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

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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

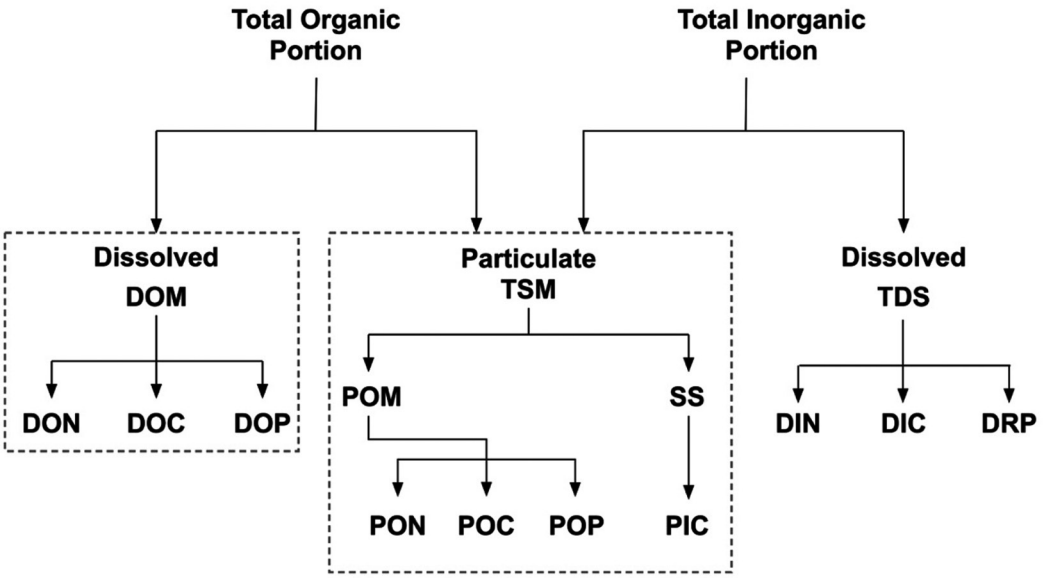


Figure 1 – Diagram of dissolved and particulate constituents in river water with an emphasis on carbon contributions. The dissolved and particulate components comprise of organic and inorganic portions that may occur as dissolved (i.e., <0.7 µm) or particulate (>0.7 µm). Elements in the dashed box potentially 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)).

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 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 proxy for determining the SSC of stream water as changes in turbidity relate to a predictable change in SSC (Gipple, 1989; Gipple, 1995, Gray and 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

Table 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 Gipple (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.

components of TSM affect measurements of turbidity differently (Table 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.

In New Zealand several studies have drawn attention to the use of turbidity as a proxy measure for suspended sediment (e.g., Davies-Colley and Close, 1990) and have demonstrated the use of a number of other proxy variables for determining suspended sediment, like water clarity (e.g., Davies-Colley, 1988; Davies-Colley and 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; Gipple, 1995). Therefore, the optical properties of water are not only dependent on the SSC, but also the presence of organic material.

Scatter in suspended sediment-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 (Gipple, 1989; Gipple, 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 (Gipple, 1989; Davis-Colley and 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 (Gipple, 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; Fig. 1) to determine the flux of carbon to the oceans and sequestration (e.g., Scott *et al.*, 2004; Coynel *et al.,* 2005; 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, 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 suspended sediment. 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.

Methods

The Glendhu Experimental Catchments were established in the Lammerlaw Ranges (Fig. 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 and Watson, 1991; Fahey and 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

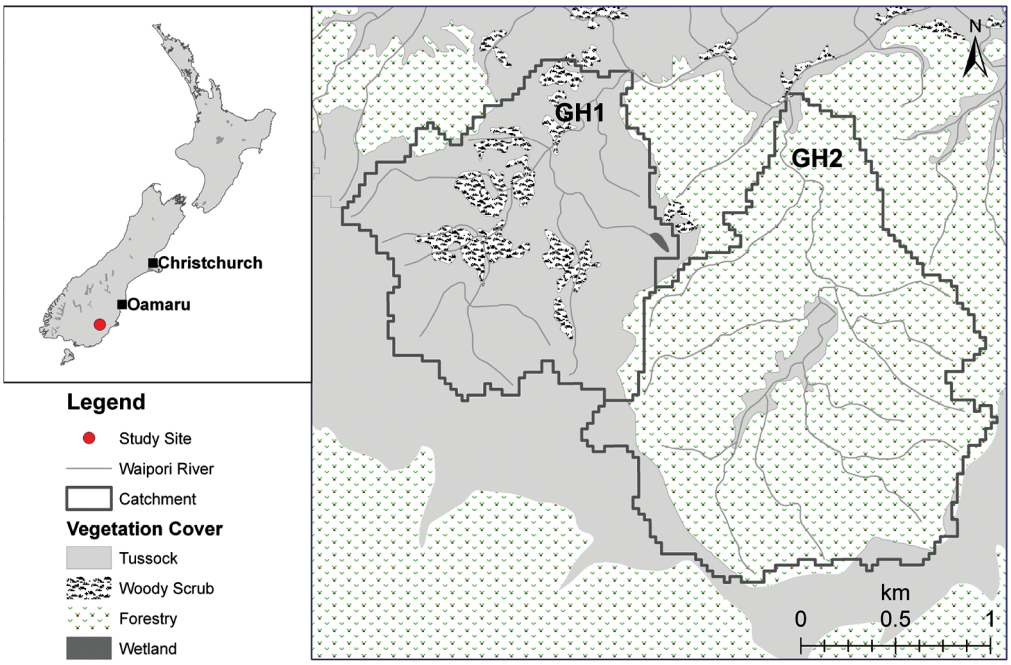


Figure 2 – Location of the Glendhu Experimental Catchments in the Lammerlaw Ranges in Otago. The smaller catchment (GH1) is tussock grassland with manuka scrub, and the larger catchment (GH2) is plantation forestry that is partially cleared

the upper Waipori catchment (Fig. 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.

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) 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 500°C and 550°C, 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 and Bilotta, 2014). The standard approach is to apply a van Bemmelen factor, which ranges from 1.4 to 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.

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 2). Turbidity, POM, TSM, and percentage of TSM as POM 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), 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 (Fig. 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 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

	Mean	Median	Max	Min	Count
Tussock					
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 (%wt)	46	45	86	10	60
Forestry					
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 (%wt)	60	60	95	23	124

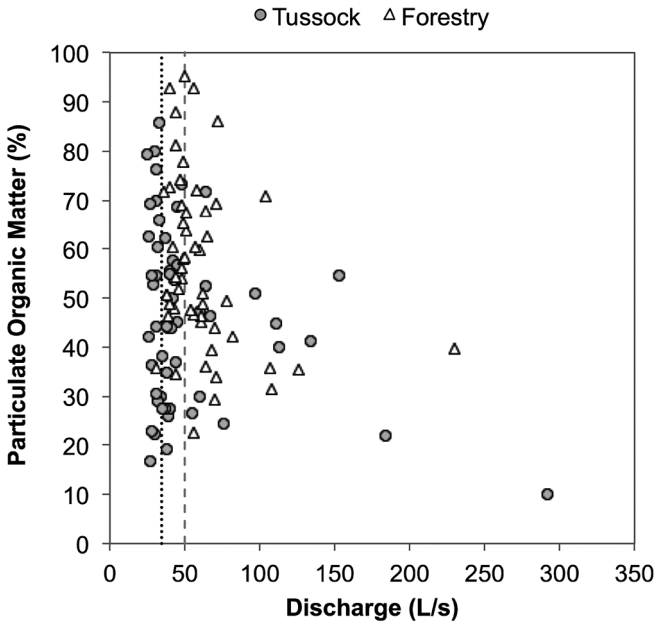


Figure 3 – Portion of total suspended material as particulate organic matter (POM) (as a percentage of dry weight) plotted relative to stream flow at time of sample collection. Median daily stream flow over the 18-month period is indicated by the dotted line (tussock catchment, GH1) and the dashed line (forested catchment, GH2).

Table 3 – Comparison of suspended load characteristics of the Glendhu Experimental forestry (GH2) and tussock (GH1) catchments using a non-parametric Mann-Whitney U-test. All parameters show a statistically significant difference between the catchments at the 95% confidence level (indicated by *), apart from suspended sediment concentration (SSC).

Variable	p-value	Confidence interval
Turbidity	0.00 *	(1.34, 2.90)
POM	0.00 *	(2.03, 4.52)
SSC	0.26	(-0.41, 1.85)
TSM	0.00 *	(3.55, 7.83)
POM (% of TSM)	0.00 *	(-19.71, -8.37)

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 (Fig. 4). For example, the largest three rainfall events during the study period occurred on 22 May 2016 (50 mm over 19 hours), 18 February (46 mm over 8 hours), and 28 May (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, 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, when 39 mm fell over 8 hours on 17 February followed by 46 mm the next day, represents an intense rain fall 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 (Fig. 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.

To evaluate the impact of rainfall on POM, three storm events between August and October (transition to spring) were examined in closer detail. Daily rainfall totals for an event between 5 and 8 October 2016 were

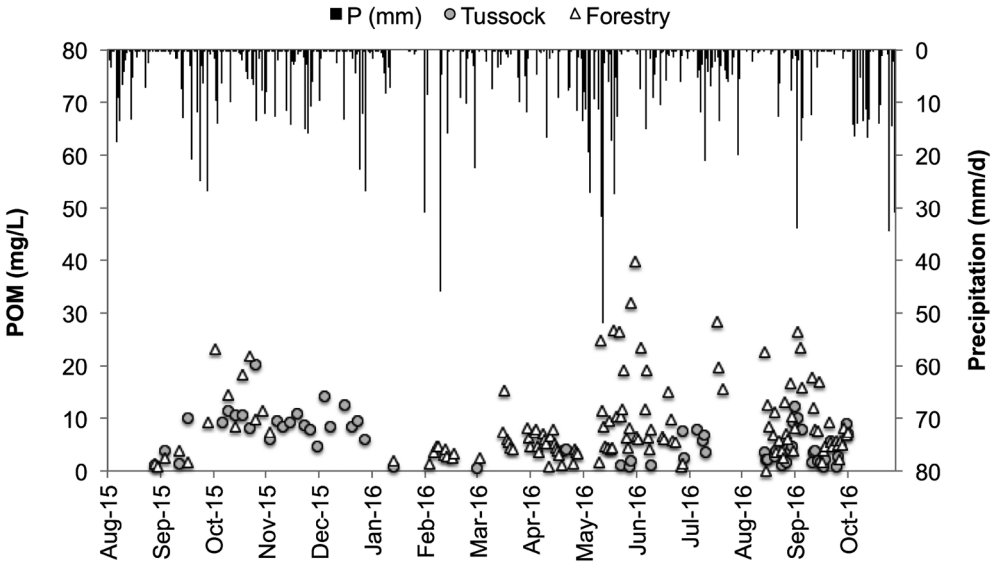


Figure 4 – Particulate organic matter concentration (POM) relative to daily precipitation for the tussock (circles) and forestry (triangles) Glendhu Experimental Catchments

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 Sep 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} (Fig. 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 (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, and a further 11 mm falling on 6 September over 8 hours. Both catchments responded rapidly, peaking at 1300 L s^{-1} in the tussock catchment and 700 L s^{-1} in the forestry catchment. In 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 (Fig. 6).

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 (Fig. 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 (Fig. 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 (Fig. 7a–c). The turbidity, SSC and POM data from the tussock and forestry

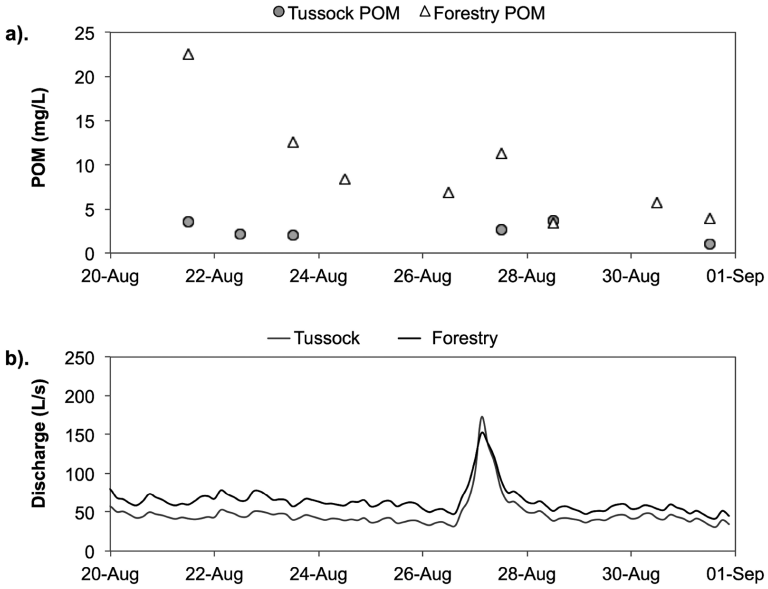


Figure 5 – Variations in particulate organic matter (POM) concentration prior to, and during, a small rainfall event in August 2016, where: a) shows the POM concentration in the tussock (circles) and forestry (triangles catchment) and b) shows the streamflow

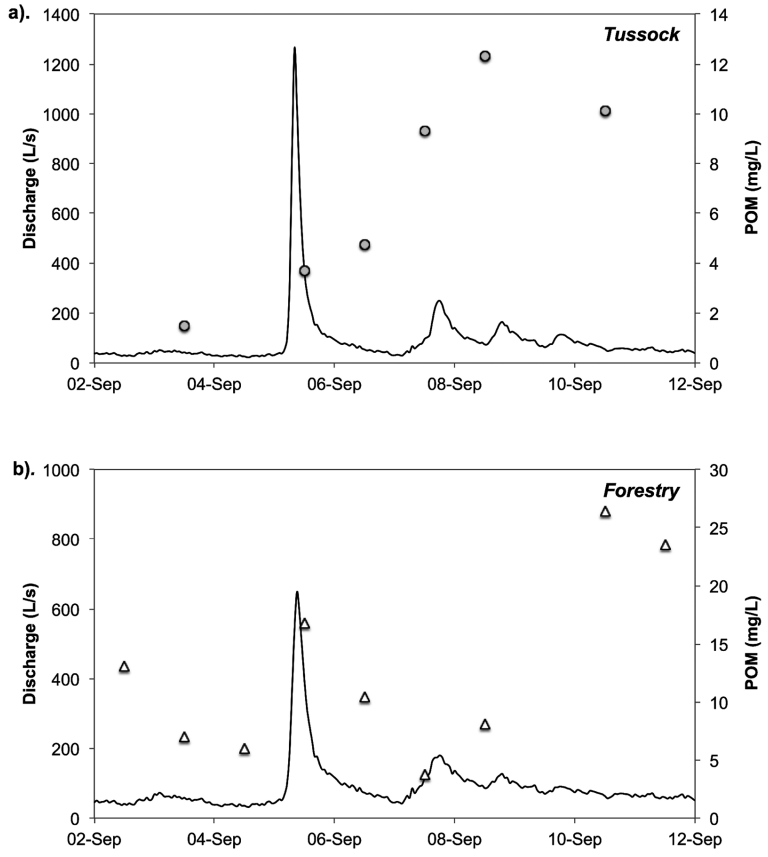
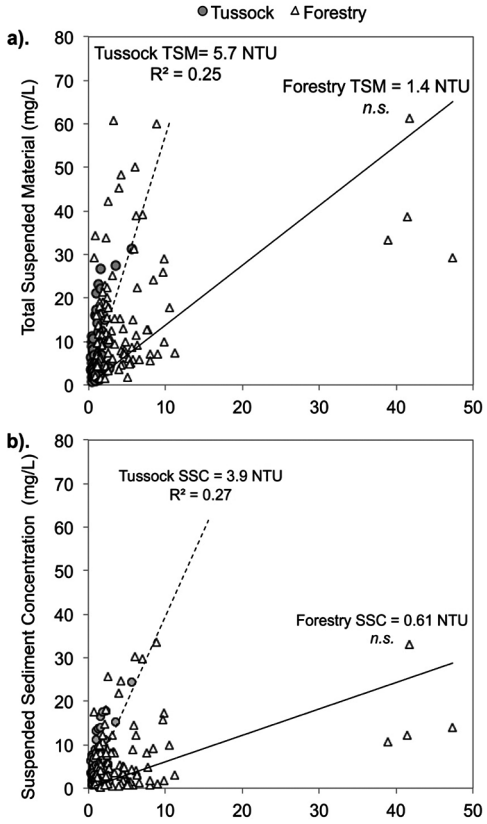


Figure 6 –Variations in particulate organic matter (POM) prior to, and during, a rainfall event in September 2016, where: a) shows the POM concentration in the tussock catchment (circles) and b) shows the POM concentration in the forested catchment (triangles), both relative to stream discharge



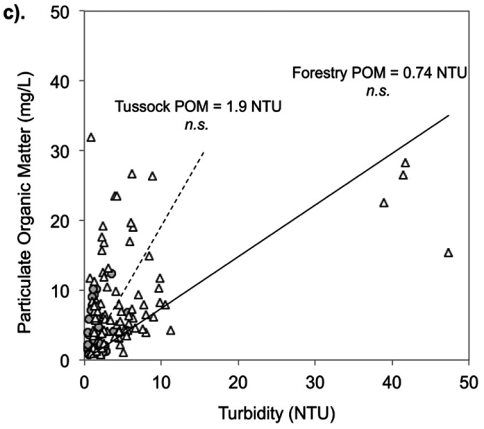


Figure 7 – Variability in: a) total suspended material; b) suspended sediment; and c) particulate organic matter concentrations relative to turbidity in the tussock and forestry catchments. Fitted lines indicate the predicted regression relationships between the variables, and n.s. indicates no statistically significant regression relationship.

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 (Fig. 8).

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

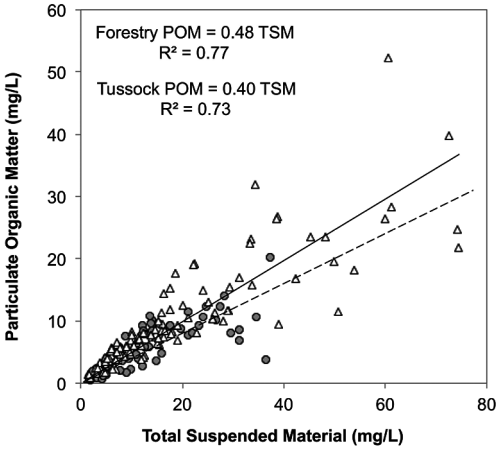


Figure 8 – Particulate organic matter relative to total suspended material, indicating a strong linear relationship (e.g., as total suspended material increases so too does the concentration of organic matter) in the tussock (circles) and forested (triangles) catchments.

Table 4 – 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). The analysis only includes samples where the concentration for each fraction was greater than the method detection limit of 0.4 mg L^{-1}. 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

(Table 4). In spring in the forest 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.

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.

Particle properties and water colour

The use of turbidity as a proxy for determining SSC relies on the assumption that suspended particles do not alter in physical properties as concentration varies (Gipple, 1989). A similar study of five small forested catchments also found that turbidity and suspended sediment relationships were weak, but improved when consideration of particle characteristics (e.g., size, shape) and water colour were taken into account (Gipple, 1989). 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 and 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 and attenuation 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 (Gipple, 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 (Gipple, 1995). The DOC from dissolved organic matter includes organic acids such as fluvic or humic acid, and tannins derived from organic decay. Gipple (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 proxy 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 and MatJafri, 2009). The Glendhu catchments episodically show a yellow-brown water colour (Fig. 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

Figure 9 – Streamflow through the v-notch weir draining the Glendhu Experimental tussock catchment (GH1). The water shows a distinct yellow that is frequently observed in both GH1 and GH2 catchments

of both dissolved and particulate organic matter are present, it may produce a SSC to 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, 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 and MatJafir, 2009).

POC in New Zealand rivers

In the wider Waipori catchment, of which the Glendhu Experimental Catchments are headwaters, there are two previous studies that have included measurements of suspended sediment. 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 >9000 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.,* 2005; 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.,* 2005; 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 catchment. Further work is required to resolve what other processes are the controlling variables of POM, particularly in relation to identifying the sources of POM and how these sources are attenuated during storm events.

Source of POM

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 is presently undergoing clearance, 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 catchment.

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 dissolved organic material

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 National Policy Statement for Freshwater Management (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. 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 form (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.

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