

# CHARACTERISATION OF NATURAL ORGANIC MATTER (NOM) IN LITTER LEACHATES FROM DRINKING WATER CATCHMENTS

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## ABSTRACT

Pruning, thinning and harvesting of planted *Pinus radiata* forests have the potential to export large amounts of terrestrial natural organic matter (NOM) to surface waters. The characteristics of NOM are a function of its precursor material. The chemical composition of NOM has the potential to interfere with water treatment processes, by fouling membranes and reacting with the disinfection process. In this study, litter leachates from two drinking water catchments were compared; a mixed vegetation native forest and a catchment dominated by *Pinus radiata*. Greater amounts of NOM were leached from native forest litter when compared to pine forest litter. However, NOM in pine forest litter leachate was characterised by lower molecular weight and more protein-like compounds. These compounds are more difficult to remove during water treatment and considered reactive with the water treatment process. Due to the management activities occurring, planted pine forests have the potential to transport large quantities of harder to treat and reactive NOM to surface waters. Understanding the differences in NOM chemistry between vegetation types will allow water utilities to better predict the quantity and quality of NOM transported to surface waters in drinking water catchments.

## KEYWORDS

Natural Organic Matter (NOM), drinking water treatment, soil, pine forests, protein-like compounds, humic-like compounds

## 1 INTRODUCTION

Forested catchments largely influence surface water quality through vegetation type, topography, soils, hydrology, and land management. An extensive knowledge of the vegetation cover in drinking water catchments is vital to ensuring clean drinking water that is protected at the source. Within New Zealand, planted forests cover 1.7 million ha, with 90% of that area in *Pinus radiata*, some inevitably occurring in drinking water catchments. A review of New Zealand's planted forests and the effects on water quality show that mature planted forests behave similarly to native forests (Baillie & Neary, 2015). However, management and timber harvesting near streams have a great effect on water quality resulting in increases in nutrients, warmer waters and large sediment loads (Baillie & Neary, 2015).

Natural organic matter (NOM) is a heterogeneous mix of organic compounds found in all natural water derived from either internal (autochthonous) or external (allochthonous) sources. Terrestrial NOM is defined as NOM that is transported to surface waters by overland flows through a catchment after precipitation events, or from interflow and groundwater inputs to surface waters. Terrestrial NOM is derived from vegetation and includes compounds like cellulose and lignin which are modified by interactions which occur in the environment from microbial degradation and solar irradiation. The rate and processes in which NOM is transformed is an area of ongoing research. New research suggests that environmental conditions can degrade compounds of soil NOM normally considered stable (Lehmann & Kleber, 2015).

The complex interactions between physical and biological processes in the soils as well as the hydrology and climatic conditions in a catchment will play an important role in the quality and quantity of terrestrial NOM produced. The study of NOM in soils is an evolving science with new views on how recalcitrant soil NOM is defined. The old standing view that the molecular structure dictated how labile organic matter is beginning to be challenged with the understanding that physicochemical and biological influences from the environment will determine how organic matter is degraded and the quality that persists (Schmidt et al., 2011). Research is

beginning to redefine organic matter that is considered resistant to degradation by accepting the understanding that a compound of organic matter persists as a function of the environment in which it is placed, not by the chemical quality (Kleber, 2010). The next step is understanding how changes in the quality of terrestrial NOM transported to water sources effects the aquatic ecosystem and ultimately water treatment processes.

The quality of terrestrial NOM which enters aquatic systems will dictate the water quality of surface waters and NOM characteristics in these waters. NOM in surface waters can have significant impacts on drinking water quality and treatment processes. NOM in waters is the main reason for coagulant and disinfection use in water treatment. As well, NOM may interfere with treatment by fouling membranes and causing bacterial regrowth in distribution systems (Matilainen, Vepsäläinen & Sillanpää, 2010). The humic component of NOM which originates from terrestrial sources, has the potential to form disinfection by products (DBPs) during water treatment (Ribau Teixeira, Rosa & Sousa, 2011). Characterising NOM is the only way to determine how it will affect water treatment processes, however this can be difficult due to the varying and complex nature of NOM. A range of techniques have been developed to characterise NOM including spectroscopic, molecular weight, and fluorescence analysis. The combination of these techniques can help provide a comprehensive characterisation of the compounds in NOM.

The main objective of this study was to characterise NOM leached from catchments differing in vegetation type. Specifically, differences were examined between a catchment dominated by New Zealand native tree species and a catchment dominated by planted *Pinus radiata*. Samples were obtained from the forest floor and mineral soil to account for differences in the leachate from different soil layers and levels of decomposition. This study aimed to improve the understanding of how planted forests and their management practices can affect NOM characteristics and the implications for surface waters and drinking water treatment.

## 2 METHODS

Organic layer and mineral soil samples were collected from three different sampling sites in two drinking water catchments, one dominated by planted pine forest (*Pinus radiata*) and one dominated by native New Zealand forests (Photograph 1). At each site a litter layer, organic layer, and mineral soil were collected. The litter layer was determined as the fallen plant material which still retained original structure and was approximately 1 – 3 cm deep in native forest and 5-7 cm deep in the planted pine forests. The organic layer contained both decomposed material in which the origin could still be identified and non-distinguishable decayed organic matter and was approximately 1 – 5 cm in depth with planted pine forests having deeper organic layers. The mineral soil was collected for the first 5 cm across both forest types. Mineral soil samples were taken at 0-10 cm depth after removing the organic layer. Samples were transported back to the laboratory and dried at room temperature.

Photograph 1: Sampling site and soil layers for pine (left) and native (right) forests



Litter layer samples were cut into approximately 2 cm pieces and homogenized before leaching. Samples were leached at a dry to wet ratio of 10 grams to 1 L of Milli-Q water for 24 hours by rotating in the dark at room temperature. All samples were filtered through 0.45  $\mu\text{m}$ -cellulose acetate membrane filters before analysis.

Dissolved organic carbon (DOC) concentrations were measured using a Shimadzu TOC-5000 A. Measurement for  $UV_{254}$  was conducted using a UV-Visible Spectrophotometer at a wavelength at 254 nm using a 1.0 cm quartz cell. Humic substances absorb a broad range of wavelengths between 254 nm and 400 nm, however  $UV_{254}$  is commonly used by water utilities as a surrogate parameter for organic matter in water, specifically more aromatic organic matter. Specific UV absorbance at 254 nm ( $SUVA_{254}$ ) is DOC normalized  $UV_{254}$  and is strongly correlated to the percent aromaticity of the organic matter in a sample (Weishaar et al. , 2003). The  $SUVA_{254}$  variable was calculated using equation 1.

$$SUVA_{254} = \frac{UV_{254}}{DOC} * 100 \quad (1)$$

Molecular weight and size distributions were measured by using high performance size exclusion chromatography (HPSEC) using a DIONEX HPLC unit equipped with a Shodex Protein KW-802.5  $5 \times 10^4$  column with a Shodex GPC KW-G Guard column (Pelekani et al. , 1999). Polystyrene sulfonate (PSS) molecular weight standards with the following molecular weights 4600, 8000, 18 000, 35 000 Daltons and acetone (58 Daltons) were used as reference standards. Fluorescence excitation-emission matrices (EEMs) were measured with a Horiba Fluoromax (Jobin Yvon Horiba) spectrofluorometer. EEMs were created by measuring the fluorescence intensity for excitation wavelengths from 240 – 600 nm and emission wavelengths from 200 – 600 nm.

### 3 RESULTS AND DISCUSSION

#### 3.1 DISSOLVED ORGANIC CARBON CONCENTRATIONS AND UV-VIS PARAMETERS

Mean DOC concentrations in native littler layer leachate was 75.00 mg/L compared to the pine litter layer which leached 27.04 mg/L (Table 1). The same trends were observed for the organic layer and mineral soil layers. These findings suggest that water leached from native forests has the potential to transfer higher concentrations of NOM to local water bodies. Lower amounts organic matter have been found in the soils below the stands of *Pinus radiata* when compared to adjacent native forests (Turner et al., 2001). In contrast, studies from Australia have reported higher DOC concentrations from pine forests surface flow compared to native woodland (Awad et al., 2015).  $SUVA_{254}$  was greater in the organic layer and mineral soil under *Pinus radiata* forests compared to the native forest. This indicates that NOM leached from pine forests into surface waters may have higher aromaticity compared to adjacent native forests.

Table 1:  $UV_{254}$ , DOC, and  $SUVA_{254}$  in litter and organic layer and mineral soil under native and pine forest. Values represent mean  $\pm$  SE ( $n = 3$ )

	$UV_{254}$ ( $cm^{-1}$ )	DOC (mg/L)	$SUVA_{254}$ (L/mg-m C)
<b>Mixed Vegetation - Native Forest</b>			
Litter Layer	$1.765 \pm 0.031$	$75.00 \pm 4.89$	2.35
Organic Layer	$0.889 \pm 0.001$	$31.55 \pm 5.35$	2.82
Mineral Soil	$0.749 \pm 0.001$	$23.72 \pm 2.65$	3.16
<b>Pine Forest</b>			
Litter Layer	$0.782 \pm 0.047$	$27.04 \pm 0.040$	2.89
Organic Layer	$0.746 \pm 0.055$	$19.04 \pm 2.11$	3.92
Mineral Soil	$0.389 \pm 0.042$	$8.36 \pm 1.78$	4.66

Between soil layers for each forest type, the litter layer leached higher concentrations of DOC than the organic layer and mineral soil layer. DOC concentration from leachates decreased as soil depth increased. However,  $SUVA_{254}$  increased with depth indicating a larger degree of aromaticity. The increase in  $SUVA_{254}$  through the top forest layers has also been found in other studies (Gabor et al., 2014).  $SUVA_{254}$  was shown to increase through the litter layer and then decrease with increasing depth in the mineral soil (Gabor et al., 2014). This initial increase in the aromaticity is due to humification, or the conversion of lower molecular weight organic compounds to more condensed higher molecular weight polymers. Mineral soils are expected to have lower  $SUVA_{254}$  than the organic layers but this was not observed. The possible reason that we did not observe a

decrease in  $SUVA_{254}$  in the mineral soil may be due to sampling depth and the mineral soil still contained large amounts of humic materials.

### 3.2 HIGH PERFORMANCE SIZE EXCLUSION CHROMATOGRAPHY AND FLUORESCENCE SPECTROSCOPY

The molecular weight and size distribution is an important part of the physical and chemical characterisation of NOM. High molecular weight (HMW) NOM is generally characterised as greater than 5000 Daltons. The molecular weight distributions of the leachates peaked around 6000 Daltons and were similar for different layers of the native forest (Figure 1). However, the intensities differed between layers with lowest milliabsorbance units (mAU) for the mineral soil leachates due to lower DOC concentration (Figure 1; Figure 2). Pine forest had similarities between the molecular weight distributions of the organic and mineral soil layers (Figure 2). The litter layer of the pine forest leachate had a low molecular weight (LMW) shift with major peaks at 3000, 1500, and 500 Daltons.

NOM of LMW is comprised of amino acids and carbohydrates that are considered labile components of organic matter which can be mineralized quickly by bacteria. More humic-like compounds are characteristic of HMW and are considered more aromatic and hydrophobic than LMW organic matter (Hur, Park & Schlautman, 2009). The organic layer from the native forest has a HMW peak that was not seen in the other soil layers. This HMW organic matter corresponds to the humification that occurs during the degradation of the litter layer. The *Pinus radiata* litter layer showed more significant LMW peaks compared to the native forest litter layer. This may be due to the fresh nature of the pine needles which are more recalcitrant to decomposition and therefore leaching more amino acid like organic matter.

Figure 1: HPSEC molecular weight distribution of native forest soil layers.

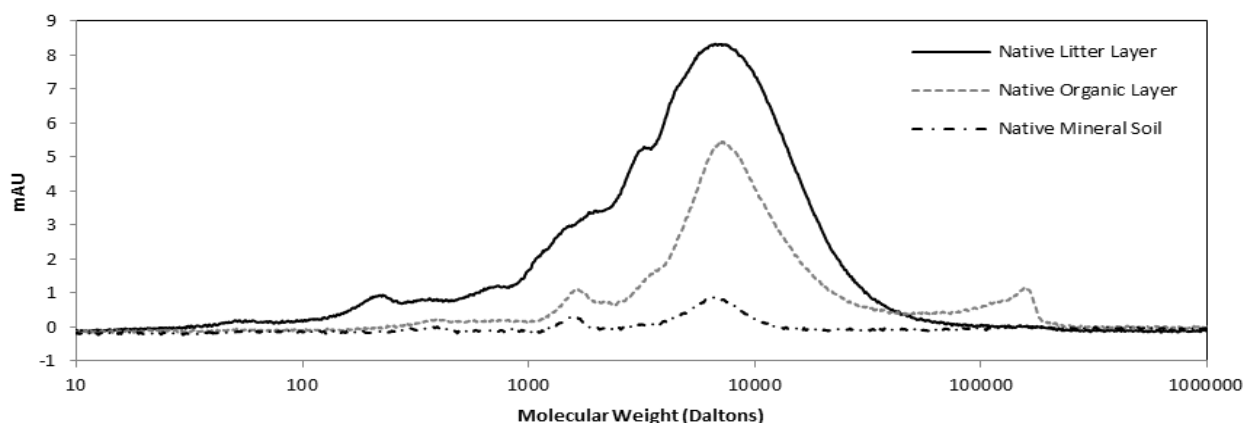
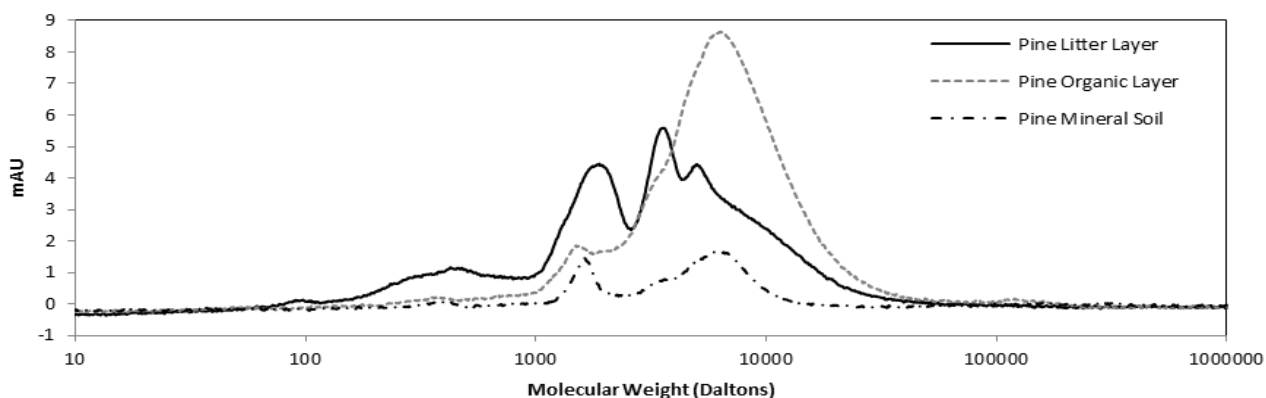


Figure 2: HPSEC molecular weight distribution of planted pine forest layers.



Fluorescence spectroscopy allows for the characterisation of NOM by fluorescence signatures that are displayed in three dimensional contour maps, EEMs, which can be used to characterise various components of NOM. The primary fluorescence peaks found in aquatic NOM are shown in Table 2. Visual inspections of the fluorescence EEMs show similarities as well as differences between the fluorophores of native versus *Pinus radiata* litter leachates (Figure 3; Figure 4). Leachates from both forest types had primary fluorescence at 240 nm excitation and 400 – 460 nm emission which corresponds to peak A, or humic-like organic matter (Table 2).

Table 2: Common observed fluorescence peak names and descriptions as detailed by Coble (1996) and Fellman et al. (2010)

Peak Name	Component	Excitation and Emission Maxima (nm)	Description
A	Humic/Fulvic-Like	Ex <260, Em 400-460	High molecular weight and aromatic humic acids, primarily terrestrial origins
C	Humic/Fulvic-Like	Ex 320-360, Em 420-460	High molecular weight humic acids, primarily terrestrial origins
T	Tryptophan-Like	Ex 270-280, Em 330-370	Amino acids, indicates intact proteins or less degraded peptide material
B	Tyrosine-Like	Ex 270-275, Em 304-312	Amino acids, may indicate more degraded peptide material

The more protein-like fluorescence, peak B/T, was seen to some extent in each leachate but was the primary fluorophore for the pine litter layer (Figure 4a). More protein-like fluorophores corresponds with the LMW pine litter layer. However, it should be noted that the source of protein-like fluorescence may also be attributed to small polyphenolics such as tannins that are leached from fresh plant matter (Cuss & Guéguen, 2015). *Pinus radiata* needles are considered recalcitrant with slower decomposition rates and fresh needles may leach more tannin compounds when compared to native forests (Girisha et al., 2003). Between forest floor layers, there was a decrease in the protein-like components with soil depth, which is consistent with the humification of the organic matter within the samples.

Figure 3: EEM scans for native forest leachate a) litter layer, b) organic layer; c) mineral soil.

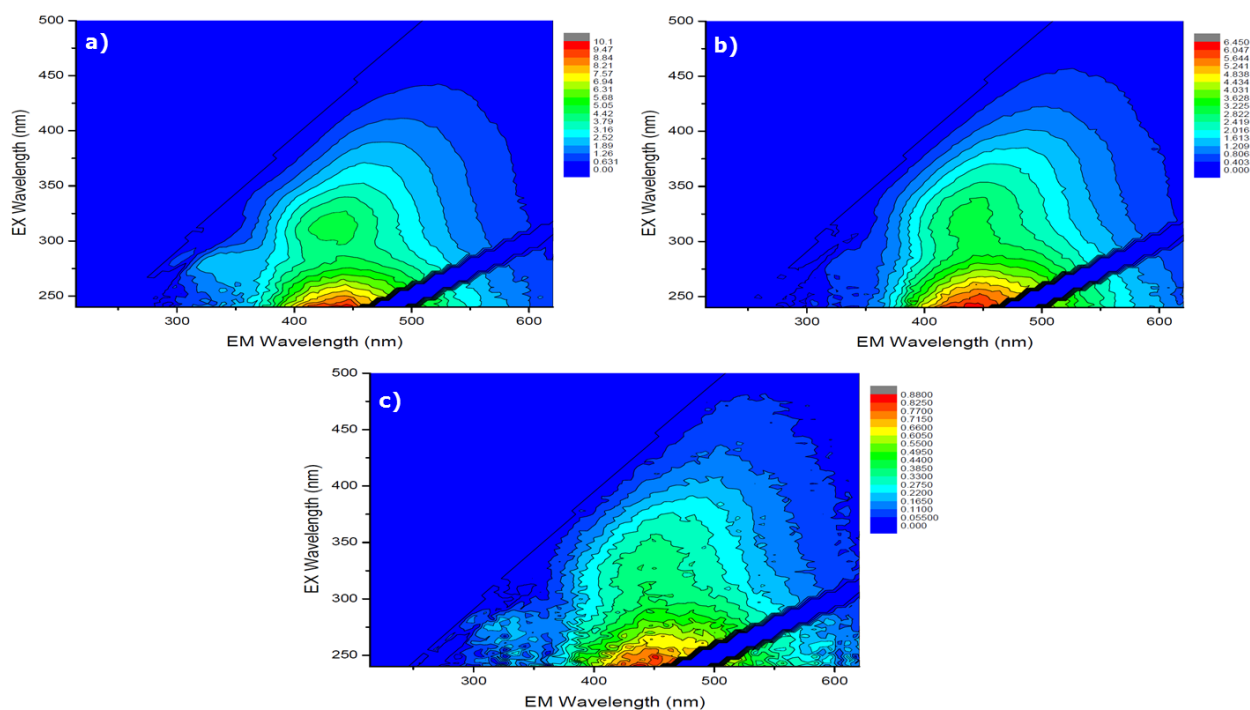
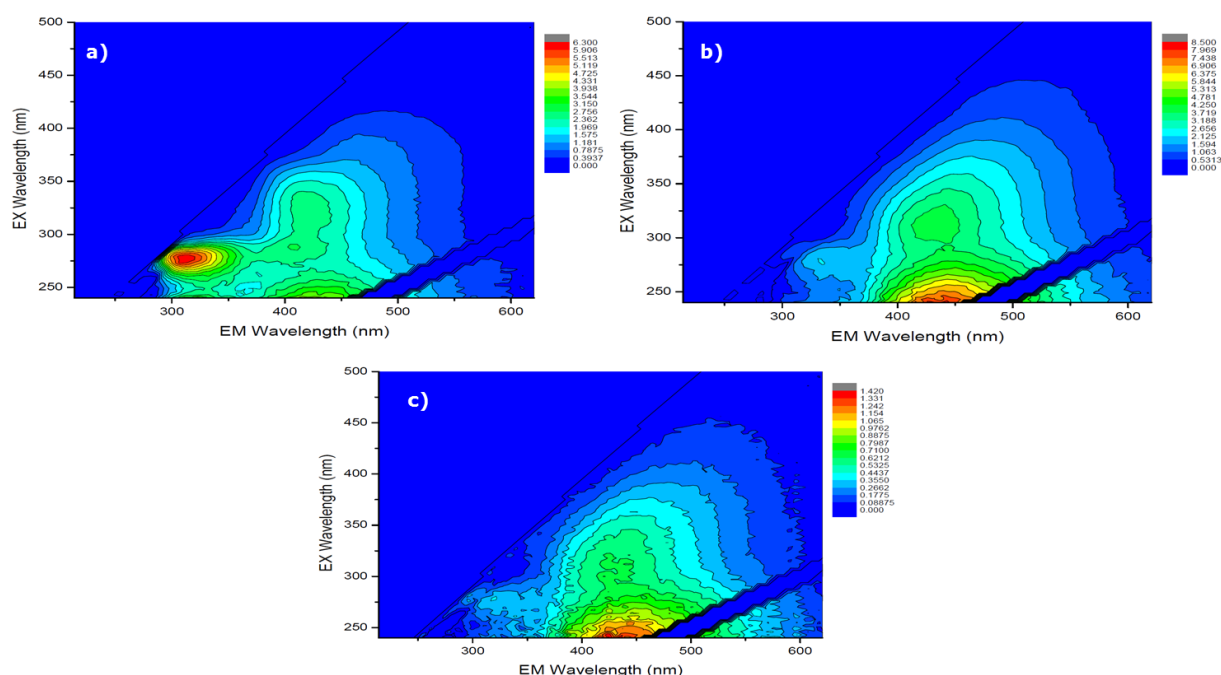


Figure 4: EEM scans for pine forest leachate a) litter layer, b) organic layer; c) mineral soil.



### 3.3 IMPACT ON SURFACE WATER QUALITY

These experiments were performed to provide a better understanding of how land use in a given water catchment can affect water quality in surface waters. Terrestrial NOM enters aquatic ecosystems through groundwater and surface flow. The hydrology of catchment will be the greatest control over how much NOM is exported and land use within a catchment will have a direct impact on the quality of NOM entering surface waters.

Based on our findings the concentration of NOM leached from *Pinus radiata* is lower when compared to the native forest catchments. Therefore, pine forest management such as pruning, thinning and harvesting has the potential to transport lower concentrations of DOC to surface waters once trees have matured, however forest cycles and management activities may affect NOM exported from these ecosystems. Clear-cutting and reharvesting activities have the potential to export large sediment loads to surface waters, due to the lack of vegetation and heavy rainfalls, and in turn may increase NOM quantity in these waters. The increase of terrestrial NOM to surface waters can decrease the light penetration which can influence lake stratification and lake turnover. Native forest in a catchment, with no management activities, will deliver consistent quantity and quality of NOM to surface waters with minor variability in quality and quantity over the year due to seasonal influences.

NOM which is characterised as LMW and high protein-like fluorescence is considered highly labile and will be rapidly consumed by heterotrophic bacteria. HMW and humic-like NOM are slowly degraded but in lakes which have high residence times and increased light, photochemical reactions can occur which will degrade this recalcitrant NOM. NOM produced from planted *Pinus radiata* forests was found to have NOM of LMW leached from the litter layer, and more protein-like fluorescence. The mineralization of this NOM by heterotrophic bacteria can stimulate phytoplankton production and release nutrients which will influence rates of primary production (Solomon et al., 2015).

### 3.4 IMPACT ON WATER TREATMENT

*Pinus radiata* planted forests are located throughout New Zealand and in some areas within drinking water catchments. NOM plays an important role in drinking water treatment due to the potential for DBP formation and membrane fouling which can inhibit treatment. NOM characterised as HMW and highly aromatic is easily removed during coagulation in drinking water treatment, while LMW hydrophilic NOM is more difficult to remove using conventional treatment. The aromatic HMW NOM has a higher potential to create DBPs during the disinfection stage of treatment (Matilainen, Vepsäläinen & Sillanpää, 2010). However, some studies have shown hydrophilic LMW NOM can also produce certain DBPs during treatment.

Planted *Pinus radiata* litter layers have the potential to leach LMW and high protein-like NOM to surrounding surface waters. This NOM is more difficult to remove by coagulation and can react with the disinfectant stage to produce DBPs. HMW humic-like NOM produced by native forest leachate has the greatest propensity to cause DBP formation but is easily removed during coagulation. However, the increased quantity of NOM which is leached from native forests may effect treatment by influencing alum dosages for these surface waters. The same increases in quantity of NOM may be seen in planted pine forests where management activities occur. This study did not take into account the age of the forest or canopy cover of the catchments where samples were taken. Differences in the quantity of organic matter leached into surface waters will be directly related to hydrology, forest age, and hydrologic events within that catchment. While the pine samples in this study leached lower amounts of DOC per dry weight than native forest, surface waters in planted pine forests may see increased DOC concentrations. Management activities, such as clear-cutting, would cause decreased interception and evapotranspiration of precipitation, therefore increasing sediment loads as well as terrestrial NOM to surface waters.

## 4 CONCLUSIONS

Differences were seen the chemical quality of NOM from *Pinus radiata* and native forest litter and soil layers. Native forest litter layer and soil layers leached aromatic humic-like NOM with HMW. While more reactive with the water treatment process, this type of organic matter is easily removed during coagulation. *Pinus radiata* litter samples leached LMW protein-like organic matter which is more difficult to remove during the water treatment process and has the potential to be reactive. LMW organic matter will also be more bioavailable to bacteria, altering primary productivity in surface waters.

The management and protection of surface water catchments, particularly drinking water catchments, are important to ensuring clean waters. Due to the large amount of planted pine forests in New Zealand, a better understanding is needed on how these forests will affect the quality and quantity of NOM transported to surface waters when compared to native forests. It is known that during certain points of a planted pine forest rotation, such as clear-cutting, there will be an increase in overland flow and erosion occurring, especially on steep slopes. These effects will be present until a few years after a new planting. A better understanding on how different phases of the forestry cycle effect water quality in catchments in needed, particularly in the understanding of terrestrial and aquatic NOM dynamics. Further research should also focus on different hydrologic events that are expected to occur due to climate change, such as prolonged dry periods and intense rainfall events, and how terrestrial NOM will be transported through native and planted forests at different phases. These understandings will allow for water utilities to have a better understanding of how their catchments behave and how NOM will change in order to optimize treatment processes.

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