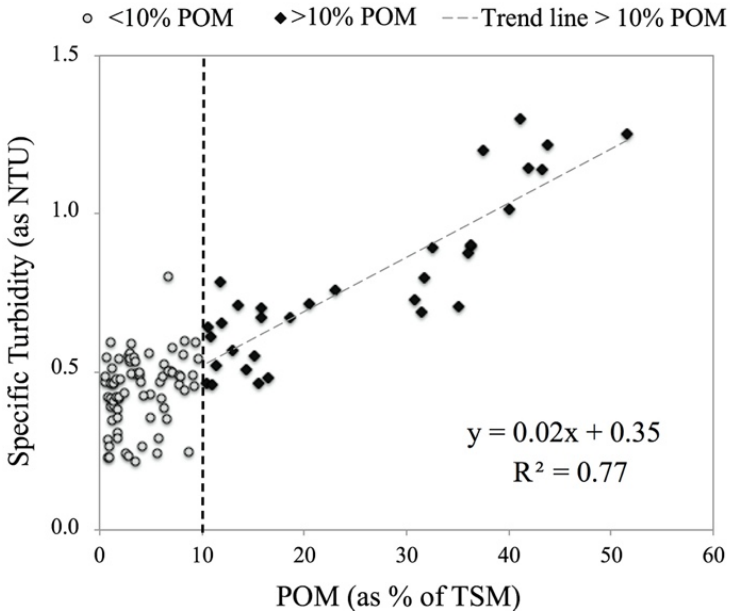

Figure 6.7 Plot of suspended sediment samples collected over two hydrographic events (Haast in February 2019, and Ahuriri in March 2019). As the percentage of POM increases in suspended sediment, there is a decrease in the stability of the specific turbidity (as K_N) (that is, the ratio of turbidity (NTU) to suspended sediment concentration).

6.5.4 Turbidimeter sensitivity to particle size

The sensitivity of a particular turbidimeter to particle size is determined by the wavelength of the light used that controls the scale of regular or irregular scatter. The HACH2100Q-is (measuring turbidity in units FNU) operates to the ISO7027 method using an infrared narrow band light source (860 nm) and is reportedly better suited to the measurement of small particle sizes since variation in instrument sensitivity is more common due to heterogeneous particle size (Clifford *et al.,* 1995; Sadar, 1999; Omar & MatJafri, 2009). By comparison, the use of a wider band light source (400–600 nm) like the tungsten filament used by the HACH2100P (measuring turbidity in units NTU) is suited to detection of a greater range of particle sizes, but is less suitable for the detection of fine particulates (Sadar, 1999; Pavelich *et al.,* 2002; Gray & Gartner, 2009; Merten *et al.,* 2014). The experimental observations, however, suggest that both instruments show a marked change in response between specific turbidity (as K_N and K_F) and particles smaller than 6 µm.

The settling experiment identified that the relationship between sediment and turbidity depends on the proportion of UFPM and its composition. As particle size decreases the specific turbidity increases. Specific turbidity (or sensitivity) is the inverse of the slope coefficient of the SSC-turbidity relationships and as the instrument sensitivity to fine

material increases (i.e., higher specific turbidity with finer material), the subsequent SSC-turbidity slope (β) decreases. This is likely due to the intense scatter caused by fine particles that is largely undetected by the 90-degree nephelometric detectors, resulting in a low turbidity response. This effect is due to the use of side-scattering sensitive turbidimeters, when non-nephelometric methods i.e., optical backscatter sensors (e.g., Lewis *et al.,* 1996) are used (that is they detect scattered light at 30 to 40 degrees from the incident light source) or dual-path sensors (turbidity in percentage units not necessarily calibrated to formazin), the effect of low turbidity response at UFPM is not generally observed (e.g., Foster *et al.,* 1992; Gippel, 1995). Therefore, turbidimeter sensitivity to particle size is highly dependent on instrumental method and may be an often-overlooked source of uncertainty when rating SSC to turbidity.

The settling experiment purposely constrained particle size to hydrodynamic size classes to control the suspension of particles in a fluid. Therefore, the sensitivity determined here is relative to hydrodynamic particle sizes likely observed in field conditions and represents the response of turbidity to different shaped or compositional material that remains suspended in a water column proportional to that of a spherical quartz grain.

6.5.5 SSC – Turbidity slopes are driven by UFPM

The implications of turbidity being sensitive to variations in particle size and composition has a direct effect on SSC-turbidity relationships (e.g., Wass & Leeks, 1999). The settling experiments identified a reduction in the regression slope coefficient (β) of turbidity as NTU and FNU to SSC as the percentage of fines increased in a sample (Figure 6.7). Increased instrument sensitivity for UFPM highlights its influence on nephelometric turbidity measurement by both methods, and the subsequent SSC-turbidity relationships. For instance, turbidity better predicts the concentration of UFPM (< 6 µm) and contributes most to the turbidity of natural waters. Particulate material that is < 6 µm (i.e., the UFPM) can attenuate light up to 7.5 times more than the > 6 µm fraction as (e.g., Gippel, 1995; Lewis, 1996; Holliday *et al.,* 2003) and therefore the experimental work carried out for New Zealand alpine rivers suggests a framework in which relationships with steeper slopes (~ 2, see Hicks *et al.,* 2004) represent the dominance of sand- and silt- derived turbidity, whereas lower slopes (< 1) suggest the dominance of UFPM. Therefore, in natural waters it may be difficult to detect small changes in suspended sediment, unless they are related to changes in the

composition or concentration of fine material. Specific turbidity, however, may be a useful metric for examining potential changes in particle size, colour, organic matter composition, and mineralogy, and provide for better critical reflection on the appropriateness of developing SSC-turbidity relationships, specific to the nephelometric method chosen.

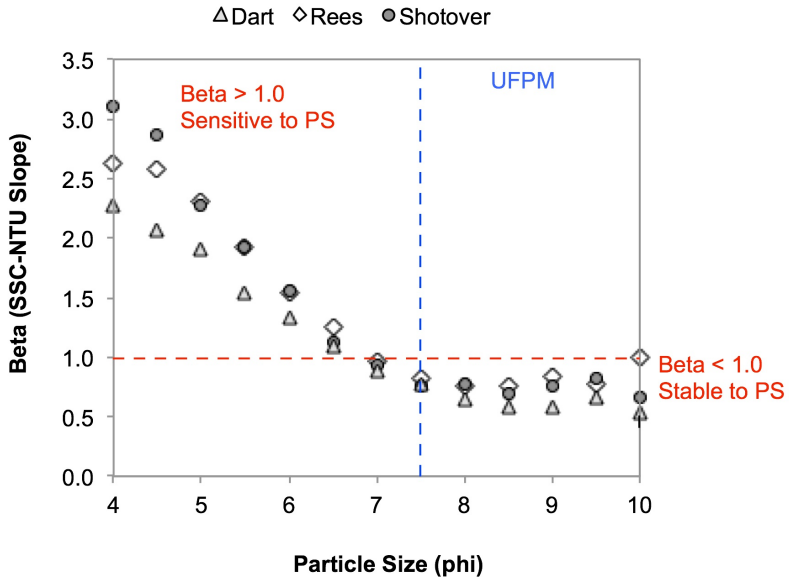

Figure 6.8 Plot of the regression slope coefficient (beta) for hydrodynamically-derived particle size classes derived from 5 replicate runs of different concentration doses of suspended sediment during a settling tube experiment. The larger the particle size (PS), the higher the slope coefficient (beta) between turbidity (in NTU) and suspended sediment.

6.6 Conclusions

Observations made over hydrographic responses in southern New Zealand alpine catchments and laboratory settling experiments show that specific turbidity is responsive to heterogeneous suspended material. This heterogeneity is common in most rivers, highlighting that the acknowledged catchment characteristics that control variation in sediment concentration inherently cause variations in PSD and composition. The influence this has on specific turbidity is two-fold; increased sensitivity of specific turbidity is a function of particle size and shape, with the greatest variability observed at the UFPM boundary; and the influence of composition whereby increased sensitivity is observed with increasing proportions of organic material in the UFPM fraction. Shown here is the role of particle size and the fundamental controls on sediment entrainment, transport, and deposition inferred from specific turbidity trends. So that for sediment distributions with a higher

proportion of coarse silts and larger sand sized particles, there are fewer particles and a smaller ratio of surface area per unit mass, and thus less light is intercepted by a particle in suspension, and a lower specific turbidity response, the opposite is true for suspensions with higher proportions of fine material, particularly UFPM (63 – 6 μm).

Specific turbidity as a metric should be used more routinely to identify the potential effects of UFPM and organic composition on SSC-turbidity relationships; and this may help understand where and when sediment concentration determined from turbidity needs to consider the effects of the local PSD and composition of the ultra-fine fraction. Such considerations are important as the effect of particle size variation and composition on the interaction between the concentration of sediment and turbidity could have deleterious effects on SSC-turbidity ratings, although acknowledgment is largely not documented. Here the present study suggests that implications for SSC-turbidity ratings are likely to be most acute in environments where there are distinct supply-related controls on the mobilization and suspension of UFPM (<6 μm) in the riverine environment, compared to coarser material that cause changes in PSD, or composition.

7 Turbidity Dependence on Particle Size and Composition of Riverine Suspended Material Across New Zealand's NRWQN

Research article published in *River Research and Applications* in 2019[5]. See Appendix 11.2.

7.1 Abstract

Turbidity, an index of light side-scattering, depends on the mass concentration of suspended sediment (SS) within water. Turbidity of river waters is regulated by the presence of suspended particulate matter and is used to identify visual changes in response to SS. Data from the New Zealand National River Water Quality Network is used to calculate 'specific turbidity' (*K*; turbidity normalised to mass concentration of suspended particulates). Specific turbidity is shown here to be an effective metric to assess the effect of suspended material composition and particle size distribution of suspended particulate matter over different landscape characteristics. Of the catchment characteristics considered in this study, specific turbidity was most sensitive to lithological factors, and relatively insensitive to land use and soil parameters. Decreasing particle size has a positive linear response to *K*, attributed to the higher proportion of ultra-fine particulate material that is generated by certain lithologies, underscoring the lithological influence on *K*.

[5] Minor changes to the narration of this research article have been made to improve coherency between chapters. Title has been modified slightly to reflect contribution to doctoral thesis. Title of published article A national-scale study of spatial variability in the relationship between turbidity and suspended sediment concentration.

7.2 Introduction

Turbidity is a useful continuous monitoring metric for understanding riverine visual clarity and suspended sediment (SS) fluctuations, but its use can be problematic (Rymszewicz *et al.,* 2017). Turbidity is a measure of all light attenuation in water, and uses fixed angle sensors to detect the scattering caused by suspended particulates, and depending on the turbidity method used, the source light may be reduced by absorption caused by coloured dissolved organic matter (CDOM). Such interferences mean that when turbidity is used as a surrogate for suspended sediment there are potential limitations to its use to derive SSC-turbidity ratings. Natural sediments are a complex mixture of sizes, shape and density, non-spherical and/or organic composition, and non-standard suspended particles scatter light very differently to formazin calibration standards. For example, particle size and the particle size distribution (PSD) of fine SS has a significant effect on light attenuation and turbidity measurements (e.g., Foster *et al.,* 1992; Davies-Colley & Smith, 2001; Holliday *et al.,* 2003; Davies-Colley *et al.,* 2014; Merten *et al.,* 2014; Hughes *et al.,* 2015; Bright *et al.,* 2020a (see: Chapter Six)). Organic materials and CDOM, by comparison, are light absorbing (Gippel, 1995), so the presence of irregular shaped organic detritus, or organic coatings with different refractive properties interferes with turbidity measurements (Sadar, 1998). The cumulative effect of the heterogeneous size, shape, and composition of natural river sediments inevitably introduces noise into turbidity measurements, and may have the effect of making SS–turbidity ratings unstable (e.g., Gippel, 1989; Bright & Mager, 2016 (see: Chapter Three)).

One approach to understanding the effect of suspended material particle size and composition on light scattering and turbidity is to derive the specific turbidity *(K).* Specific turbidity, as used by Foster *et al.* (1992) and Gippel (1995) as examples, is a parameter used to quantify the light attenuation effect of nephelometric turbidimeters and calculated as the ratio of attenuation turbidity per unit mass of suspended sediment) and is normally denoted as unitless, since it is equivalent to the inverse of the beta slope coefficient derived in SSC-turbidity regression equations, when plotted through the origin. Although few studies explicitly use *K,* it is well documented that turbidity is highly responsive to differences in particle grain size, shape and composition (e.g., Wass & Leeks, 1999; Hughes *et al.,* 2015). For example, increasing portions of fine material (< 63 µm, silts and clay) alter the behaviour of light scattering and will cause an increase in *K* because fine grained particles scatter light

more efficiently (e.g., Foster *et al.,* 1992; Gippel, 1995; Lewis, 1996; Wass & Leeks, 1999; Davies-Colley & Smith, 2001; Holliday *et al.,* 2003; Omar & Matjafri, 2009; Merten *et al.,* 2014). Conversely, particulate organic material and CDOM that occur when particulate concentrations of inorganic SS are low, cause absorption of light (Foster *et al.,* 1992; Gippel, 1995; Ziegler, 2002; Merten *et al.,* 2014). Invariably, the nature of suspended riverine material reflects intrinsic and extrinsic catchment characteristics (e.g., soil order, land cover, climate, topography, and lithology) that regulates the inherent particle characteristics of material available to be transported through a river network. Therefore, the assumption that the PSD of SS remains stable across spatial scales and with flow conditions, or as sediment and soil erosion mitigation tools are implemented in environmental management interventions, may not be valid (e.g., Wass & Leeks, 1999; Landers & Strum, 2013, Dymond *et al.,* 2017). The impacts of PSD (e.g., Clifford *et al.,* 1995; Gippel, 1995; Merten *et al.,* 2014) or organic matter (e.g., Sadar, 1998; Ziegler, 2002; Hatten *et al.,* 2012; Bright *et al.,* 2018 (see: Chapter Five)) have typically been derived from catchment-specific assessments, or laboratory-based experiments that measure controlled changes in turbidity and sediment properties (e.g., Foster *et al.,* 1992; Clifford *et al.,* 1995; Hatten *et al.,* 2012; Merten *et al.,* 2014; Bright & Mager, 2016 (see: Chapter Three); Rymszewicz *et al.,* 2017). Thus the derivation of *K* has been mostly confined to laboratory-based observations of turbidity attenuation effects, and its application across regional scales to understand SSC-turbidity relationships is limited. Therefore, there is an opportunity to revisit the use of K, as a tool for understanding turbidity responses across a diverse range of landscape units.

In New Zealand turbidity is a widely used regulatory tool for managing waterways and was included as one of three metrics that quantify water clarity in the National River Water Quality Network (NRWQN) routinely measured across 77 sites (Smith & Davies-Colley, 1992). Suspended particulate material was not routinely measured as part of the NRWQN, but in 2011, total suspended solids (TSS) was included temporarily as part of a study focused on the visual clarity of New Zealand rivers (e.g., Davies-Colley *et al.,* 2014). The NRWQN provides a valuable long-term record of visual clarity, turbidity, and light absorption (g_{440}), and provides an opportunity to assess catchment-scale characteristics that control light attenuation, measurement of turbidity, and the use of *K* at regional scales.

The aim of this paper is to examine the influence of catchment characteristics on suspended sediment concentration–turbidity (SSC–turbidity) ratings across New Zealand. In particular,

it is considered whether the relationship between SS and turbidity is a function of soil order, land cover, climate, topography, and/or lithology. Other indices of light attenuation (e.g., light beam attenuation, see: Davies-Colley *et al.* 2014) have previously been shown to be more successful at estimating concentrations of suspended particulate material, however, light beam attenuation is not yet a widely used tool in environmental monitoring. Rather, the focus here on turbidity because of its broad range of applications in river research and monitoring, and because a regulatory threshold for turbidity of 5 NTU applies (ANZECC, 2000). It is examined whether the composition of the suspended material (as organic matter content indicated by absorption i.e., optical density measured by spectrophotometer), volatile suspended sediment (VSS) concentration; or particle size distributions, are more influential on SS–turbidity ratings. The approach has been to derive this information from an existing nationally significant database (NRWQN), and examine the use of *K* as an indicative metric of SS–turbidity ratings; and more broadly assess the suitability of *K* for wider use as a metric to understand the controls on, and function of suspended sediment flux.

7.3 Method

7.3.1 NRWQN data

New Zealand is environmentally diverse in terms of lithology, soils, land cover, and climate, and provides a 'natural laboratory' to assess the optical response of rivers. The National River Water Quality Network (NRWQN) ran from 1989 – 2015 and was comprised of 77 sites from 35 large river systems across New Zealand that were monitored monthly by NIWA Taihoro Nukurangi for 14 water quality parameters (see: Davies-Colley *et al.,* 2011). In 2011 suspended particulate material was analysed, with total suspended solids (TSS) and VSS included as part of monthly monitoring (see: Ballantine *et al.,* 2014; Davies-Colley *et al.,* 2014). The most recent five-year period of data (2011 – 2015) from the NRWQN was used as the basis of this paper (Table 7.1). Turbidity (measured in units NTU) and absorption coefficient data for g_{440} (m^{-1}) was used. The absorption coefficient at 440 nm is directly relevant to the visual clarity of water as it relates to light absorption in the visible range of the spectrum (Davies-Colley & Vant, 1987). Data was used for the period of 2011 – 2015 so that the results of this study were consistent with the land use conditions present for the study period when SS was collected.

Table 7.1 National River Water Quality Network variables collected by NIWA Taihoro Nukurangi, that were used by the study, and the analytical methods.

Variable	Count	Record	Method
Flow (m^3 s^{-1})	60	2011–2015	Instantaneous discharge determined from gauging or rating.
Visual Clarity (m)	60	2011–2015	Visual water clarity determined in the field from horizontal black disc (see: Davies-Colley, 1988).
Turbidity (NTU)	60	2011–2015	Nephelometer (HACH 2100A) to March 2012, thereafter Hach model 2100AN
Abs g440 (m^{-1})	60	2011–2015	Absorption coefficient of a membrane filtrate @ 440 nm calculated from 440 & 740 nm absorbances. [1] (see: Davies-Colley & Vant, 1987).
TSS (mg L^{-1})	7	2011	TSS measured by standard gravimetric methods (see: APHA 2005 Method 2540D; Davies-Colley *et al.,* 2014) using glass fibre filters, that were subject to loss on ignitions at 400 ºC for 6 hours to determine the inorganic SS and VSS components.
Inorg. SS (mg L^{-1})	7	2011	
VSS (mg L^{-1})	7	2011	

[1] 740 nm absorbance is measured to provide a correction for residual filter-passing light scattering, because true absorption at 740 nm is negligible.

There is a dearth of information about the composition and PSD of SS in New Zealand. Hicks *et al.* (2004) defined seven generalised PSDs for different lithology types for New Zealand as part of a New Zealand-wide suspended sediment yield predictive model. Given the lack of other comparative data, these PSDs were used to estimate the sand, silt, and clay fractions of the NRWQN suspended sediment (as % wt of sample). Unfortunately, the cumulative PSDs given by Hicks *et al.* (2004) exclude fine silt and clay material < 4 µm, and so do not bracket the optically most-efficient particles of around 1.2 µm size (see: Davies-Colley & Smith, 2001: Figure 3).

7.3.2 Specific turbidity and statistical analyses

Specific turbidity (*K*) was calculated as the ratio of turbidity (in units NTU and FNU) to the TSS (see: Merten *et al.,* 2014). Spatial patterns in *K* were mapped using ArcGIS (v15) and grouped by Hierarchical Cluster Analysis (HCA) using Wards linkage and squared Euclidean distance in SPSS (v22). Existing geospatial datasets (Table 7.2) provided metrics of catchment land use, lithology, soil order, climate conditions, and topography for all 77 NRWQN catchments and used as independent input variables for multiple linear regressions in SPSS (v22) (Table 7.2).

Table 7.2 Basin, lithological, soil, and land cover catchment variables used in multiple regression modelling, and data sources.

Type	Predictor	Units	Source
Catchment	Catchment Size Mean Flow Stream Order FRE3 Mean annual rainfall Suspended sediment yield (SSY) Slope	km^2 $m^3 s^{-1}$ mm/a $t km^{-2} a^{-1}$ %	Catchment polygons, mean flow, stream order, and FRE3 sourced from NZ River Environment Classification. [1] Rainfall calculated from MfE average rainfall 1972–2013, based on NIWA virtual climate station network.[2] SSY from NIWA SSY estimator.[3] Slope defined from LRIS NZLRI database (v3). [4]
Lithology	Lithology (NZLRI ED1)	%	Lithology extracted and consolidated into 24 lithology types from NZLRI database data (v3). [4]
Soil	Soil Type (NZSC) Carbon Content Erosion	% %	Soil type from LRIS FSL defined in NZLRI database (v3). [4] Carbon content (% estimate) from LRIS FSL defined in NZLRI (v3).[4] Erosion categories defined by LRIS NZLRI database (v3). [4]
Landcover	Alpine vegetation, crop, exotic forest, indigenous forest, grassland, pasture, scrub, shrub, snow and ice, tall tussock grassland, urban, gravel rock and landslide, lake river and pond.	%	Landcovers defined by LRIS Land Cover Database and consolidated into 16 landcover types (v4.1). [5]

Note: All variables with % are calculated as % of catchment area.
[1] New Zealand River (MfE) Environment Classification (2016). Ministry for the Environment Online Data Portal. See also Booker (2015).
[2] Average Annual Rainfall, 1972 – 2013 (2015). Ministry for the Environment Online Data Portal.
[3] Suspended Sediment Yield Estimator (Hicks *et al.,* 2011).
[4] NZLRI New Zealand Soil Classification (v3) (2010). Landcare Research NZ LRIS Online Portal.
[5] Landcover Database (v4.1) (2015). Landcare Research NZ LRIS Online Portal.

7.4 Results

7.4.1 Catchment influences on specific turbidity

Median turbidity for the 77 NRWQN catchments ranged from < 1 NTU – 77 NTU, with 17 of the 77 rivers (22%) showing median turbidity values greater than the local regulatory 5 NTU threshold. Median inorganic SS from < 1 mg L^{-1} – 335 mg L^{-1} for the 2011 period. *K* values ranged 20-fold from 0.2 – 2.1, with the highest *K* occurring in the central South Island, for example in the Waitaki catchment (TK5, TK6) where headwater glacial lakes provide distinct pulses of fine material (Figure 1). The lowest values occurred in tributaries of the

upper Clutha/Mata-Au, Grey/Māwheranui (GY2, GY3) in the South Island, and Tarawera (RO1, RO2) and Rangitaiki (RO3, RO5) catchments in central North Island (Figure 7.1). The original framework of the NRWQN defined sites as having significant lowland impact from land use change and agriculture relative to 'baseline' sites with only small amounts of pastoralism. However, land use intensification has encroached into most of these baseline sites since inception, so that few are non-impacted or 'pristine' catchments. Despite transformations of land use change since the site classifications in 1989, sites classified as 'impacted' by anthropogenic land uses in the NRWQN generally had higher SS, VSS, TSS, turbidity, and specific turbidity compared to 'baseline' sites (Table 7.3).

Table 7.3 Summary statistics for 77 sites within the New Zealand NRWQN that are categorised as baseline and impacted.

Variable	Median	Minimum	Maximum
Baseline [1] *(n=32)*			
Inorganic SS (mg L^{-1})	1.4	0.3	52.0
VSS (mg L^{-1})	0.3	0.1	2.5
TSS (mg L^{-1})	1.7	0.3	56.6
Turbidity (NTU)	1.5	0.4	9.1
Specific Turbidity (*K*)	0.8	0.2	1.9
Impacted [2] *(n=45)*			
Inorganic SS (mg L^{-1})	7.1	0.3	335.0
VSS (mg L^{-1})	0.8	0.1	3.3
TSS (mg L^{-1})	8.0	0.4	349.0
Turbidity (*NTU*)	4.1	0.7	76.8
Specific Turbidity (*K*)	0.6	0.2	3.3

[1] Baseline – Upstream, lightly impacted sites
[2] Impacted – downstream affected by cumulative impacts of point discharges, pollution, and land use.

Hierarchal cluster analysis of *K* across 77 sites identified 6 *K* clusters that ranged in median *K* from 0.6 – 2.0 (Figure 7.2; Table 7.4) and suggests that catchment characteristics affect *K*. Clusters 1 and 2, and 3 and 4 are more closely related to each other respectively, as are clusters 5 and 6, but are most different to clusters 1 to 4. The clusters are not based on geographical location, as only one of the identified clusters was specific to the North Island (e.g., Cluster 5, *K* of 2.0). The other five clusters showed a mix of North and South Island catchments, with no distinct east–west division. Land use, topography, soil type, and lithology differed between clusters, suggesting a general effect on *K* (Table 7.4). For example, clusters 4 (median *K* of 0.6) and 1 (median *K* of 0.8) both comprised of large, mixed land use catchments primarily with pasture or forest land cover, and collectively include 52 of the 77 catchments, but contained very different soil and lithology types.

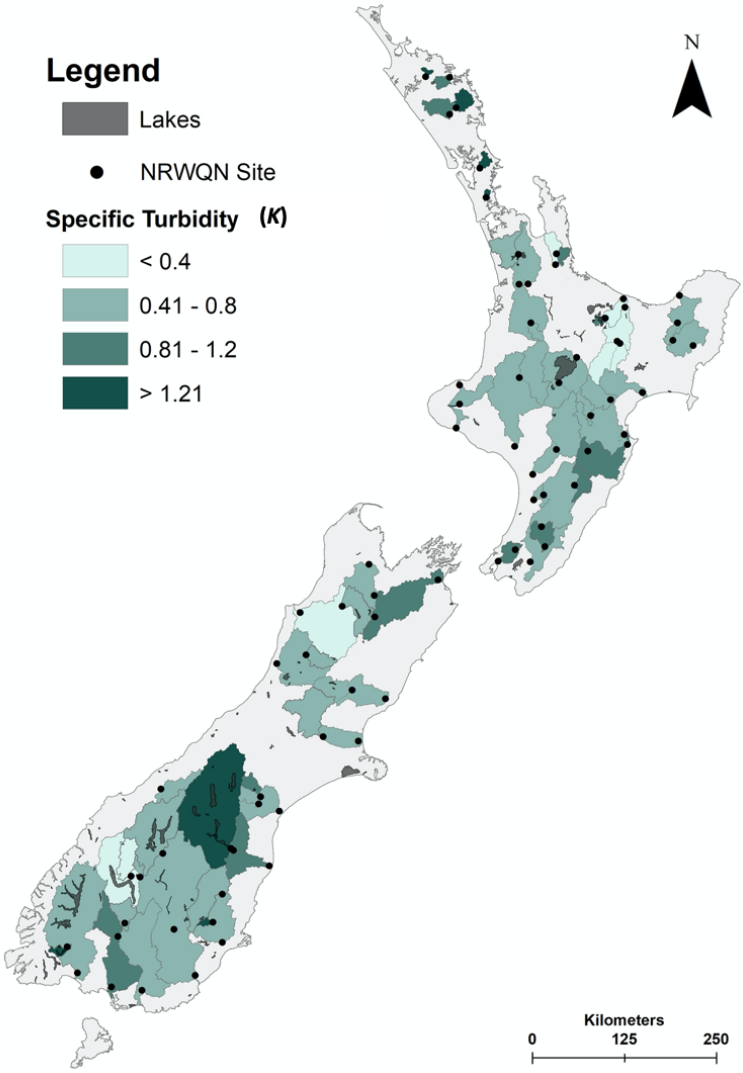

Figure 7.1 Specific turbidity (K) for 77 catchments from New Zealand National River Water Quality Network (NRWQN) derived from suspended sediment and turbidity data sourced from NIWA Taihoro Nukurangi.

Cluster 6 (median *K* of 1.5) was mostly agricultural catchments (e.g., Taieri DN2, Waiau DN10, Wairu WH4, Hoteo AK1), whereas Cluster 3 (median *K* of 0.2) was mostly tussock and former alluvial gold mining catchments (Shotover AX2, and Kawarau AX3) or plantation forestry (Rangitaiki RO3). Cluster 2 (median *K* of 1) includes steep catchments with mixed land use (e.g., Tukituki HV1, Hakatakamea TK5, Ruamahanga WH2). SS and VSS concentrations varied between the identified clusters (Table 7.4), as does the slope coefficient of the SS–turbidity relationships (that were derived for 66 of the 77 NRWQN sites).

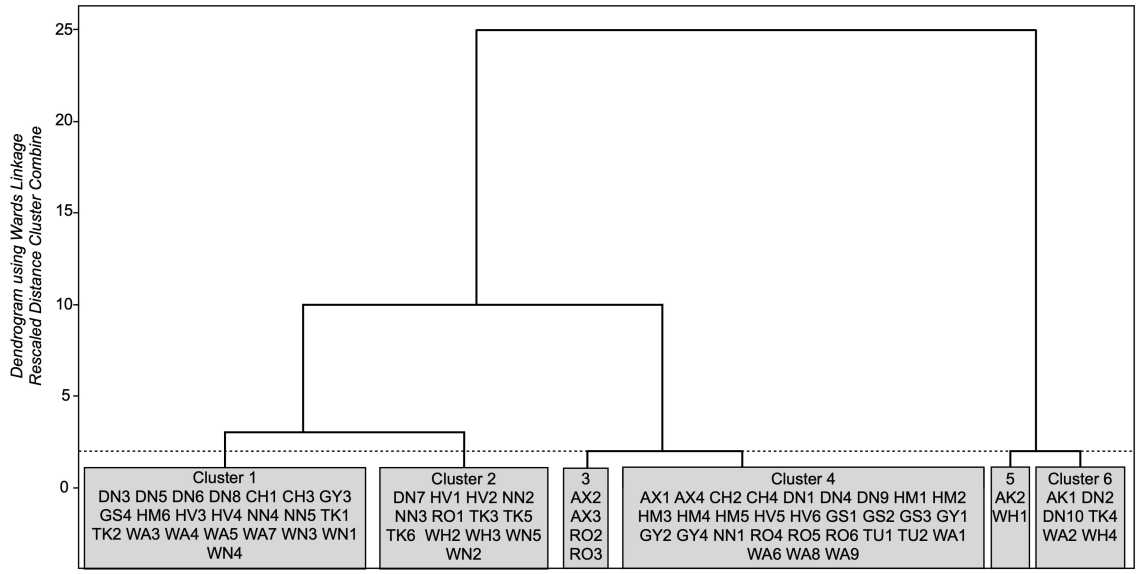

Figure 7.2 Hierarchical cluster membership dendrogram for 6 specific turbidity (K) clusters derived from 77 sites from the New Zealand National River Water Quality Network (NRWQN).

7.4.2 Organic influences on specific turbidity clusters

VSS, as a measure of organic solids was strongly associated with turbidity (NTU) (Spearman's $\rho = 0.74$ and $p < 0.05$) and suggests the organic component of suspended particulate material increases concomitantly with turbidity. Similarly, turbidity was associated with the absorption coefficient g_{440} (Spearman's $\rho = 0.60$ and $p < 0.05$), so that as CDOM within the visible part of the light spectrum (400 – 600 nm) increases in the water column, there is a concordant response in turbidity. Thus, the underlying factors that release organic solids and CDOM into the environment contributes to the turbidity of river water; either as an associated effect, or that these parameters may be a source of interference with turbidity measurements. *K* was calculated as the ratio of turbidity (NTU) to inorganic SS (mg L^{-1}), and therefore any response of *K* to VSS, or CDOM is a function of any remaining light attenuating material within a sample, when accounting for the mass concentration of organic material. *K* was inversely associated with VSS (Spearman's $\rho = -0.46$ and $P < 0.05$) and not associated with g_{440}. Therefore, scattering as a result from VSS likely contributes to the turbidity of river water, and the effect of CDOM on *K* is insignificant, although may depend on turbidimeter method. Such associations are expected given that CDOM only generates an absorption response, whereas *K* responds to scattering caused by particulates.

Table 7.4 Catchment area (km^2) and modelled runoff (R)(m/a), turbidity (NTU), suspended sediment (SS as mg L^{-1}), volatile suspended sediment (VSS as mg L^{-1}) and the proportion of VSS relative to total suspended solids (VSS%), specific turbidity (K), and the slope coefficient (β) of the SS–turbidity relationships, across the 6 clusters defined by hieratical cluster analysis and significance determined by Kruskall-Wallace (p-value < 0.05 at 95%) (*).

Cluster	*n*	Area km^2 *	*R*	NTU	SS *	VSS *	VSS %	*K* *	*β* *	Description
1 Low SS Low VSS Low VSS%	22	1,390	1.0	3.0	3.6	0.3	10.0	0.8	1.6	**Large mixed catchments** with agriculture and forest. Steep slopes with moderate to severe erosion. Brown, recent, anthropic soils. Greywacke, ashes, alluvium. e.g., Wairau, Hurunui, Ngaruroro, Upper Buller
2 Low VSS Low SS	13	458	1.0	1.5	0.9	0.2	13.0	1.0	1.8	**Steep catchments** with mixed use; indigenous forest, agriculture, tussock. Moderate to severe erosion. Brown, pumice, ultic soils. Greywacke and alluvium. e.g., Makaroro, Ruramahanga, Upper Motueka, Upper Oreti.
3 High SS Low VSS%	4	1,112	1.2	3.6	18.9	1.5	7.1	0.2	4.1	**Large forested catchments in NI**[1] **or large tussock catchments in SI**[2] with minor agriculture. Steep slopes with moderate erosion. Brown, pallic, podzol soils. Schist and volcanic. e.g., Shotover, Tarawera
4 Moderate SS, and VSS%	30	2,672	1.1	3.7	7.7	0.9	11.5	0.6	2.0	**Large mixed catchments** with agriculture and forest, primarily in North Island. Steep slope with moderate erosion. Brown, Podzol, Pumice soils. Ashes, alluvium, greywacke. e.g., Waiau, Lower Buller, Wanganui, Waikato
5 Low SS High VSS%	2	102	0.9	4.2	1.4	0.5	24.1	2.0	1.3	**Northland forest with urban settlement** with rolling slope and negligible erosion. Brown and ultic soils. Sandstone and greywacke. e.g., Rangitopuni, Waipapa
6 High VSS%	6	264	1.4	1.6	3.7	0.5	23.6	1.5	1.2	**Agricultural catchments** with indigenous forest. Rolling slopes, moderate erosion. Brown and Pallic soils. Sandstone and schist. e.g., Hoteoa, Sutton, Wairu

[1] NI – North Island of New Zealand
[2] SI – South Island of New Zealand

7.4.3 Optical properties and catchment characteristics as predictors

Iterative regression models were run to explore the dependence of *K* on intrinsic and extrinsic catchment characteristics. Model 1 was based on catchment characteristics, including optical properties, rainfall (mm/a), runoff (m/a), suspended sediment yield (SSY) (t km^{-2} a^{-1}), and catchment size (km^2), but excluded lithology, vegetation class, and soil cover. The output showed that optical water properties provided a good linear fit ($r^2 = 0.47$) dominated by three variables: absorption coefficient at 440 nm (g_{440}), VSS (mg L^{-1}), and visual clarity, suggesting that the underlying contributing factors to *K* also affect water colouration and organic particulates.

A subsequent model run with catchment lithology only (Model 2) showed a good linear regression ($r^2 = 0.49$) based on mixed lithologies, igneous rock types (ash, lapilli, and volcanic), greywacke and muds. However, strong autocorrelation amongst these variables (D-W 1.2) precludes further use of this model. When the lithological classes from Model 2 were included in Model 1 (catchment characteristics *and* lithologic classes, excluding land cover and soil class data) a strong linear regression ($r^2 = 0.71$) from 12 variables was derived (Model 3). These variables included optical properties, visual clarity and g_{440}, and a subset of lithological classes, with igneous rock types dominating (including volcanic, plutonic, ultramafic and ash deposits), then metamorphic rock types (schist) and sedimentary (loess, and sandstone). Model 3 also included potential for extreme erosion and high suspended sediment yield, although these provided only a minimal contribution to the overall goodness of model fit.

When land cover class was run through multiple regression, it produced a poor fit ($r^2 = 0.1$) with *K*, and when combined with the catchment characteristics of Model 1, the model selected optical water properties over any land cover criteria. This suggests that land cover does not strongly influence *K*, as many of the catchments have mixed land use. Soil order similarly was a poor predictor of *K* ($r^2 = 0.3$), derived from pumice, ultic, gley, and melanic soils. When soil classes were combined with the catchment characteristics from Model 1, a good linear regression model was produced ($r^2 = 0.61$). The combination of all iterative model runs suggests that catchment characteristics and lithological classifications are far more influential predictors than either land cover or soil type.

When all variables were included, a strong linear regression model (the 'best') was produced (r^2 = 0.81); containing: optical properties (visual clarity, g_{440}, VSS); soil characteristics (recent soils, and medium soil carbon %); SSY, lithological classes (volcanic, sandstone, greywacke); topographic classes (extreme erosion potential, flat to undulating topography); and the presence of permanent snow and ice (Table 7.5). Of these variables only volcanic lithology, SSY and VSS concentration were inversely related to *K* (negative coefficients: Table 7.5). The iterative approach here to multivariate regression shows that *K* can be reasonably-well predicted from catchment characteristics and lithological classifications alone and is relatively insensitive to land cover and soil type; however, for a few catchments, like the Waitaki (TK4) glacial weathering that produces fine particulate material may be an important predictor.

Table 7.5 Independent catchment characteristics listed in hierarchal order of importance in linear model for specific turbidity (K)(determined by stepwise linear multivariate regression), with slope coefficients (Beta – β), model fit (r^2) and Durbin-Watson statistic (D-W) used to determine statistical significance.

	Model Parameter	β	r^2	D-W
Specific Turbidity (*K*)	Visual Clarity (m)	0.080	0.81	2.1
	Recent soils[1]	0.010		
	Volcanic lithology[1]	-0.010		
	SSY (t km^{-2} a^{-1})	-0.001		
	Sandstone lithology[1]	0.010		
	Erosion extreme[1]	0.020		
	Absorption g_{440} (m^{-1})	0.220		
	Soil carbon medium level[1]	0.003		
	VSS (mg L^{-1})	-0.070		
	Greywacke[1]	0.003		
	Flat-undulating topography[1]	0.004		
	Snow and ice[1]	0.080		

[1] Indicates parameter expressed as a percentage of total catchment area

7.4.4 Particle size distribution effects on specific turbidity

K increases as the clay content (as % wt of PSD) increases (Figure 7.3a), whereas sand (as % wt of PSD) causes a reduction in *K* (Figure 7.3b). Catchments with siltstone and sandstone showed a greater proportion of clay in the PSD (e.g., Clusters 5 and 6) suggesting that the fine grain parent material undergoes comminution and ends up with an overall higher portion of clay. Volcanic and schist lithologies produce river sediments with relatively less clay and are associated with a lower specific turbidity (e.g., Cluster 3). Of the 77 NRWQN sites, 66

had sufficient data to derive SS–turbidity relationships where $r^2 > 0.40$. Slope coefficients (β) of the SS–turbidity ratings for these 66 NRWQN sites showed the effect that increasing portions of sand have on the slope coefficients of SS–turbidity ratings. For example, when the % wt of sand increases in suspended sediment samples, the slope coefficient is steeper (e.g., Weak Volcaniclastic, Westland Schist, Fiordland Gneiss). The linear slope coefficient of SS–turbidity is inversely proportional to *K*, so that the relationship between % wt of sand and the slope coefficient (β) is the inverse to that of Figure 7.3b.

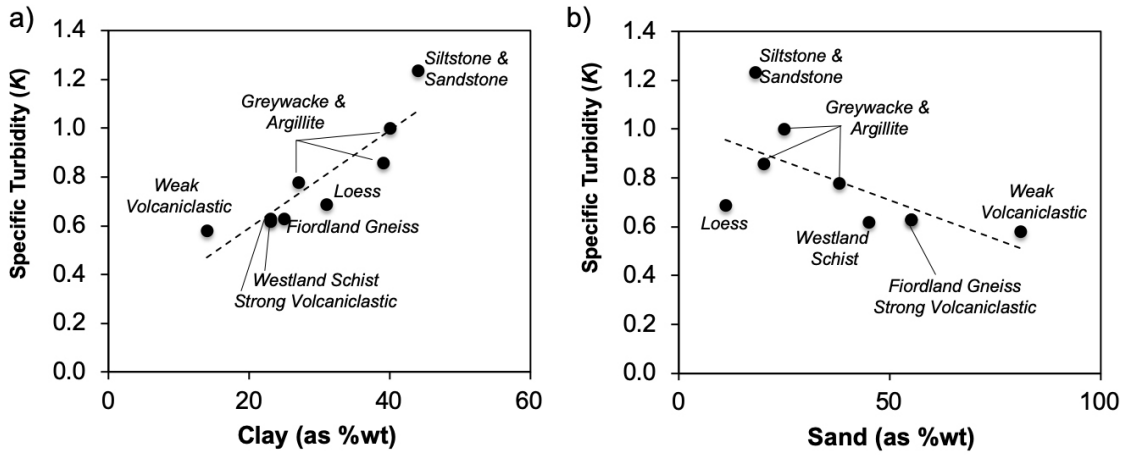

Figure 7.3 Median specific turbidity (K) relative to a) clay (as % weight of particle size distribution); and to b) sand (as % weight of particle size distribution) for the seven common lithology types across New Zealand, as defined by Hicks et al. (2004).

7.5 Discussion

7.5.1 Influence of intrinsic catchment variables on specific turbidity

K is unevenly distributed across New Zealand; however, the assessment here suggests that *K* responds mostly to catchment lithology and is underpinned by differences in organic composition and particle size distributions. Specific turbidity clusters also corresponded to landscapes that have higher levels of intensification from human activities (e.g., plantation forestry, or agriculture). Because specific turbidity is dependent on the PSD and composition of suspended sediments (e.g., Wass & Leeks, 1999; Hughes *et al.,* 2015), the catchment characteristics identified through multiple regression modelling reflect the processes that regulate the composition of suspended materials and sediment grading through fluvial systems.

Catchment lithology provides a framework for understanding the conditions under which suspended material composition and particle size vary spatially and is particularly relevant for the rivers that show median turbidity above the regulatory threshold and understanding why this occurs. For example, volcanic, sandstone, and greywacke lithology units represent the different attrition rates (Attal & Lavé, 2009) of rock that have a direct effect of light attenuation from different sized particulates. In conjunction with SSY, organic particulates (VSS), visual clarity, and absorption coefficient underscore the dependence of particulate concentration and composition that directly control light attenuation. Whereas recent soils, erosivity, undulating topography, carbon content of soil, and snow and ice in a catchment, provide examples of some landscape characteristics that give rise to, or provide mechanisms for, higher transport of sediment to the fluvial environment.

7.5.2 Optical properties control specific turbidity

Turbidity was determined in this study by a nephelometric method where light attenuation is proportional to scattering measured at 90° (± 30º) to the light source; based on EPA Method 180.1 (Sadar, 1998). Nephelometric turbidity is known for its vulnerability to interferences from particulate organic matter (POM) and CDOM as organic composition alters light attenuation processes in water (e.g., Foster *et al.,* 1992; Gippel, 1995; Ziegler, 2002; Merten *et al.,* 2014; Bright *et al.,* 2018 (see: Chapter Five)). A strong association between the g_{440} was identified, which is an index of dissolved organic matter in water, to turbidity. Absorption g_{440} represents CDOM that is detectable within the operating range of method EPA180.1, so it is possible this is a potential interference on turbidity measurements. The increased presence of light absorbing material, like the components that comprise CDOM (e.g., fatty acids, amino acids, carbohydrates, and hydrocarbons) have been previously identified as causing a negative bias in turbidity by reducing the light scattering effect (see: Davies-Colley & Vant, 1987; Gippel, 1995; Hope *et al.,* 1994; Omar & Matjafri, 2009). The mechanisms behind this are unknown and warrant further investigation but could be related to changes in refractive index through chemisorption of CDOM onto particle surfaces, creating organic coatings, or to electrostatic changes that may aid particle dispersion.

7.5.3 Lithological attrition effect particle size and specific turbidity

The attrition of river sediment produces distinct PSDs by persistent abrasion and fragmentation (Attal & Lavé, 2009), and as a result there is a notable effect on the observed *K*, and associated slope coefficient (β) of SS–turbidity relationships. This effect is commonly reported in studies focused on turbidimeter sensitivity where the fine fraction of suspended sediment has a more notable effect on turbidity measurements due to the intense light attenuation effect of fine particulate materials (e.g., Foster *et al.,* 1992; Gippel, 1995; Lewis, 1996; Sadar, 1999; Wass & Leeks, 1999; Holliday *et al.,* 2003; Omar & Matjafri, 2009; Merten *et al.,* 2014; Bright *et al.,* 2020b (see: Chapter Four)). The observation that *K* increases as the portion of clay (as % wt of PSD) increases, and the decreasing linear trend with sand (as % wt of PSD), is consistent with the general principles of light scattering. The nephelometric turbidity method is based on the principle that suspended particles produce regular side scatter at 90° (± 30°) to the incident light source, that gives a predictable turbidity response for spherical particles, but not for plate shaped clay-sized particles (Sadar, 1998; Kitchener *et al.,* 2017). So, when suspended sediment contains a higher portion of platy clay-sized material, there is an increase in specific turbidity.

Since *K* is the inverse of the SS–turbidity slope coefficient, SS–turbidity ratings respond to particle size. For New Zealand rivers the slope coefficient of SS–turbidity ratings approximate 2 (see: Hicks *et al.,* 2004). However, as reported here slope coefficients range from 1.4 – 2.4 (Table 7.6) across seven lithology classes and provides a framework for interpreting SS–turbidity relationships based on catchment lithology (e.g., Wass & Leeks, 1999). The attrition of different lithology types differs due to rock properties including; initial grain size distribution, clast shape and cleavage planes, tendency for abrasion, and texture (Nibourel *et al.,* 2015). Attrition rates for the Southern Alps of New Zealand show that yields of sand and silt differ between schist, greywacke, and nephrite lithologies (Cox & Nibourel, 2015). For example, schist produces more sand, whereas greywacke produces very little sand and the PSD comprises almost entirely silt. Applying a generalised PSD for the NRWQN has shown that SS–turbidity ratings with steeper slopes likely represent the dominance of sand- and silt- derived turbidity (e.g., Weak Volcaniclastic and Westland Schist). Lower slopes (~ 1) (e.g., silt and sandstone, greywacke and argillite) suggest the dominance of finer material that has the effect of reducing the slope coefficient. The general effect in relation to light attenuation is that particulate material that is < 6 µm attenuates light up to 7.5 times more than the > 6 µm fraction (e.g., Gippel, 1995; Lewis, 1996; Davies-

Colley & Smith, 2001; Holliday *et al.,* 2003), which gives a higher *K* response, but inversely a lower slope coefficient. Although PSDs were not measured directly for all locations, it appears that the nature of lithological attrition is an important driver of *K* and may be a valuable index explaining changes in SS–turbidity ratings, particularly in locations undergoing land use transformation. It is possible that *K* may be useful for identifying a change in suspended sediment particle sizes that could be connected to specific landscape characteristics. Evidently further work is warranted to explore the usefulness and appropriateness of *K* for environmental monitoring purposes, or in situations where existing turbidity and SS records need to be reconciled for the effect of particle size following landscape changes.

Table 7.6 Dominant lithologies of New Zealand defined by Hicks et al. (2004) and the cumulative particle size distribution data as % weights, and percentage of fine particulate material (FPM) with median specific turbidity (K) and the slope coefficient (Beta - β) of the SS–turbidity relationships.

	Sand (%wt)	Silt (%wt)	Clay (%wt)	% FPM (< 63 µm)	*K*	*β*
North Island [1]						
Greywacke & Argillite	25	35	40	50	1.0	1.6
Siltstone & Sandstone	18	38	44	51	0.8	1.4
South Island [1]						
Fiordland Gneiss	55	20	25	33	0.6	1.8
Axial Greywacke & Argillite	38	35	27	33	0.9	1.5
Foothills Greywacke & Argillite	20	41	39	48	0.9	1.7
Westland Schists	45	32	23	30	0.6	2.4
Common[1]						
Loess	30	42	29	33	0.6	1.5
Strong Volcaniclastic	55	22	23	29	0.8	1.7
Weak Volcaniclastic	81	5	15	13	0.6	2.4

[1] Particle size distributions based on lithology as determined from Hicks *et al.* (2004).

Landscapes are mosaics of varying land use types, topography, and lithology, and therefore increases in sediment concentration that generally occur as the result of landscape disturbance, or in response to natural perturbations from rainfall events or slope-failure, can occur at different locations within catchments. For example, if catchments are prone to different sources of suspended material, whether that is from slope failure, or introducing a component of land use disturbance (e.g., pastoral intensification, or plantation forestry), it may change the size of material available for sediment transport (Navratil *et al.,* 2011; Landers & Strum, 2013). The implication is, that if transformations in land use predispose a

catchment to release finer-grade material, there may be an increase in turbidity that is disproportionate to the increase in suspended sediment mass, because fine grain particles produce proportionately more turbidity, per mass, than sand particles when using nephelometric turbidity. From an environmental monitoring perspective, this means that if a nephelometric turbidity regulatory threshold is specified, it may be exceeded more quickly by the release of fine silt and clay sized particles than by disturbance that produces coarser, sand grade material (Owens *et al.,* 2005). The counter is that fine grained material is potentially more environmentally detrimental to receiving environments, where fine grained material builds up in riverbeds and acts to clog interstitial space, and reduce vadose zone exchange, and be potentially harmful to aquatic species (Wood & Armitage, 1997; Owens *et al.,* 2005; Brunke & Gonser, 1997). Careful consideration to different sediment sources is therefore required when applying different rating curves for SS–turbidity, especially if the monitoring effort is to try to understand landscape disturbance and SS response from turbidity records.

7.6 Conclusions

Specific turbidity differs across the NRWQN of New Zealand and is influenced by the underlying lithological composition and how that controls rock disaggregation and propensity for attrition to certain material size classes. Lithological type and optically distinct variables that directly control light attenuation, and landscape characteristics (e.g., soil type, erosivity, topography) that enable availability and transport of sediment and organic material, are the main processes that affect specific turbidity. As such, these factors contribute to different SS–turbidity relationships. Shown here is that K, that normalises turbidity for the mass concentration of sediment, is a useful metric for exploring underlying differences in material composition, when combined with data related to particle size and organic composition. While other indices, such as light beam attenuation that is based on visual clarity (m), have been shown to be a more successful at estimating concentrations of riverine particulate material, these approaches are not yet widely used tools in environmental monitoring. Therefore, it is proposed that in the interim, specific turbidity could be a useful metric for classifying the effects of organic composition and particle size of riverine suspended materials where existing records of SS and turbidity are available. Additionally, the influence of CDOM on turbidity measurements remains problematic and

further work is needed to understand how CDOM interacts with particulate material. It is suggested that the use of turbidity as a surrogate for determining suspended sediment concentration must consider the effects of particle size and organic interferences, and therefore propose greater use of specific turbidity as a metric for delineating the influence of composition and PSD changes on the appropriate measurement of suspended sediment.

8 Synthesis

8.1 Research Summary

Optically distinct components of riverine suspended material restrict use of turbidity in all suspended sediment monitoring situations. The conditions in which these restrictions apply are not well understood. Therefore using turbidity in suspended sediment monitoring to understand land use disturbance and natural processes requires careful consideration of the monitoring methods used. This thesis shows that sediment is only one component of the material eroded and transported in riverine systems when landscape transformations and perturbations occur, and provides context for the catchment characteristics that give variable particulate compositions with a variety of properties, and noisy turbidity responses. The research outputs of this thesis have shown that the suspended load can be a complex mixture of inorganic mineral suspended sediment and biogenic particulate organic matter (POM) that are controlled by intrinsic and extrinsic catchment characteristics. Typically, it is the inorganic sediment portion that is of most interest and quantified using surrogates like turbidity, and the organic influence on the clarity of river waters and turbidity is largely ignored. The present study shows that organic and inorganic materials are optically distinct and behave differently with nephelometric turbidimeters, and therefore this has implications for the wide use of turbidity in suspended sediment monitoring and research. As such, effective measurement of riverine sediment flux with simple surrogates like turbidity is deeply problematic and requires careful consideration of its application and use.

Overall this thesis has established that:

- Biological fouling from POM and coloured dissolved organic matter (CDOM), and variation in particle size of suspended particulate material cause turbidity to be a poor surrogate for the suspended sediment concertation (SSC);
- POM can be a significant component of suspended load, and is particularly acute under baseflow;
- The proportion of POM relative to the total suspended material (i.e., POM%) is controlled by a variety of extrinsic and intrinsic catchment characteristics that predispose landscapes to the erosion of organic rich material;

- Organic carbon comprises approximately half of the POM transported as part of the suspended load, and therefore particulate organic carbon (POC) is linked to the catchment denudation processes that control POM export;
- The organic composition (POM and CDOM), and particle size distribution of suspended material, under both event and base flow conditions, control light attenuation and turbidity in river waters. This has impacts on the nephelometric determination of turbidity making use of turbidity as a surrogate for SSC problematic;
- Specific turbidity (that is turbidity normalised for mass concentration of particulates) is a useful indicator for the detection of organic composition (POM and CDOM), and particle size that explain variation in turbidity response at base flow and event flow;
- Specific turbidity trends show that POM and particle size are temporally and spatially variable, and therefore the common assumption that suspended sediment do not change in their particle properties or composition over time, or due to soil erosion mitigations, is not valid; and
- Suspended sediment-turbidity ratings are fraught in locations with high proportions of POM or significant proportions of ultra-fine particulate material. In some catchments with specific characteristics, POM or ultra-fine particulate material dominates the turbidity response.

These findings broadly contribute to understanding under three themes, that are discussed in more detail below.

1. Particulate Organic Material can be a Significant Component of Total Suspended Material

Organic matter flux on a regional scale has not been studied in depth in New Zealand, and contributes to a distinctly Southern Hemisphere perspective, and the flux yields are broadly consistent with global observations (e.g., Wu *et al.,* 2007; Zhang *et al.,* 2009; Madej, 2015). Regional perspectives of regional POM fluxes are limited, and this thesis has linked POM to POC yields by calculating a van Bemmelen conversion factor of 1.3 for riverine carbon for southern New Zealand. Typically, this conversion factor is estimated as being a value of 2, ranging 1.4 – 2.5 (Pribyl, 2010), but these ratios are largely derived for soils (Ahn & Jones,

2013); and may not be representative of the multiple carbon sources that comprise of POM in fluvial systems. The van Bemmelen factor calculated here is a value at the lower end of the generalised range, and signifies that baseline fluvial POM flux determined from fluvial POM likely derives a van Bemmelen factor <1.5, and may be a consequence of both allochthonous and autochthonous carbon sources that are present in fluvial POM, and that different ratios exist between terrestrially-derived soils and other carbon-sources. Or, that the traditional range of van Bemmelen does not adequately represent raw or recent soils that may be produced in alpine regions in New Zealand. For example, Ahn and Johnes (2013) and Périé and Ouimet (2007) show considerable differences in van Bemmelen factors exist between different soil types.

Significant is the general implication of high organic matter on the poor statistical fit between SSC and turbidity. The thesis has shown that this effect is most apparent in the presence of POM and variable particulate size distributions. The contribution of this thesis is the linkage between poor suspended sediment-turbidity ratings being most acute in the presence of CDOM that gives waters a characteristic yellow hue. The significance of POM on suspended sediment monitoring has not been accounted for at this scale, or across a range of diverse landscapes, as evident in southern New Zealand. POM concentration is also associated with lithology and transport competence that is controlled by event hydrology, and therefore, behaves like suspended sediment due to its concomitant transport. However, the proportion of POM (i.e., POM%) at base flow responds to both intrinsic and extrinsic catchment characteristics and is affected by the availability of organic material and mechanisms for transport including vegetation cover, topography, and hydrology. This thesis contributes to better understanding of the variability, patterns, and controls on riverine organic matter fluxes and yield in a distinctly Southern Hemisphere example, that is largely absent from existing research. POM% has acted as an indicator for identifying the relevance of these transport mechanisms and may have value as a metric to infer landscape controls on riverine fluxes of organic matter. Focus on baseflow levels is an uncommon approach, as event flow export is typically considered more relevant due to the large volume of particulate material exported during higher flows, however, the data shows that organic and inorganic material at lower flows are relevant to annual loads, and across southern New Zealand it is evident that baseline riverine organic matter and suspended sediment is spatially organised and connected to broader hillslope processes.

2. Turbidity is Sensitive to Composition and Particle Size Distribution

The turbidimeter comparison studies presented as part of this thesis further consolidate the burgeoning research into this issue. The approach used in this thesis differs, however, given the use of natural suspended sediments collected from alpine and organic rich rivers in spate, rather than relying on synthetic or deposited samples (e.g., Gippel, 1995; Merten *et al.,* 2014) and has observed the behaviour of variable particle sizes and organic compositions over event flow. The thesis shows the effect of optically distinct components of naturally derived suspended particulate material that controls light attenuation and gives variable turbidity responses. Specific turbidity is a measure of sensitivity (e.g., Gippel, 1995; Merten *et al.,* 2014) although its application across sediment research is not widely used. This thesis, however, has identified the use of specific turbidity as a means of understanding where and when turbidity is most sensitive, and is a novel contribution to turbidity science focused on light attenuation processes. Given the broad use of turbidity in research and suspended sediment monitoring, specific turbidity has a place alongside suspended sediment monitoring with turbidity to better understand variability in composition and particle size, that despite common assumptions, are rarely stable. Like observed across southern New Zealand, the same effect of composition and particle size was observed across New Zealand's National River Water Quality Network. Therefore, the implications are broadly relevant across large spatial scales, and highlights the relevancy of catchment specific light attenuation responses across a national record of turbidity when used in suspended sediment monitoring. Therefore the thesis provides information pertinent to evaluating the applicability of comparing turbidity records over time, or between catchments, that is commonly done without thought for the factors that control variable light attenuation responses.

3. Implications for Use of Turbidity as Surrogate for Sediment Monitoring

The implication of variability in turbidity response to composition and particle size is that nephelometric turbidity methods do not necessarily produce consistent predictive relationships between turbidity and SSC. Observed noise in relationships is common, although the effect is not quantified. Organic composition of suspended riverine material can be highly variable, and particle size variations are in part responsible for observed noise in suspended sediment-turbidity relationships. The missed opportunity is that specific turbidity is the inverse of the slope coefficient of suspended sediment-turbidity relationships, and therefore changes in specific turbidity represent variability of suspended sediment-

turbidity relationships, that are driven by compositional and particle size variations. This validates that for mixed composition samples, or where significant portions of ultra-fine material (<6µm) are part of the particle size distribution, turbidity cannot be reliably used as a predictor for inorganic sediment concentration. This poses an interesting question in relation to use of turbidity for suspended sediment monitoring, that traverses the five research papers included in this thesis by examining the individual components, and their combined effect. The outputs from this thesis culminates in Chapter Seven that applies the learnings from this thesis to the National River Water Quality Network. This fills the identified gap in the existing literature and connects POM and suspended sediment to one another by using POM% as an indicator for the catchment denudation processes that determine composition (and therefore particle size), and the effect this has on light attenuation and suspended sediment-turbidity relationships.

Statistical analysis of the landscape controls that affect specific turbidity showed that for New Zealand the lithology type, and therefore attrition rates, and optically distinct variables that control light attenuation, along with landscape characteristics (e.g., soil type, erosivity, topography) affect specific turbidity. Therefore, extrinsic and intrinsic catchment characteristics define the composition and particle size distribution of riverine suspended material, and this is bespoke to individual catchments. These factors contribute to different suspended sediment-turbidity relationships, as shown across New Zealand, there is significant variation in the slope coefficient that is assumed to approximate 2 (Hicks *et al.,* 2011), however, these assumptions miss the key drivers that lead to variable suspended sediment-turbidity responses. So that for the same value of turbidity in two different catchments the estimated SSC based on suspended sediment-turbidity could be over- or under- predicted based on the optical properties of the suspended material present. National records of suspended sediment-turbidity provide a framework for estimating the likely properties of the material suspended in rivers measured by nephelometric turbidity, and offers an opportunity to apply this to existing SSC-turbidity records and calibrate for the effects of particle size, organic matter or water colour . Furthermore, specific turbidity may be an effective indicator that represents the integration of the processes that control source availability and transport competence. Researchers and environmental managers should therefore consider the following questions when evaluating use of turbidity and validity of exiting suspended sediment-turbidity records:

- Can suspended sediment be derived from turbidity at a particular site, and can noise in existing suspended sediment-turbidity relationships be explained by higher portions of organic matter or fine particulate material?
- Are there certain landscape characteristics within a catchment that predispose the suspended flux to higher proportions of organic matter, or show a preference for the attrition of certain particle size fractions?
- Do existing suspended sediment-turbidity relationships vary in time and space, within and between catchments, and is this indicative of variable light attenuation responses to organic matter or particle size?

Despite these identified limitations, turbidity can be a successful metric for monitoring suspended sediment in certain landscapes, for example where organic matter is an insignificant component of the suspended material flux (e.g., alpine or glacial environments) (e.g., Mager *et al.,* 2018) or where landscape characteristics produce homogenous suspended materials (e.g., small, single land cover catchments) (e.g. Gippel, 1995). The difficulty is that these conditions rarely exist (e.g., Landers & Strum, 2013), and the conditions under which turbidity is a suitable surrogate for monitoring suspended sediment are catchment (and potentially temporally) specific (Gippel, 1989; Lewis *et al.,* 2007). Turbidity is a poor surrogate in catchments where sources of sediment are switched on and off (Duvert *et al.,* 2010; Navratil *et al.,* 2012), or where organic material is intermittently cycled through the riverine system (Ittekkot & Arain, 1996; Robertson *et al.,* 1999), because the light attenuation and optical response of rivers is variable. Therefore turbidity is inconsistent, and this introduces the observed noise in suspended sediment-turbidity relationships, and explains why in some catchments a suspended sediment-turbidity rating may be very difficult to calibrate.

8.2 Future Work

Despite the recent surge in understanding the implications of sediment on freshwater ecosystems at a broader integrated catchment management perspective, there remains a paucity in understanding the independent controls that influence the mix of mineral and organic material fluxed through rivers. Further research should be directed to assessing the properties of riverine suspended material across a range of landscapes. The present study has begun to address this, although there remains substantial scope for further work. For example, if specific turbidity or other normalised metrics should be applied to existing and future turbidity and SSC records so that the suitability of turbidity for determining SSC can be assessed before ratings are developed.

Specifically, further research should be directed to:

- Source discrimination of sediment and organic matter in mixed land use catchments, especially in impacted versus indigenous catchments as method tests for various source tracing techniques. Initial studies have shown promise of these techniques (Gibbs, 2008; Vale *et al.,* 2016; Upadhayay *et al.,* 2018), but it is needed more expansively across varying landscape types to understand the source and timing of sediment and organic matter release to the fluvial environment, and the landscape characteristics that control these processes;
- Increase the collection of particle size data of suspended sediment so that sediment properties can be better understood in relation to the light attenuation effect and turbidity response, and be used to assess suitability of turbidity method;
- Further evaluation of the implications of particle size and suspended material composition on other turbidity methods, and water clarity surrogate technologies; and
- Strategic investment is needed at a national level if turbidity is unsuitable for continued use in some landscapes, the assessment of other indices, such as measures of visual clarity, for monitoring SSC is required.

One aspect of this future direction (source tracing) was considered for inclusion in this thesis. Analytical work contributing to a source tracing experiment has been completed but is not included in the final document due to a delay in the delivery of the analytical data within the PhD timeframe. The source tracing experiment was started in 2018 and focused in the Taieri Catchment of Otago, and has used a relatively new sediment source tracing technique that

uses environmental biotracers (Compound Specific Stable Isotopes (CSSI)) to link sediment samples collected from stream flow or depositional areas with sources from outside the fluvial environment (see: Gibbs, 2008). As the technique uses the isotopic signature of the fatty acids within soil and sediment samples that are bespoke to vegetation type, the technique that is primarily used to source discriminate sediment, also discriminates the organic matter component. Sample collection selected the major land covers in the Taieri catchment (pasture, tussock grassland, low productivity grassland, and exotic forest) across a range of topographies, so that the sources of sediment and organic matter can be identified. The project also quantified the geochemical signature of soils and sediments as tracers for the inorganic sediment component and follow the approach described by Vale *et al.* (2016), and compare this to the source discrimination of the CSSI method. The objective of this thesis is to add value to the existing understanding of intrinsic landscape characteristics that preference higher proportions of organic matter or inorganic sediment, and test method suitability to this application. Few studies have been completed in New Zealand (Gibbs, 2008; Vale *et al.,* 2016) but it is needed more expansively across the country to understand the presence and significance of riverine organic matter in comparison to mineral sediment, and the implications for optical water quality, carbon flux, and relevance of soil erosion control programmes.

The present study, along with Hicks *et al.* (2004), and Hicks *et al.* (2019) are the primary sources of particle size data that are relevant to New Zealand riverine suspended sediments, and there is a substantial shortfall in available data to resolve the complexities of turbidity response to particle size factors. A surge in further work based in New Zealand is occurring (e.g., Dymond *et al.,* 2019; Hicks & Haddadchi, 2019; Horton *et al.,* 2019; Smith *et al.,* 2019). Hicks *et al.* (2019) has shown use of the Sequoia LISST-SL2 with laser diffraction technology (see: Section Two; Table 2.1) that measures particle size distribution in-situ when cable-suspended in stream flow (Hicks *et al.,* 2019; Mikkelsen & Agrawal, 2019). Although successful at collecting depth and flow integrating SSC with particle size data, it is expensive and does not yet offer continuous monitoring opportunities. Thus, further work in understanding the particle size distribution factors are forthcoming, and will substantially improve the dearth of particle size related information in New Zealand.

Continued work examining the optical water quality parameters that were collected as part of the New Zealand National River Water Quality is also under development. The national record provides a 30 year record of visual clarity that has previously been examined by Davies-Colley *et al.* (2014) for use as a surrogate in suspended sediment monitoring. Similar to specific turbidity that normalises turbidity to the mass concentration of particulates, the specific beam attenuation coefficient (i.e., the optical cross-section of particulates) normalises light attenuation estimated from visual clarity for mass concentration of particulates. As such, the beam attenuation coefficient is a potentially useful metric for assessing the parameters that control light attenuation in river waters, and is arguably a better metric for monitoring changes in visual water clarity and the impacts of suspended sediment on ecosystems. Preliminary analysis of the specific beam attenuation coefficient suggest that landscape controls are relevant, like for specific turbidity, and therefore this warrants further investigation for suitability of use in suspended sediment monitoring across different landscapes.

8.3 Turbidity and Environmental Monitoring in New Zealand

Substantial change to New Zealand's strategic framework for freshwater management has occurred since implementation of the Resource Management Act in 1991. Although is it recognised that this is a dynamic space, and standardised methods for environmental monitoring has improved the consistency of environmental data collection. As part of the National Environment Monitoring Standards (NEMS) workflow, a standard for the measurement of turbidity has been developed, with a further standard for determining the suspended sediment underway. However, along with the present study, other research in New Zealand has identified the non-comparability of turbidity methods due to the different response of different sensors (i.e., those operating to EPA 180.1 and ISO 7027) (Jeff Watson, personal communication, November 2019), and even between sensors of the same method (Hughes *et al.,* 2019). This raises the question as to whether the current technology available is appropriate, particularly in New Zealand where the landscape is a mosaic of land uses and landscape typologies (e.g., volcanic, alpine, coastal floodplains, rolling hill country).

Pertinent to the continued use of turbidity, as suggested within the NEMS, will be maintaining the common use of technology (Jeff Watson, personal communication November, 2019), which could be costly and take time to implement, therefore continued use of current turbidity monitoring is inevitable for at least the short term. Despite this however, inconsistent turbidity response even when using the same sensor technology suggest that comparability of turbidity is unlikely, and procedures for maintaining consistency between sensors is paramount (Jeff Watson, personal communication November, 2019). Therefore, investigation into the validity of other indices, such as visual clarity, is highly important but should also consider the spatial and temporal trends that have been identified in the current study.

As highlighted several times within this thesis, the continued use of turbidity is pragmatic, but problematic. Scientists, researchers, and environmental managers alike must consider whether continued use of turbidity is appropriate given the limitations outlined in this thesis. Particularly as a regulatory tool, turbidity cannot be fairly or reasonably used as a standalone threshold due to the over- or under- prediction of SSC that can occur for the same values of turbidity, depending on the properties of the suspended material. So that, for a value of 5 NTU, which is a common threshold in New Zealand regional water plans, based on a suspended sediment-turbidity relationships with a slope coefficient of 2, the equivalent concentration of suspended sediment would be 10 mg L^{-1}, however, a suspended sediment-turbidity slope coefficient of 1.3 (as observed in organic rich catchments, or where fine suspended sediment dominant) a concentration of 6.2 mg L^{-1} would be derived (Figure 8.1). Even under such a simple example it is clearly evident that the effects of land use disturbance would be unequally evaluated between the two examples. The issue this poses to use of turbidity as a regulatory threshold for sediment flux and landscape disturbance is that it might unduly burden landholders in some locations, relative to others. This uncertainty is a significant issue that must be addressed through careful selection of turbidity methods or must at least be justified for use in certain catchments.

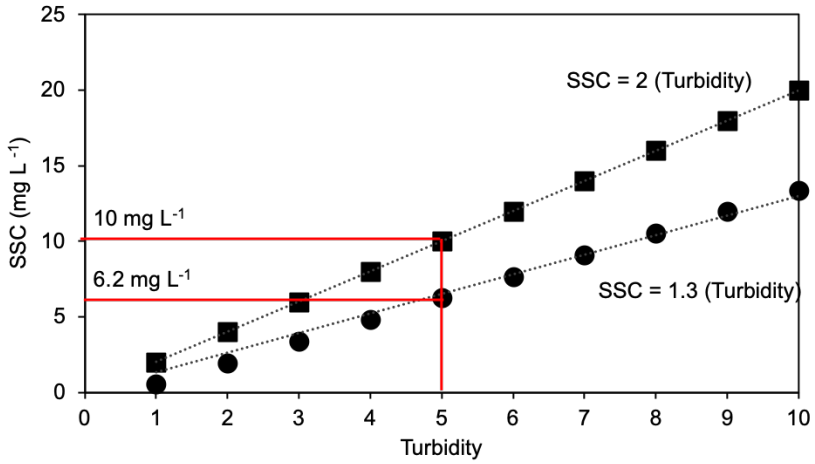

Figure 8.1 Synthetic suspended sediment concentration (SSC) and turbidity for two different possible relationships, where the estimation of SSC from the same value of turbidity is different.

As discussed in Chapters Three to Seven, consideration of the composition and particle size of suspended particulate materials, and the sources within diverse catchments must be taken into account when deriving suspended sediment from turbidity. The implications can be troublesome for suspended sediment-turbidity relationships and are particularly acute to regulatory frameworks where limits on suspended sediment are imposed through thresholds of turbidity, such as those imposed in Australia and New Zealand. By comparison, other countries set their limits on suspended sediment and turbidity is a secondary measure, for example the European Union, Canada, and United States of America (Table 8.1) (Collins *et al.,* 2011; Grove *et al.,* 2015). These regulatory frameworks focus attention on suspended sediment, since that is the variable of harm to aquatic form and function, although suggest use of turbidity as a means of making assessments (e.g., Canada, United States of America) or recommend a threshold of turbidity for implementing assessments (e.g., European Union). However, as described above, a single value of turbidity, as mandated in Australia and New Zealand, does not necessary equate to an exact suspended sediment concentration that is comparable across locations, or may not have direct relevance to the environmental values the thresholds are designed to protect (Grove *et al.,* 2015). These existing targets are subject to the inherent problems associated with suspended sediment monitoring, namely the use of imperfect surrogates like turbidity, that when applied over diverse environments mean water quality recommendations are more like benchmarks rather than regulatory thresholds (Collins *et al.,* 2011). For example, of the New Zealand rivers that were included in the

National River Water Quality Network 22% had median turbidity values that exceeded the regulatory 5 NTU threshold (see: Chapter Seven). These catchments included a mixture of South Island alpine catchments with paraglacial landforms, and catchments across both the North Island and South Island with large areas of pastoral agriculture and pockets of other significant land uses, like plantation forestry. Therefore, it is not appropriate to enshrine a single threshold into regulation that is appropriate for all these landscapes that may produce distinct suspensions of suspended material reflective of catchment characteristics other than those produced by anthropogenic disturbance.

In light of these turbidity method limitations, investment in alternatives is warranted, although other indices will require substantial validation before abandoning use of turbidity, however, little discussion of visual clarity indices is evident in these regulatory frameworks (Table 8.1). Visual clarity, while included in Australian and New Zealand frameworks, and measured as part of the New Zealand National River Water Quality Network, has received substantially less recognition for suitability in suspended sediment monitoring, despite its wide use in other disciplines. The use of visual clarity is hampered by the development of continuous measurement technologies, rather the method requires discrete point measurements to be collected in the field using a Secchi or black disk (Davies-Colley *et al.,* 2014; West *et al.,* 2013; West & Scott, 2016). Despite this, some refer to visual clarity as the preferred metric over turbidity, as visual clarity, unlike turbidity, has more environmental relevance as it is calibrated to a *proper* scientific quantity, i.e., visual range measured in metres (Smith *et al.,* 1997; Smith & Davies-Colley, 2001; West & Scott, 2016). Despite this, turbidity as a relative index of water cloudiness continues to be expansively used for continuous measurement applications, often by default. In the short term (until alternatives are available) a balance must be found between the spatially extensive collection of continuous turbidity for estimating suspended sediment, and the need for exact quantification of suspended sediment and its composition. The future development of New Zealand's regulatory framework should develop a limit set on suspended sediment where this is the variable of interest, and follow international protocols like that of the European Union. In this way standardised techniques (i.e., the turbidity NEMS) for the measurement of turbidity can only be used as a measure of suspended sediment when an existing suspended sediment-turbidity relationship has been established, and validated. It is these decisions, and the intended use for comparability, or environmental consequence that should drive the use of any surrogates in suspended sediment research and monitoring.

Table 8.1 Summary of regulatory frameworks for Canada, United States of America, European Union, and Australia and New Zealand, with general descriptions of relevant thresholds and monitoring criteria for suspended sediment and turbidity, and where relevant visual clarity. (Adopted from: Bilotta and Brazier (2008) and Collins et al. (2011).

			General Threshold Limits		
Authority	Policy	Country	Suspended Sediment	Turbidity	Visual Clarity
Canadian Council of Ministers of the Environment (CCME)	Canadian Environmental Quality Guidelines for protection of Freshwater Aquatic Life	Canada	Low flow, high flow, and short lived concentration change limits set. General limit 25 mg L^{-1}.	Turbidity as measure for change from baseline levels[1] applied to actual and potential spawning sites. Thresholds range 5 – 8 NTU.	
United States Environmental Protection Agency	National Recommended Water Quality Criteria US EPA 2007 Ecoregional Criteria Solids Suspended and Turbidity	United States of America	Suspended solids should not reduce depth for photosynthetic activity.	Turbidity use in aesthetic quality assessments. Turbidity to set limit on suspended particulate matter Thresholds range 5 – 50 NTU.[2]	
European Union Freshwater Fisheries Directive	Freshwater Fisheries Directive (78/659/EEC) and (2004/44/EC); Quality of Water Intended for Human Consumption (98/83/EC); Water Framework Directive (2000/60/EC)	European Union	Concentrations should not exceed 25 mg L^{-1} in waters suitable for salmonid and cyprinid fish populations.	Maintain levels <4 NTU for drinking water.[3] Marine and freshwater application to assessing effects of sediment, and application to other water quality parameters.[4]	
Australian and New Zealand Environment and Conservation Council (ANZECC) Agriculture and Resource Manage Council of Australia and New Zealand	Australia and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC 2000)	Australia and New Zealand	Suspended sediment limits based on turbidity for different regions.	Turbidity limits applied to lowland rivers, freshwater lakes and reservoirs. Thresholds range 2-50NTU depending on region.	Visual clarity monitored by Secchi disc, and not be reduced by more than 20%. Swim-ability defined by 1.6m horizonal visual range.[5]

[1]CCME (2002). Canadian Water Quality Guidelines for the Protection of Aquatic Life – Total Particulate Matter
[2] EPA (2002). EPA Ecoregional Criteria
[3] WHO (2017). Drinking Water Parameter Cooperation Project.
[4] Water Framework Direction (2015). Water Resources, England and Wales, 2015 No 1623.
[5]ANZECC (2000) Australian Water Quality Guidelines for Fresh and Marine Waters – National Water Quality Management Strategy. Australian and New Zealand Environment and Conservation Council: Canberra, Australia.

9 Conclusion

The transfer of sediment from the terrestrial surface to the fluvial system is an important component of sediment routing systems, however, the mechanisms that effect inorganic sediment delivery also influence organic matter delivery. This thesis has addressed: 1) how much particulate material under base flow is conveyed through rivers in southern New Zealand, and the relative importance of organic matter flux; 2) how different landscape units contribute to the particulate load; and 3) how the use of turbidity as a surrogate for suspended sediment is affected by differences in particulate composition, size and optical properties.

Organic matter is transported concomitantly with suspended sediment, and allochthonous organic matter sources delivered from outside the fluvial environment are a small, but important component of all suspended load in New Zealand rivers. By quantifying the particulate organic matter flux, this thesis also has been able to report conservative estimates of organic carbon yields for southern New Zealand, which has not been previously quantified. Riverine organic matter has different optical properties to inorganic sediment, and as such its presence in water affects turbidity, and the assessment of the role of organic matter provides a novel contribution to existing research showing that suspended sediment, POM and turbidity and intimately connected.

Additionally, this thesis has critically reflected on the use of turbidity as an environmental indicator as mandated in New Zealand regulatory thresholds. It is the composition (POM and CDOM) and particle size factors (proportion of clay, silt and sand) that complicate the use of surrogates like turbidity, particularly when the purpose of turbidity data collection is to derive records of suspended sediment. Therefore, although turbidity is a pragmatic tool, its use is problematic, being particularly flawed in certain landscapes. Discontinuing use of turbidity is unlikely an option given the that turbidity is imbedded is existing monitoring frameworks, however, metrics like POM% and specific turbidity may be useful tools for diagnosing the appropriate conditions for turbidity use as a suspended sediment surrogate. The use of these metrics should be used more widely for classifying the effects of organic composition and particle size on riverine suspended materials, and be used to evaluate whether turbidity is suitable and validate existing records.

These overarching themes of the role of particulate organic matter, sediment characteristics, and turbidity were the focus of this thesis, and resolved by considering six research questions, which are:

RQ1: Is POM an important component of stream suspended load, and does it affect suspended sediment-turbidity relationships?

Particulate organic matter can be a substantial component of stream suspended load (Chapters Three and Four). Chapters Five, Six, and Seven show that particulate organic matter and coloured dissolved organic matter have different light attenuation responses to inorganic suspended sediment. This introduces noise in suspended sediment-turbidity relationships.

RQ2: How much POM is transported by southern New Zealand rivers, and what is the association of this POM to suspended sediment and carbon flux?

Suspended sediment composition across southern New Zealand is non-homogenous, primarily due to organic composition where particulate organic matter can be a significant component of the suspended material fluxed through rivers: <10%, or much higher at 50 – 80% (Chapters Four). POM contributes a significant proportion of organic carbon to oceanic sequestration.

RQ3: How much POC is discharged through rivers in Southern New Zealand and what is the POC yield for 84 southern New Zealand catchments?

The riverine organic flux exports 0.04 – 0.4 t km^{-2} a^{-1} of particulate organic carbon into Fouveaux Strait, and between 0.4 – 2.7 t km^{-2} a^{-1} into the South East Pacific Ocean (Chapter Four). This particulate organic carbon comprises around 23% of the organic matter exported to the southern oceans.

RQ4: What extrinsic and intrinsic catchment characteristics control POM concentration and POM proportions?

Intrinsic (within catchment) and extrinsic (external to catchment) variables inherently affect particulate organic matter by enabling and conditioning slopes for the erosion of particulate organic matter with sediment. Intrinsic variables, such as discharge and flow characteristics, landcover, and lithology affect the concentration and proportion of particulate organic matter of the total suspended particulate materials (Chapter Four).

RQ5: What effect do organic composition and particle size have on turbidity measurements derived from different nephelometric methods (EPA 180.1 and ISO 7027)?

Chapters Five, Six, and Seven show that that different nephelometric turbidity methods produce inconsistent responses. This is due to variability in composition and particle size that affect the light source of nephelometric turbidimeters. Particulate organic matter causes an unpredictable scattering effect, and coloured dissolved organic matter can absorb light within the visual light spectrum. Particle size controls the shape and density of inorganic suspended sediment, and controls refractive and scattering principles. Therefore, variation in composition (POM and CDOM) and particle size factors (proportion of clay, silt and sand) give different turbidity values.

RQ6: What influence do catchment characteristics have on suspended sediment–turbidity ratings across New Zealand?

Turbidity (recorded as unit NTU) across the New Zealand National River Water Quality Network is suspectable to variations in particle size and composition of suspended particulates (Chapter Seven). This has a notable effect on SSC-turbidity relationships and has limitations for the comparability, and relevancy, of suspended sediment data derived from turbidity in New Zealand. Extrinsic and intrinsic catchment characteristics define the composition and particle size distribution of riverine suspended material across New Zealand, and therefore suspended sediment-turbidity ratings are bespoke to individual catchments.

Turbidity is a pragmatic, but problematic surrogate for suspended sediment monitoring, especially where particulate organic matter, coloured dissolved organic matter, or the lithology of a catchment preferentially erodes to ultra-fine suspensions of clay and silt. These factors make turbidity an unsuitable surrogate for suspended sediment concentration in many landscape units across New Zealand.

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11 Appendix

11.1 Research Outputs During PhD

Conference Presentations and Posters as Lead Author:

2019 The effect of fine particulates and particle size on nephelometric turbidity. Oral presentation New Zealand Hydrological Society conference in Rotorua.

2018 Particulate organic matter, suspended sediment and turbidity in Otago, New Zealand tussock grasslands. Poster at European Geosciences Union General Assembly conference in Vienna, Austria.

2018 Particle facilitated transport of metals in Southland and Otago, New Zealand. Poster at Integrated Hydrosystem Modelling conference, Tübingen, Germany.

2017 Organic matter, suspended sediment and turbidity in Otago Tussock Grasslands. Oral presentation at New Zealand Hydrological Society conference in Napier.

2017 Turbidity's sensitivity to organic matter. Oral presentation at New Zealand Hydrological Society conference in Napier.

2017 Particulate organic matter and its influence on predicting suspended sediment concentrations when derived from nephelometric turbidity. Oral presentation at International Society for River Science conference in Hamilton.

2017 Stream Flow Particulates and Turbidity: Shedding light on Organic Matter and Suspended Sediment. Oral presentation part of the Department of Geography, University of Otago seminar series.

2016 Why do suspended-sediment turbidity relationships fail? Oral presentation at New Zealand Hydrological Society Conference in Queenstown.

Workshops:

2018 New Zealand Hydrological Society Technical Workshop "Discover the real dirt in hydrology", held in Palmerston North.
Oral Presentation: Turbidity – More than just Sediment

2017 New Zealand Hydrological Society Technical Workshop "Are you making a difference in field hydrology?", held in Dunedin.

2017 Horizons Regional Council workshop with Environmental Science Team and NEMS Steering Group Members.
Oral Presentations:
1. Suspended Sediment Turbidity Relationships
2. Stream Flow Particulates and Turbidity, the Impact of Particulate Organic Matter

Publications and Reports:

Bright, C.E., & Mager, S.M. (2020). A national-scale study of spatial variability in the relationship between turbidity and suspended sediment concentration. *River Research and Application, 1-11.* DOI: 10.1002/rra.3679.

Bright, C.E., Mager, S.M., & Horton, S.L. (2020). Response of nephelometric turbidity to hydrodynamic particle size of suspended fine sediments. *International Journal of Sediment Research, 35,* 444-454. DOI: 10.1016/j.ijsrc.2020.03.006.

Bright, C.E., Mager, S.M., & Horton, S.L. (2020). Catchment-scale influence on riverine organic matter in southern New Zealand. *Geomorphology, 353.* DOI:10.1016/j.geomorph.2019.107010

Mager, S.M., Bright, C.E., and Horton, S.L. (2018). Glendhu Forestry Water Quality Monitoring Project: Summary Report.

Bright C.E., Mager, S.M. and Horton, S.L. (2018). Predicting suspended sediment concentration from nephelometric turbidity in organic-rich waters. *River Research and Applications*, *2018, 1 –9.* DOI 10.1002/rra.3305.

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Bright, C.E. and Mager, S.M. (2016). Contribution of particulate organic matter to riverine suspended material in the Glendhu Experimental Catchments, Otago, New Zealand. *Journal of Hydrology (NZ), 55, 2,* 89 – 105.

11.2 Research Papers

1. Contribution of particulate organic matter to river suspended material in the Glendhu Experiment Catchment, Otago, New Zealand.

Reference
Bright, C. E., & Mager, S. M. (2016). Contribution of particulate organic matter to riverine suspended material in the Glendhu Experimental Catchments, Otago, New Zealand. *Journal of Hydrology (NZ), 55,* 89–105.

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Contribution of particulate organic matter to riverine suspended material in the Glendhu Experimental Catchments, Otago, New Zealand

C. E. Bright and S. M. Mager

Department of Geography University of Otago, PO Box 56, Dunedin, New Zealand
Corresponding author: chrissy.bright@otago.ac.nz

Abstract

Turbidity is a widely-used water quality indicator that is used to infer the volume of suspended sediment transported through riverine systems. In New Zealand, regional limits on turbidity are a component of water plans, where excessive turbidity is often used to indicate land disturbance. Turbidity of river water is a function of both organic and inorganic constituents. Measurement of inorganic suspended sediment is common; however, to date there has been little work determining how much of the total suspended material in rivers may be organic material, and how this affects relationships between suspended particulates and turbidity. The objective of this study was to determine what portion of total suspended material occurs as particulate organic matter and what effect this has on the relationship between suspended sediment and turbidity. Particulate organic matter was determined by a loss on ignition method that supplemented traditional methods for determining suspended sediment concentration. In the Glendhu Experimental Catchments, Otago, New Zealand, particulate organic matter contributed 45% of the total suspended material from a tussock catchment and 60% of the total suspended material from a forested catchment, although concentrations were highly variable: 0.6–20.3 mg L^{-1} (equivalent to 10-80%) in the tussock catchment and 0.7–39.7 mg L^{-1} (equivalent to 23–95%) in the forested catchment. These data suggest that particulate organic matter can represent a large portion of total suspended material in these catchments. The presence of dissolved organic material may also interfere with turbidity measurements, and contribute to uncertainty in deriving turbidity-suspended sediment relationships in organic-rich rivers.

Keywords

turbidity; suspended material; particulate organic matter; suspended sediment concentration

Introduction

Quantifying the amount of particulate material in rivers and streams is an important aspect of monitoring water quality because it is associated with the transport of nutrients, contaminants, pesticides, heavy metals, and pathogens (Griffiths, 1981; Walling, 2005; Gray and Gartner, 2009; Hughes *et al.*, 2012). Total suspended material (TSM) is composed of organic and inorganic fractions, and both types of suspended material are important contributors to stream water turbidity (Fig. 1). Turbidity is an inverse measure of water clarity, therefore turbidity increases due to the presence of suspended material, gases and some dissolved

2. Catchment-scale influence on riverine organic matter in southern New Zealand.

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Author Contribution
Lead author, project design and implementation (CEB), field data collection and laboratory analysis (CEB, SMM, SLH), data analysis and interpretation (CEB), editorial drafting and editing (CEB, SMM), valuable review and editing inputs from (SLH).

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Catchment-scale influences on riverine organic matter in southern New Zealand

C.E. Bright *, S.M. Mager, S.L. Horton

School of Geography, University of Otago, PO Box 56, Dunedin, New Zealand

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ABSTRACT

Riverine particulate organic matter (POM) is a critical vector for nutrient cycling of carbon at both regional and global scales. POM and suspended sediment (SS) are transported concomitantly through rivers, and their concentrations change in association to landscape transformations and natural fluctuations. The proportion of POM to SS mobilised in rivers under base flow is an important component of carbon flux to oceans, and is a useful metric for understanding hillslope–river coupling and hydraulic connectivity. We quantified POM during base flow conditions in southern New Zealand to assess the role of different catchment characteristics that control the spatial variability of organic matter in the fluvial environment. The proportion of POM to total suspended material (TSM) can be <5%, or much higher at 50–80% across southern New Zealand, with the highest concentrations associated with lowland agricultural catchments. Particulate organic carbon yields were estimated to be between 0.04 and 2.7 t km^{-2} a^{-1} discharged into the Pacific Ocean. The POM% responds to both intrinsic and extrinsic catchment characteristics, affecting the availability of organic material and mechanisms for transport including vegetation cover, topographic controls, and hydrological controls. Across southern New Zealand it is evident that riverine organic matter is spatially organised and connected to broader hillslope processes, albeit difficult to predict at the catchment scale.

1. Introduction

Riverine particulate organic material (POM) sequesters 90–240 Mt a^{-1} of carbon globally and is a small, but significant, component of the global carbon budget (Hope et al., 1997; Lyons et al., 2002). It is estimated that POM accounts for up to 20% of total carbon export, 60% of total nitrogen export, and 90% of total phosphorus export (Meybeck, 1982; Sanchez-Vidal et al., 2013). Thus, riverine POM is a critical vector for nutrient cycling at both regional and global scales, particularly in carbon cycle studies with an emphasis on determining particulate organic carbon (POC) fluxes (e.g., Meybeck, 1993; Ludwig and Probst, 1996; Robertson et al., 1999; Lyons et al., 2002; Wu et al., 2007). POC is a subset of total organic carbon (TOC), with the other component being dissolved organic carbon (DOC). POM flux is connected to hillslope processes, denudation, and suspended sediment (SS) flux; so that understanding the flux of POC (as a subset of POM) requires consideration of extrinsic (external to the catchment, e.g., rainfall) and intrinsic (within catchment, e.g., land cover and hydrology) catchment characteristics to inform source land uses and pathways.

Discharge is a critical intrinsic catchment variable driven by rainfall in catchments, although the observed behaviour of organic matter with discharge is complex, often confounded by antecedent conditions and storm fluctuations (Hope et al., 1994; Coynel et al., 2005; Sabater et al., 2006). Catchment hydrology, including runoff generation and hydrological flow pathways affect the quantity and quality of organic matter by controlling the contribution of allochthonous or autochthonous sources (Hope et al., 1994; Robertson et al., 1999; Sanchez-Vidal et al., 2013). POM concentration typically increases with discharge, although the relationship is often weak as organic matter can be delivered to, or become, temporarily diluted as flow changes (e.g., Zhang et al., 2009). Consequently, base flow and event flow POM responses are typically observed separately (Meybeck, 1982; Coynel et al., 2005; Zhang et al., 2009; Sanchez-Vidal et al., 2013; Madej, 2015), although focus is primarily on event flow behaviour. Discharge typically explains <30% of the variation in concentration and ratio of POM to suspended material, and unit stream power explains <20%; suggesting that there are other more significant controls (Naiman, 1982; Madej, 2015).

Carbon supply is affected by season, influencing sediment and organic matter storage and their release into the fluvial environment (Hope et al., 1994). Season controls the timing of organic matter availability, and the input to streams depends on biological demand. The release of carbon from catchments is strongly controlled by the effects temperature and rainfall impart on biological production (Meybeck, 1982; Hope et al.,

* Corresponding author.
E-mail address: christina.bright@hotmail.com (C.E. Bright).

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RESEARCH ARTICLE

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Predicting suspended sediment concentration from nephelometric turbidity in organic-rich waters

Christina E. Bright | Sarah M. Mager | Sophie L. Horton

Department of Geography, University of Otago, Dunedin, New Zealand

Correspondence
Christina Bright, Department of Geography, University of Otago, PO Box 56, Dunedin, New Zealand.
Email: chrissy.bright@otago.ac.nz

Abstract

Nephelometric turbidity is an optical index for the side scattering of light caused by fine particles suspended in water. When a mixed composition of suspended inorganic and organic materials, including dissolved organic material, is present, turbidity measurements can be affected by the different optical properties of the organic and inorganic materials present, and different turbidimeters are more or less sensitive to these influences. Two different methods of nephelometric turbidity measurement were assessed (using instruments confirming to two different turbidity standard methods: EPA 180.1 and ISO 7027). We investigated the influence of particulate organic matter and coloured dissolved organic matter on relationships between turbidity and suspended sediment concentration for rivers in diverse Otago catchments, in the South Island of New Zealand. The presence of organic matter and dissolved colour affected turbidity measurement owing to light absorption; however, turbidity measurement following the ISO 7027 standard, which specifies near infrared radiation at wavelengths where organic absorption is very weak, was less affected by organics. As a result, rating equations between suspended sediment and turbidity may be significantly different with ISO 7027 compared with EPA 180.1 methods.

KEYWORDS

nephelometry, particulate organic matter, suspended sediment concentration, turbidity

1 | INTRODUCTION

Turbidity, quantified in nephelometric units, is a widely used surrogate indicator of suspended particles in water bodies employed by researchers and environmental monitoring agencies (Kitchener, Wainwright, & Parsons, 2017). In the broadest sense, water turbidity is inversely related to water clarity, in terms of light penetration and visual clarity, because the presence of suspended particles within a water column acts to decrease light penetration and visual clarity and causes light scattering, of which turbidity is a relative index of the side scattering of light (Davies-Colley & Smith, 2001). Poor water clarity diminishes light penetration through the water column and causes reduced photosynthesis and aquatic habitat quality, whereas reduced visual clarity has a deleterious impact on recreational water use, aesthetic values, and human health (Davies-Colley & Close, 1990; Davies-Colley & Smith, 2001; Hughes, Davies-Colley, & Elliot, 2015; Sadar, 2004; Smith, Davies-Colley, Knoef, & Slot, 1997). From an environmental monitoring perspective, turbidity is an inexpensive and convenient proxy measure of the "cloudiness" of water and provides an inexpensive relative index of the amount of particulate contaminants from land use disturbance, principally as suspended sediment concentration (SSC; Ankcorn, 2003; Gray & Gartner, 2009). However, turbidity is not a physical quantity; rather, it is a convenient relative index, used to predict the quantity of suspended particulates in a water column (Davies-Colley & Smith, 2001; Kitchener et al., 2017). Its use is problematic, however, because particles have different light scattering properties; and these particulate properties (e.g., size, shape, and composition) contribute different amounts of light scatter that result in noisy or poor relationships between the physical quantity of suspended sediment and observed turbidity.

Turbidimeters come in many different forms but, in principle, operate by using a light-emitting source that interacts with water

4. Response of nephelometric turbidity to hydrodynamic particle size of fine sediments.

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Bright, C.E., Mager, S.M., & Horton, S.L. (2020). Response of nephelometric turbidity to hydrodynamic particle size of suspended fine sediments. *International Journal of Sediment Research, 35,* 444-454. DOI: 10.1016/j.ijsrc.2020.03.006.

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Original Research

Response of nephelometric turbidity to hydrodynamic particle size of fine suspended sediment

Christina Bright*, Sarah Mager, Sophie Horton

School of Geography, University of Otago, PO Box 56, Dunedin, New Zealand

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ABSTRACT

Turbidity is used as a surrogate for suspended sediment concentration (SSC), and as a regulatory tool for indicating land use disturbance and environmental protection. Turbidity relates linearly to suspended material, however, can show non-linear responses to particulate organic matter (POM), concomitant with changes in particle size distribution (PSD). In the paper the influence of ultra-fine particulate matter (UFPM) on specific turbidity and its association with POM in suspended sediment are shown for alpine rivers in the Southern Alps of New Zealand. The approach was two-fold: a field-based investigation of the relations between SSC, POM, and turbidity sampled during event flow; and experimental work on hydrodynamic particle size effects on SSC, POM, PSD, and turbidity. Specific turbidity changes over event flow and are sensitive to increasing proportional amounts of sand, UFPM, and POM in suspension. Furthermore, the UFPM is the size fraction (<6 μm) where POM increases. The implications of the current study are that the slopes of turbidity-SSC relations are undesirable in locations that may be dominated by cyclic release of POM or distinct pulses of fine-grained material. At locations where the turbidity-SSC slopes approximate 2, the POM proportion is usually <10% of the total suspended load. However, when turbidity-SSC slopes are <1 this is likely caused by high amounts of side-scatter from UFPM concomitant with higher proportions of POM. Thus, the use of turbidity as a proxy for determining SSC may have serious consequences for the measurement of representative suspended sediment data, particularly in locations where POM may be a significant contributor to overall suspended load.

1. Introduction

Riverine suspended material is a mixture of mineral and biogenic material that are produced by land disturbance and physical weathering. Understanding the sources and pathways of suspended sediment is one of the main approaches to determining physical weathering rates in geomorphology (e.g., Milliman & Meade, 1983; Turowski et al., 2010; Walling & Fang, 2003), however, quantifying material in suspension also is an indicator for environmental degradation (e.g., Davies-Colley et al., 2014). Thus, inquiry into suspended material in rivers principally operates in two ways: as a measure of erosion and mass wasting processes, and as an indicator of land disturbance, most often associated with the effects of land cover change (e.g., forest clearance) and ensuring aquatic ecosystem health (e.g., Davies-Colley & Smith, 2001). Quantifying suspended material is challenging, and standard methods require the collection of discrete grab samples and laboratory analysis; and so, its continuous measurement is laborious. Instead, researchers and environmental managers alike opt to quantify riverine suspended sediment using turbidity as a proxy (e.g., Foster et al., 1992; Gipple, 1989), by establishing ratings between in situ turbidity and suspended sediment measurements. However, the physical characteristics of suspended material, that is, particle size, shape, color, density, and refractive index behave differently and yield different optical outputs, which undermine the precision of measured suspended sediment to turbidity relations (Kitchener et al., 2017; Sadar, 1999). Despite the recognition of these different optical properties, nephelometric turbidity persists as a convenient measure in environmental monitoring programs, as a proxy indicator of land disturbance and suspended sediment.

Suspended particulate load is usually <2 mm in size, comprised mostly of silt (2–63 μm) and clay (<2 μm) sized material (Omar &

* Corresponding author.
E-mail address: christina.bright@hotmail.com (C. Bright).

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5. A national-scale study of spatial variability in the relationship between turbidity and suspended sediment concentration.

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Bright, C.E., & Mager, S.M. (2020). A national-scale study of spatial variability in the relationship between turbidity and suspended sediment concentration. *River Research and Application, 1-11.* DOI: 10.1002/rra.3679.

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Data statement
Underlying data for this study was provided by NIWA Taihoro Nukurangi, sourced from New Zealand's National River Water Quality Network (NRWQN).

Author Contributions
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A national-scale study of spatial variability in the relationship between turbidity and suspended sediment concentration and sediment properties

Christina E. Bright | Sarah M. Mager

School of Geography, University of Otago, Dunedin, New Zealand

Correspondence
Christina E. Bright, School of Geography, University of Otago, PO Box 56, Dunedin, New Zealand.
Email: christina.bright@hotmail.com

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Abstract

Turbidity, an index of light side-scattering, depends on the mass concentration of suspended sediment (SS) within water. Turbidity of river water is regulated by the presence of suspended particulate matter and is used to identify visual changes in response to SS. We used data from the New Zealand National River Water Quality Network, to calculate "specific turbidity" (*K*; turbidity normalised to mass concentration of suspended particulates). Specific turbidity is shown here to be an effective metric to assess the effect of suspended material composition and particle size distribution of suspended particulate matter over different landscape characteristics, and the effect on SS-turbidity relationships. Of the catchment characteristics considered in our study, specific turbidity was most responsive to lithological factors, and relatively insensitive to land use and soil parameters. Decreasing particle size has a positive linear response to *K*, attributed to the higher proportion of ultra-fine particulate material that is generated by certain lithologies, underscoring the lithological influence on *K*. SS-turbidity relationships, therefore, vary spatially across New Zealand's national record of water clarity, and *K* is considered a useful index for inter-catchment comparison of SS than turbidity alone.

KEYWORDS
NRWQN, organic matter, particle size distribution, suspended sediment, turbidity

1 | INTRODUCTION

Turbidity is a water quality indicator that is widely used in regulatory monitoring across regional and national scales as a surrogate measure of sediment concentrations. Its use, for example in Canada, the United States of America, European Union, and Australia and New Zealand (Bilotta & Brazier, 2008; Collins et al., 2011), is directed towards a low-cost, readily available method for environmental monitoring limits as a means of establishing drinking water, recreational, and/or environmental thresholds (Ankcorn, 2003; Gray & Gartner, 2009). Turbidity is a useful continuous monitoring metric for understanding riverine visual clarity and suspended sediment (SS) fluctuations, but its use can be problematic (Rymszewicz et al., 2017). As a measure of light attenuation in water, turbidity probes and metres use fixed angle sensors to detect light scattering caused by suspended particulates (Sadar, 1998). Different turbidity methods use different spectrums of wavelength, and in some methods the type of source light may be reduced by absorption caused by coloured dissolved organic matter (CDOM), and such interferences may impede deriving SS–turbidity ratings (Ankcorn, 2003; Gipple, 1995; Hongve & Akesson, 1998; Omar & MatJafri, 2009).

It is, however, well established that turbidity–SS relationships can be highly variable over temporal scales; both seasonally and during individual hydrographic events (e.g., Gipple, 1995; Jastram et al., 2010; Landers & Strum, 2013; Lewis, 1996; Navratil et al., 2011; Walling, 1988; Wass & Leeks, 1999). Natural sediments are a complex

11.3 Raw Data

1. Southern New Zealand POM

Southern New Zealand Turbidity, SSC, POM and carbon data (period 2012 - 2018)

Key for water quality parameters

NTU - Turbidity (as NTU)
FNU - Turbidity (as NFU)
POM - Particulate organic matter (mg L^{-1})
SSC - Suspended sediment concentration (mg L^{-1})
POM% - Percentage of POM of TSM
TOC - Total organic carbon (mg L^{-1})
DOC - Dissolved organic carbon (mg L^{-1})
POC % of TOC - Percentage of TOC that is POC (derived POC=TOC-DOC)
DOC Yield - Dissolved organic carbon yield (t/km2/y)
POC Yield - Particulate organic carbon yield (t/km2/y)
SSY - Suspended sediment yield (t/km2/y)

River	NTU	FNU	POM	SSC	TSM	POM %	TOC	DOC	POC % of TOC	DOC Yield	POC Yield	SSY
Acton			1.6	7.1	8.7	18.0	2.9	2.1	41.8	8.3	4.8	28.5
Ahuriri	2.3	3.8	2.6	6.3	17.2	45.8	2.7	1.4	75.5	3.5	4.7	15.4
Ahuriri-Upper	485.0		3.5	425.4		1.0	3.0	1.3	87.8	1.8	3.6	580.8
Aparima			0.9	5.1	5.9	14.5	4.3	3.9	1.3	2.6	0.0	3.4
Aparima Upper (West)			0.5	2.1	2.5	18.0	2.5	2.3	15.8	1.9	0.3	1.8
Arrow	6.5	17.9	3.4	9.7	26.4	11.7	4.9	3.2	53.5	1.5	1.2	7.3
Bannock Burn	0.9	0.8	0.4		0.4	100.0				0.0	0.1	0.0
Birch-hill	1.4	2.9	1.1	5.7		52.2	1.8	1.3	45.5	2.0	1.3	6.7
Buckler Burn	23.3	33.6	2.9	69.3	72.2	4.1				0.0	4.3	131.7
Bush	7.5		2.0	7.5		20.3	2.0	1.1	74.1	2.3	4.4	18.1
Camerons	2.0		2.0	6.6		21.4	2.7	1.7	57.1	5.6	4.8	18.2
Cardrona	2.3	4.4	2.2	8.5	8.8	18.8	4.5	3.5	36.6	1.1	0.5	2.6
Clutha	6.4	13.3	0.6	3.9	4.5	14.3	2.5	2.2	13.8	16.8	2.7	30.4
Dart	174.0	675.0	4.4	227.0	1193.0	1.9	4.5	2.3	73.6	17.0	30.9	4054.5
Deep Stream	1.3	1.6	1.2	3.0	2.3	40.6	5.8	5.2	18.0	3.5	0.9	3.5
Deeps	4.6	6.5	2.7	17.0	19.7	13.7	3.6	2.2	58.6	1.3	1.2	9.8
Dobson	4.5	6.5	1.1	12.9	12.8	10.6	1.6	1.1	59.7	1.9	1.7	24.0
Eglinton			0.5	4.4	4.9	10.2	2.0	1.8	18.6	4.0	0.9	9.8
Flagstaff	2.5	3.1	1.1	2.5	3.4	30.6	2.9	2.4	33.0	0.8	0.4	1.9
Fraser	1.3	1.6	0.9	0.9	1.8	50.9	4.5	4.0	10.2	2.6	0.3	0.6
Glendhu (GH1)	0.7	1.1	0.6	0.6	0.9	67.0	3.8	3.5	17.8	1.2	0.2	0.4
Glendhu (GH2)	1.0	1.3	0.9	0.7	1.0	74.3	3.1	2.7	14.4	1.4	0.3	0.6

River	NTU	FNU	POM	SSC	TSM	POM %	TOC	DOC	POC % of TOC	DOC Yield	POC Yield	SSY
Glendhu Waipori	0.8	1.7	0.6		0.7	88.5				0.0	0.3	0.0
Godley	6.8	7.3	1.0	13.1	14.1	7.0	1.3	0.8	58.9	3.0	3.0	51.3
Greenstone	1.1	2.5	1.3	5.0		19.8	2.3	1.7	43.5	5.3	2.9	14.5
Hakataramea	0.7	0.9	0.8	3.9	4.7	17.3	1.7	1.3	1.7	0.3	0.0	0.9
Hawea	3.7	4.8	0.2	3.2	3.4	5.7	6.3	6.2	2.4	21.3	0.5	11.1
Hooker	46.7	75.8	2.6	47.9	125.8	3.1	2.3	1.1	84.7	6.4	11.7	385.3
Hopkins	121.0		58.4	513.0		10.4	30.5	1.3		3.0	106.0	1211.9
Houndburn	3.6	3.9	2.2	3.9	6.1	37.4	9.4	8.3	18.1	2.0	0.3	1.0
Hunter	3.8		2.7	7.0		27.7	2.7	1.4	75.0	2.5	3.7	12.4
Jollie	2.2	1.4	1.0	9.4	3.4	8.0	1.0	0.5	64.6	1.2	1.0	21.2
Kawarau	13.3	20.4	1.6	76.8	78.3	2.0	2.4	1.6	19.6	5.9	1.7	281.9
Kyeburn	3.4	4.9	0.8	11.0	11.0	8.2	3.0	2.6	23.7	0.9	0.8	36.7
Last Creek	0.8	0.9	0.5	1.1	1.3	44.0	2.6	2.4	25.2	1.2	0.3	1.3
Lee Stream	4.8	6.8	2.6	5.7	8.4	30.0	8.5	7.2	20.0	1.8	1.0	5.9
Lindis	3.5	4.4	0.4	5.9	6.3	5.8	5.6	5.4	5.0	0.0	0.0	0.0
Low Burn	0.8	0.9	0.7	0.1	0.9	83.3				0.0	0.1	0.0
Lug Creek	0.6	0.8	0.7	1.0	1.6	43.4	1.9	1.5	27.4	0.7	0.3	0.7
Macaulay	3.8	4.1	1.3	5.8	4.9	22.3	1.7	1.1	57.4	1.6	2.4	9.1
Maerawhenua	3.3	4.9	1.8	4.6	6.5	28.5	3.1	2.2	14.4	0.8	0.2	1.7
Makarewa			1.6	4.6	6.2	26.0	8.4	7.6	14.7	3.2	0.5	1.9
Makarora (Upper)	1.9	8.8	0.9	4.1	12.5	31.5	2.0	1.6	34.6	11.4	8.1	41.6
Manuherikia	2.7	4.2	0.9	9.1	10.0	8.9	3.4	3.0	15.8	0.7	0.1	2.1
Mararoa			0.8	2.0	2.8	27.4	1.7	1.3	7.6	1.7	0.2	2.6
Mataura	62.2	79.1	3.9	71.9	75.8	5.2	6.6	4.6	7.4	4.1	0.4	64.5
Mataura-Upper			1.5	25.7	27.1	5.5	2.9	2.2	18.7	3.7	0.9	42.1
Mataura Upper (East)			0.6	5.7	6.3	9.2	3.5	3.2	10.4	3.1	0.4	5.6
Mataura Upper (West)			0.8	2.5	3.2	24.3	1.6	1.2	25.6	0.6	0.2	1.2
Matukituki	4.2		2.6	17.4		8.0	3.6	2.3	55.6	15.7	14.4	244.1
Matukituki-Upper	8.7	13.8	0.6	10.3		8.7	2.4	2.1	19.2	9.3	2.0	43.7
Omarama	1.4	3.0	1.6	6.7	8.4	19.7	2.2	1.4	37.4	0.4	0.2	2.0
Oreti			1.4	5.2	6.6	21.8	4.5	3.8	24.5	1.3	0.4	1.7
Oreti-Upper			2.5	2.3	4.8	52.9	2.2	0.9	27.9	1.3	0.9	3.4
Otautau			9.5	30.5	40.0	23.7	11.8	7.1	3.1	3.2	0.2	13.8
Otematua	0.5	0.8	0.6	1.8	2.4	24.8	1.6	1.3	36.3	0.6	0.3	0.8
Pigburn	1.3	2.0	0.8	3.8	4.4	18.2	3.5	3.2	20.7	0.9	0.2	1.1
Pomohaka	9.3	12.3	0.9	10.6	11.5	8.2	4.8	4.3	20.2	1.8	0.4	4.5
Rees	23.0	73.0	3.1	65.0	1285.0	2.9	3.6	2.1	60.2	5.8	15.2	1330.7
Roaring Meg	2.8	4.2	1.1	5.7	6.8	15.8					0.4	2.5
Routeburn	3.1	7.7	1.4	4.1	11.6	24.6	2.0	1.3	53.5	5.5	4.9	54.5

River	NTU	FNU	POM	SSC	TSM	POM %	TOC	DOC	POC % of TOC	DOC Yield	POC Yield	SSY
Shotover	27.4	45.0	2.5	68.0	171.0	2.8	3.8	2.5	51.5	4.5	7.6	532.3
Silver Stream	0.8	0.9	0.6	2.4	1.8	36.5	5.1	4.8	9.2	1.5	0.2	1.6
Simpson	2.6	4.0	1.8	6.0	7.8	28.0				0.0	2.1	9.0
Six Mile Creek	0.7	0.8	0.5	4.0	0.8	54.8	1.7	1.5	38.0	0.7	0.4	1.7
Sowburn	0.5	0.7	0.5	1.0	0.9	46.4	1.6	1.4	35.6	0.9	0.3	1.0
Taieri @ Henley	6.9	8.7	1.7	9.0	10.7	16.1				0.0	0.6	5.8
Taieri @ Hyde	7.6	10.2	1.3	13.7	11.6	16.1	3.9	3.2	39.1	1.3	0.6	12.5
Taieri @ Middlemarch	8.5	9.5	1.6	9.5	10.8	12.4	4.5	3.8	28.7	1.5	0.7	10.4
Taieri @ Outram	5.8	11.6	2.0	12.2	13.8	18.6	6.0	5.0	20.8	1.7	1.6	19.3
Taieri @ Titoriti	5.9	8.0	1.6	7.3	8.7	13.5	3.7	2.9	33.7	1.3	1.0	24.1
Taieri @ Waipiata	2.7	3.2	1.2	3.5	4.4	27.6	4.4	3.8	20.3	1.1	0.4	1.5
Tasman	40.0	45.9	1.4	49.0	62.6	2.1	2.1	1.4	43.5	19.7	54.8	3329.6
Tasman-Upper	88.8	60.8	3.4	96.1	36.6	2.8	2.7	1.0	96.9	5.9	11.9	534.4
Temple	2.4	3.3	0.7	4.0		28.1	1.5	1.2	35.9	1.9	1.3	11.5
Tevoit	2.0	2.6	1.4	3.2	4.6	29.7	6.4	5.7	5.2	1.6	0.1	0.9
Twizel	2.0	2.5	0.7	3.1	3.8	19.4	1.1	0.7	48.8	0.5	0.4	2.2
Upukerora			0.8	4.6	5.4	14.5	3.1	2.7	19.4	4.7	1.0	7.9
Waiau			0.7	1.0	1.7	42.0	2.6	2.3	1.0	16.2	0.2	6.7
Waiau-Upper			0.9	3.9	4.7	18.0	1.9	1.5	18.2	6.4	1.5	16.5
Waikaia			0.7	4.3	4.9	13.5	3.9	3.6	12.7	2.6	0.4	3.1
Waipori Falls	1.8	2.2	1.3	1.9	2.6	39.6	3.7	3.1	31.6	1.4	0.6	1.1
Waitaki	0.7	1.3	1.5	3.6	5.0	28.9	2.0	1.3	6.7	4.1	0.4	11.2
Whetherburn	2.7	3.1	1.2	2.8	3.9	32.3	9.1	8.5	14.8	2.1	0.3	0.9

2. New Zealand National River Water Quality Network

New Zealand National River Water Quality Data (period 2011 - 2015)
Source: NIWA Taihoro Nukurangi

Key for water quality parameters

VC - Visual Clarity (m)
NTU - Turbidity (as NTU)
g340 - Absorbance coefficient at 340nm (/m)
g440 - Absorbance coefficient at 440nm (/m)
Spec. NTU - Specific turbidity calculated NTU/SSC, for turbidity as NTU
TSS - Total suspended solids (mg L^{-1})
VSS - Volatile suspended solids (mg L^{-1})
VSS% - Percentage of VSS of TSS
SSC - Suspended sediment concentration (mg L^{-1})
SS Yield - Suspended sediment yield (t/km2/y) (Discharge weighted)

Median 2011 - 2015

Site	Place	VC (m)	NTU	g340	g440	Spec. NTU	TSS	VSS	VSS %	SSC	SSY
AK1	Hoteo @ Gubbs	1.3	7.3	16.2	3.0	1.6	7.7	0.9	11.4	6.9	7.6
AK2	Rangitopuni @ Walkers	1.0	6.9	24.3	4.5	2.1	3.0	1.0	31.4	2.1	10.1
AX1	Clutha @ Luggate Br.	5.3	0.8	0.4	0.1	0.6	1.9	0.2	10.6	1.6	8.4
AX2	Kawarau @ Chards	1.4	3.3	0.5	0.1	0.2	11.1	0.4	3.2	10.9	78.8
AX3	Shotover @ Bowens Peak	0.5	8.7	1.1	0.3	0.2	56.6	1.1	1.9	52.0	145.1
AX4	Clutha @ Millers Flat	1.9	2.5	1.1	0.3	0.6	7.7	0.3	3.7	7.4	14.6
CH1	Hurunui @ Mandamus	1.5	2.3	1.6	0.4	0.8	3.0	0.2	6.4	2.8	30.9
CH2	Hurunui @ SH1 Br.	1.0	4.4	1.7	0.3	0.6	4.6	0.2	5.0	4.3	71.8
CH3	Waimakariri @ Gorge	0.5	9.1	0.9	0.2	0.7	8.2	0.2	2.7	7.7	93.3
CH4	Waimakariri above old HW Br.	0.3	19.0	0.9	0.3	0.6	26.1	0.8	3.1	25.6	146.2
DN1	Taieri @ Tiroiti	0.8	6.1	11.4	2.1	0.6	7.5	0.8	11.2	6.7	9.7
DN10	Monowai below Gates	7.1	0.6	2.8	0.5	1.5	0.6	0.3	49.1	0.3	0.8

Site	Place	VC (m)	NTU	g340	g440	Spec. NTU	TSS	VSS	VSS %	SSC	SSY
DN2	Sutton @ SH87	2.7	1.6	12.3	2.3	1.5	1.7	0.6	37.0	1.0	0.5
DN3	Taieri @ Outram	1.3	4.1	12.0	2.3	0.7	5.0	0.7	14.9	4.2	9.6
DN4	Clutha @ Balclutha	1.5	3.7	2.1	0.4	0.5	11.7	0.6	4.8	11.3	42.3
DN5	Mataura @ Seaward Down	1.0	6.3	5.8	1.1	0.7	11.0	1.2	10.5	9.9	15.3
DN6	Mataura @ Parawa	2.3	2.1	1.8	0.4	0.7	2.9	0.3	9.4	2.6	5.9
DN7	Oreti @ Lumsden	3.5	1.4	3.1	0.5	1.1	1.2	0.2	14.5	0.8	1.7
DN8	Oreti @ Riverton HW Br.	1.3	3.5	3.7	0.6	0.9	4.5	0.3	6.2	4.3	27.3
DN9	Waiau @ Tuatapere	1.7	2.5	4.7	0.9	0.6	2.2	0.4	18.3	1.7	79.2
GS1	Waipoa @ Kanakanaia	0.1	76.8	4.4	0.8	0.6	349.0		0.0	335.0	3659.8
GS2	Waikohu @ No. 1 Br.	1.5	3.7	5.8	1.1	0.6	9.0	1.4	15.6	8.0	478.5
GS3	Motu @ Waitangirua	1.2	4.5	5.9	1.1	0.6	12.1	1.7	14.0	10.4	30.3
GS4	Motu @ Houpoto	1.3	4.1	2.1	0.4	0.7	76.4	2.6	3.4	73.7	291.2
GY1	Buller @ Te Kuha	1.4	2.5	5.2	1.1	0.3	15.1	1.1	7.2	14.0	147.3
GY2	Grey @ Dobson	1.9	1.8	7.7	1.5	0.6	3.2	0.4	12.2	2.9	151.2
GY3	Grey @ Waipuna	3.4	1.1	6.1	1.2	0.8	1.8	0.2	11.4	1.6	32.4
GY4	Haast @ Roaring Billy	2.6	1.5	0.6	0.1	0.6	2.8	0.1	3.2	2.7	105.0
HM1	Waipa @ Otewa	2.0	2.2	5.2	1.0	0.5	5.2	1.2	22.5	4.0	97.6
HM2	Waipa @ Whatawhata	0.6	10.3	9.0	1.7	0.6	20.2	3.2	15.6	17.5	30.8
HM3	Waikato @ Hamilton Traffic Br.	1.5	2.3	3.3	0.7	0.6	7.8	1.6	20.4	5.9	4.2
HM4	Waikato @ Rangiriri	0.7	7.0	5.5	1.1	0.6	12.6	2.5	19.5	10.3	16.2
HM5	Waihou @ Te Aroha	0.9	4.9	4.6	0.9	0.4	14.2	2.2	15.3	12.0	26.9

Site	Place	VC (m)	NTU	g340	g440	Spec. NTU	TSS	VSS	VSS %	SSC	SSY
HM6	Ohinemuri @ Karangahake	2.9	1.3	3.6	0.8	0.9	1.6	0.5	29.4	1.2	2.3
HV1	Makaroro @ Burnt Br.	3.0	1.5	1.0	0.2	1.0	1.2	0.1	10.8	1.1	90.5
HV2	Tukituki @ Red Br.	2.4	1.9	2.6	0.5	1.0	4.7	0.4	9.1	4.3	55.7
HV3	Ngaruroro @ Chesterhope	1.2	3.4	1.4	0.3	0.7	8.0	0.3	4.1	7.7	20.5
HV4	Ngaruroro @ Kuripapango	5.8	1.0	1.0	0.2	0.8	1.3	0.2	13.4	1.3	1.9
HV5	Mohaka @ Raupunga	1.0	4.6	2.8	0.6	0.6	34.1	1.2	3.4	33.0	54.5
HV6	Mohaka @ Glenfalls	3.1	1.3	1.8	0.4	0.5	5.2	0.4	7.9	4.8	5.6
NN1	Motueka @ Woodstock	4.2	1.2	3.6	0.7	0.6	1.0	0.6	57.0	0.7	70.2
NN2	Motueka @ Gorge	9.9	0.5	1.1	0.2	1.0	0.3	0.1	42.9	0.3	2.4
NN3	Wairau @ Dip Flat	3.1	1.5	0.7	0.2	1.0	1.7	0.1	6.6	1.6	11.7
NN4	Wairau @ Tuamarina	2.6	1.6	0.9	0.2	0.9	3.5	0.3	7.1	3.3	15.8
NN5	Buller @ Longford	3.3	1.1	2.5	0.5	0.8	1.4	0.3	20.6	1.2	14.1
RO1	Tarawera @ Lake outlet	5.3	0.6	0.6	0.1	1.3	0.7	0.6	75.3	0.3	0.5
RO2	Tarawera @ Awakaponga	1.0	3.8	5.4	1.0	0.2	29.4	3.2	11.0	26.4	22.0
RO3	Rangitaiki @ Murapara	2.2	1.4	1.7	0.4	0.2	13.2	1.8	13.9	11.4	6.3
RO4	Whirinaki @ Galatea	2.2	1.7	3.2	0.7	0.4	22.0	2.5	11.1	16.4	40.3
RO5	Rangitaiki @ Te Teko	1.8	2.0	2.6	0.5	0.4	10.9	1.0	9.4	9.9	10.1
RO6	Waikato @ Reids Farm	8.2	0.4	0.5	0.1	0.6	0.6	0.2	37.5	0.4	0.4
TK1	Opihi @ GRASSY BANKS	5.2	1.1	2.3	0.4	0.7	1.1	0.1	11.7	1.0	0.2

Site	Place	VC (m)	NTU	g340	g440	Spec. NTU	TSS	VSS	VSS %	SSC	SSY
TK2	Opihi @ Rockwood	3.9	1.0	2.8	0.5	0.8	1.2	0.2	13.7	1.0	0.3
TK3	Opuha @ Skipton Br.	2.2	2.4	3.8	0.7	1.2	1.3	0.4	28.0	0.9	0.7
TK4	Waitaki @ Kurow	3.7	1.6	0.7	0.2	1.6	6.6	0.2	3.6	6.4	17.4
TK5	Hakatakamea above MH Br.	6.7	0.7	2.2	0.4	1.2	0.4	0.1	27.3	0.3	0.1
TK6	Waitaki @ SH1 Br.	1.3	5.0	0.7	0.2	1.0	7.9	0.3	4.2	7.5	53.2
TU1	Whanganui @ Te Maire	1.0	4.2	5.8	1.1	0.6	6.3	0.7	11.7	5.5	28.3
TU2	Tongariro @ Turangi	3.8	1.1	1.0	0.2	0.5	1.5	0.3	21.3	1.2	362.8
WA1	Waitara @ Bertrand Rd	0.5	9.8	9.0	1.8	0.6	8.3	1.5	17.8	7.1	496.5
WA2	Manganui @ SH3	3.8	1.2	3.0	0.6	1.4	0.9	0.3	33.3	0.7	6.9
WA3	Waingongoro @ SH45	1.3	3.7	6.1	1.2	0.7	9.4	3.3	34.6	6.1	15.0
WA4	Whanganui @ Paetawa	0.4	19.8	9.1	1.7	0.7	31.7	2.1	6.5	29.6	217.6
WA5	Rangitikei @ Mangaweka	1.3	3.6	3.0	0.5	0.8	6.8	0.5	7.8	6.3	35.5
WA6	Rangitikei @ Kakariki	0.6	10.1	3.4	0.6	0.6	19.9	1.1	5.3	18.9	59.9
WA7	Manawatu @ Weber Rd	1.3	3.8	5.7	1.0	0.9	4.5	0.5	11.1	4.0	143.7
WA8	Manawatu @ Teachers Coll.	0.9	5.8	5.6	1.1	0.6	11.0	0.8	7.5	10.0	194.6
WA9	Manawatu @ Opiki Br.	0.7	7.9	6.0	1.1	0.5	16.0	1.9	12.1	15.0	76.2
WH1	Waipapa @ Forest Ranger	3.4	1.5	5.3	1.1	1.9	0.8	0.1	16.9	0.7	0.7
WH2	Waitangi @ Wakelins	1.6	3.3	9.7	1.8	1.1	6.2	0.8	13.0	5.4	4.6
WH3	Mangakahia @ Titoki Br.	1.2	5.5	7.4	1.4	0.9	10.5	1.2	11.2	9.3	13.7
WH4	Wairu @ Purua	0.7	9.6	15.1	2.8	1.4	9.8	1.4	13.8	6.9	9.3

Site	Place	VC (m)	NTU	g340	g440	Spec. NTU	TSS	VSS	VSS %	SSC	SSY
WN1	Hutt @ Boulcott	2.1	1.9	6.5	1.3	0.9	1.9	0.4	22.2	1.5	15.7
WN2	Hutt @ Kaitoke	7.0	0.7	4.1	0.8	1.0	0.7	0.2	26.5	0.4	19.9
WN3	Ruamahanga @ Waihenga	1.5	3.5	4.3	0.8	0.8	3.4	0.3	7.6	3.2	27.8
WN4	Ruamahanga @ Wardells	2.1	2.6	4.5	0.8	0.9	5.3	0.3	5.7	5.1	37.2
WN5	Ruramahanga @ SH2	6.5	0.8	2.8	0.5	1.1	1.0	0.1	13.0	0.9	432.4