Permafrost degradation and nitrogen cycling in Arctic rivers: Insights from stable nitrogen isotope studies

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Abstract

Across the Arctic, vast areas of permafrost are being degraded by climate change, which has the potential to release substantial quantities of nutrients, including nitrogen into large Arctic rivers. These rivers heavily influence the biogeochemistry of the Arctic Ocean, so it is important to understand the potential changes to rivers from permafrost degradation. This study utilised dissolved nitrogen species (nitrate and dissolved organic nitrogen (DON)) along with nitrogen isotope values ($\delta^{15}N-NO_3^-$ and $\delta^{15}N$-DON) of samples collected from permafrost sites in the Kolyma River and the six largest Arctic rivers. Large inputs of DON and nitrate with a unique isotopically heavy $\delta^{15}N$ signature were documented in the Kolyma, suggesting the occurrence of denitrification and highly invigorated nitrogen cycling in the Yedoma permafrost thaw zones along the Kolyma. We show evidence for permafrost derived DON being recycled to nitrate as it passes through the river, transferring the high ^{15}N signature to nitrate. However, the potential to observe these thaw signals at the mouths of rivers depends on the spatial scale of thaw sites, permafrost degradation and recycling mechanisms. In contrast with the Kolyma, with near 100% continuous permafrost extent, the Ob' River, draining large areas of discontinuous and sporadic permafrost, shows large seasonal changes in both nitrate and DON isotopic signatures. During winter months, water percolating through peat soils records isotopically heavy denitrification signals in contrast with the lighter summer values when surface flow dominates. This early year denitrification signal was present to a degree in the Kolyma but the ability to relate seasonal nitrogen signals across Arctic Rivers to permafrost degradation could not be shown with this study. Other large rivers in the Arctic show different seasonal nitrogen trends. Based on nitrogen isotope values, the vast majority of nitrogen fluxes in the Arctic rivers is from fresh DON sourced from surface runoff through organic-rich top-soil and not from permafrost degradation. However, with future permafrost thaw, other Arctic rivers may begin to show nitrogen trends similar to the Ob'. Our study demonstrates that nitrogen inputs from permafrost thaw can be identified through nitrogen isotopes, but only on small spatial scales. Overall, nitrogen isotopes show potential for revealing integrated catchment wide nitrogen cycling processes.

1 Introduction

The Arctic Ocean contains ~1% of global ocean volume but receives greater than 10% of the total global riverine discharge (Frey and McClelland, 2009). This disproportionate influence of rivers means that any changes in riverine inputs will likely have significant implications on marine chemical, physical and biological processes (Holmes *et al.*, 2012). River biogeochemistry and discharge also integrate catchment wide processes, making them potentially sensitive indicators of change to the terrestrial environment (Holmes *et al.*, 2000). With diminishing sea ice and opening of surface waters to light, Arctic productivity is sensitive to riverine nutrient inputs and particularly nitrogen which is the limiting nutrient in coastal areas (Thibodeau *et al.*, 2017).

Biologically available nitrogen can exist as dissolved inorganic nitrogen (DIN) in forms of nitrate, nitrite and ammonium. DIN is calculated as the sum of these three forms (DIN = $NO_3^- + NO_2^- + NH_4^+$) (McCrackin *et al.*, 2014) and can be taken up by primary producers (Tank *et al.*, 2012). Nitrite and ammonium are highly biologically labile and so only persist for a short time before being converted into nitrate or assimilated. Nitrogen can also exist as dissolved organic nitrogen (DON) but these forms generally need to be broken down (remineralised) into DIN before uptake can occur (Tank *et al.*, 2012). DON is calculated as the difference between total dissolved nitrogen (TDN) and DIN: (DON = TDN – DIN) (Frey *et al.*, 2007). Nitrate is expected to be the dominant species so a simplification can be made to DON = TDN – NO_3^-. As part of the nitrogen cycle, exchange between these pools occurs in riverine and coastal areas depending on environmental conditions. In oxic conditions, assimilation and nitrification occur, while denitrification can be dominant in anoxic conditions (Voigt *et al.*, 2017).

Extensive areas of permafrost influence most of the riverine inputs to the Arctic Ocean. Permafrost is defined as *'any subsurface material that remains below 0^{o}C for at least two consecutive years'* (Van Everdingen, 1998). It is defined exclusively on the basis of temperature, not whether ice is present. Permafrost can stabilise ancient soils, preventing breakdown of soil organic matter and is classified based on its spatial extent and thickness. Continuous permafrost has 90-100% aerial extent and is 100-800m thick, while discontinuous has 50-90% extent and is 25-100m thick (Anisimov and Reneva, 2006).

Permafrost undergoes degradation through different mechanisms. The most common is active layer deepening, where the top layer of soil that degrades and refreezes each year becomes deeper due to increased summer temperatures and the influx of precipitation (Nelson *et al.*, 1997). This increases the depth of permafrost, allowing the active layer to penetrate previously frozen soil. Permafrost can also degrade through riverbank or coastal erosion, cutting through deep horizons of permafrost promoting rapid and often catastrophic degradation (Streletskiy et al., 2015). These mechanisms all lead to increases in soil microbial activity that release dissolved nitrogen from previously frozen organic matter (Beermann et al., 2017). The proportion of the released nitrogen species vary depending on the degree and mechanism of degradation.

Climate change is causing annual surface air temperatures within the Arctic to increase at almost twice the rate of the global average (Hassol, 2004). In 2010, air temperatures in the Arctic were 4^{o}C warmer than the reference period of 1968 – 1996 (NOAA, 2014). A further 4 to 7^{o}C increase is expected by the end of the century (Hassol, 2004). These dramatic temperature changes will result in the Arctic experiencing unprecedented impacts on its environments. Over the whole pan-Arctic watershed, river discharge is increasing by an estimated 5.6km^3y^{-1} each year based on observations from 1964 - 2000 (McClelland *et al.*, 2006). Some recent studies have revealed even greater rates occurring and predicted into the future but some uncertainty exists due to substantial variation across basins and permafrost regimes (Feng *et al.,* 2021). Discharge has already increased by ~10% in Russian rivers compared to this reference period (Peterson *et al.*, 2002). Permafrost is at high risk of degradation with climate change with estimates that 10% of permafrost in the northern hemisphere has disappeared in the last 100 years (NSIDC, 2018). Predictions of future losses vary but a recent study predicts 4.8 or 6 million km^2 of permafrost (32 or 40% of global total) would be lost for a global temperature increase of 1.5 or 2°C respectively (UNFCCC, 2015; Chadburn *et al.*, 2017).

Riverine biogeochemistry across the Arctic will be significantly affected by these changes due to liberation of nutrients and organic matter from the degrading permafrost and alterations to nutrient cycling within Arctic rivers. Although there has been considerable research into the effects of permafrost degradation on organic matter and carbon fluxes (Frey and Smith, 2005; Schuur *et al.*, 2009; Vonk *et al.*, 2013; Spencer et al., 2015), there are fewer studies on nitrogen loading in Arctic rivers and fewer still on cycling and processing. Some of the proposed dynamics of nitrogen cycling from permafrost degradation have been described in a study of Alaskan permafrost by Harms (2013). The active layer of soil is rich in fresh organic matter with a high C:N ratio. Within this layer, biotic assimilation of nitrate occurs along with denitrification in anaerobic conditions. With limited permafrost degradation, nitrogen export from this layer will largely be in the form of DON, rather than nitrate, but at relatively low concentrations. Much of the Arctic is covered in many meters of peat so it is argued that this may apply to large areas of Arctic watersheds, especially western Siberia (Frey and McClelland, 2009). As watershed mean annual air temperature (MAAT) increases past the threshold limit for permafrost (-2°C – catchment temperature where permafrost begins to degrade) DON concentrations in streams and rivers rapidly increase, with only smaller changes in nitrate concentrations, resulting in the DON:nitrate ratio increasing. The extent of permafrost degradation is the controlling factor on DON variability as greater depths of soil are exposed with increasing degradation.(MacLean *et al.*, 1999; Frey *et al.*, 2007).

In contrast, where shallow peat exists, warming and underlying permafrost degradation can cause the active layer to deepen into mineral horizons with low C:N ratios. This can lead to flow paths of groundwater being directed through these mineral horizons leading to an increased adsorption of DON and release of nitrate through subsequent mineralization and nitrification (Harms, 2013). This process can occur to a lesser extent on a seasonal cycle with groundwater influx from mineral horizons in the winter and surface runoff from organic horizons in spring and summer. Extensive future permafrost degradation in catchments with active layer deepening occurring is expected to increase the seasonal groundwater contribution leading to decreased DON concentrations and increased nitrate concentrations in streams and rivers (Walvoord and Striegl, 2007).

These studies focus on gradual active layer deepening processes. Other more rapid permafrost degradation processes such as riverine and coastal erosion are more spatially limited but could be responsible for moving nitrogen species rapidly and directly from terrestrial permafrost to riverine or coastal environments (Berhe *et al.*, 2007). This mechanism is understudied so the resulting nitrogen export is still relatively unknown.

The processing and cycling of nitrogen that occurs in-stream and in near-shore coastal areas after release from permafrost is also largely unknown. DON represents a 5x greater influx to Arctic shelf waters from rivers than nitrate across the whole Arctic but 70% of the DON is removed in shelf waters before reaching the open marine environment (Thibodeau *et al.*, 2017). The processes involved in this removal are largely unclear but riverine nitrate can have a strong remineralised signal, with sources from recycling of particulate organic nitrogen (PON) and DON (Thibodeau *et al.*, 2017). The biolability of riverine DON and exchanges with the nitrate pool are key aspects that influence the Arctic nitrogen cycle, and the impact of future permafrost degradation on these aspects has not been studied. It is important, therefore, to understand how permafrost degradation may influence each nitrogen species input across multiple Arctic river catchments and the subsequent potential changes to the riverine and coastal nitrogen cycle as a result. This study focusses solely on the dissolved species of nitrogen, where most cycling occurs.

Dual stable nitrogen and oxygen isotopes of dissolved nitrate ($\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$), and nitrogen isotopes of TDN and DON ($\delta^{15}N$-TDN and $\delta^{15}N$-DON) were used to determine cycling and source processes. During various stages of the nitrogen cycle, biological processes favour the use of the light nitrogen isotope (^{14}N) over the heavy isotope (^{15}N) due to it being more energetically favourable (Sigman and Casciotti, 2001). This leaves the residual pool with more of the heavier isotopes, thus a more positive (higher) isotopic signature. The relative extent of a certain cycling processes is proportional to the residual isotopic signature. Transformation between nitrogen pools can also induce kinetic isotopic fractionation with fractionation factors unique to each transformation process (Voigt *et al.*, 2017). Oxygen isotopes behave similarly but have different sources to nitrogen during each cycling stage so the use of the dual isotope technique can distinguish sources of nitrate and determine the relative influence of nitrogen cycling processes such as nitrification, assimilation or denitrification (Thibodeau *et al.*, 2017). Comparisons of $\delta^{15}N\text{-}NO_3^-$ versus $\delta^{18}O\text{-}NO_3^-$ can show distinct sources of nitrate and mixing between them based on the environmental conditions inducing specific isotopic fractionations to both elements. Particular nitrogen cycling processes can also be shown using this method. For example, during denitrification or biological assimilation (nitrate consumption processes), the residual nitrogen and oxygen pools become equally enriched in the heavy isotopes (Granger *et al.*, 2004), the fractionation of the two isotopes is "coupled" resulting in a near 1:1 relationship (Botrel *et al.*, 2017). In comparison, nitrification, a nitrate producing process, causes decoupled fractionation between the isotopes due to different nitrogen and oxygen sources (Sigman *et al.*, 2005).

Since DON concentrations are elevated relative to nitrate concentrations in this Arctic riverine environment (Thibodeau *et al.*, 2017), $\delta^{15}N$-DON can be measured, allowing the possible sources of DON to be determined and when combined with nitrate isotope data, some of the cycling mechanisms can also be identified. This is only the second study utilising $\delta^{15}N$-DON in the Arctic (Thibodeau *et al.*, 2017) and the first to apply it to Arctic rivers.

This study aimed to contribute to the debate on the role of permafrost degradation on changing riverine loads of nitrogen into the Arctic. Specifically determining if there is an increase of dissolved nitrogen supply into Arctic rivers and coastal zones as a result of permafrost degradation within catchments, what the proportions of nitrogen species within these inputs are and whether a unique permafrost degradation signal be detected in rivers using dissolved nitrogen species. A major focus was on the understudied area of nitrogen cycling within rivers and coastal areas. Nitrogen isotope signals in degradation zones and Arctic rivers with differing permafrost extents were utilised to provide insights into catchment scale nitrogen cycling and recycling of various forms during riverine transport.

2 Methods

2.1 Study areas and sample collection

2.1.1 Kolyma

Samples from the lower Kolyma River catchment were used to identify local scale nitrogen signals from zones affected by varying levels of permafrost degradation (Figure 1a). Samples were collected in September 2018 from surface water, filtered on-site using a 0.7µm glass fibre filter and immediately frozen. Late Autumn sampling was chosen as active layer depths reach their maximum extent at this time, allowing the greatest permafrost DOM influx to streams (Schuur *et al.*, 2008; Mann *et al.*, 2012).

PD1 is a well-studied permafrost degradation zone known as Duvannyi Yar, where a 10-12km long outcrop of permafrost is exposed along the bank of the Kolyma River. The permafrost is part of the extensive Pleistocene Yedoma permafrost that covers much of the Kolyma and Lena catchments and contains almost a third of all organic matter stored in Arctic permafrost (Vonk *et al.*, 2013). Limited freeze-thaw action prevents processing and degradation of organic matter, resulting in storage of ancient and well-preserved organic matter. Ancient ice wedges also characterise this permafrost, accounting for about 50% of the soil volume and storing some of the organic matter within it (Schirrmeister *et al.*, 2011). Yedoma permafrost is mostly continuous throughout the Kolyma catchment except at a limited number of erosional sites such as Duvannyi Yar. Here, the river erodes it at 100m per year, leading to extensive permafrost degradation throughout the soil horizon (Vasil'chuk *et al.*, 2001). This destabilizes soil profiles, leading to bank collapses and release of ancient organic matter into streams. This erosional style degradation leads to both organic layer and mineral influence in dissolved nitrogen and carbon additions, differing to active layer degradation mechanisms, where the peat depth determines which layer is exposed after degradation (Harms, 2013). Radiocarbon dating of DOC from a fluid mud stream draining from the degrading permafrost yielded an age of 20,000 years at this site. This organic matter is highly biolabile after thawing occurs and can be assimilated rapidly by aquatic microorganisms after mineralisation (Vonk *et al.*, 2012; Spencer *et al.*, 2015). Samples for this study were collected from a similar fluid mud stream.

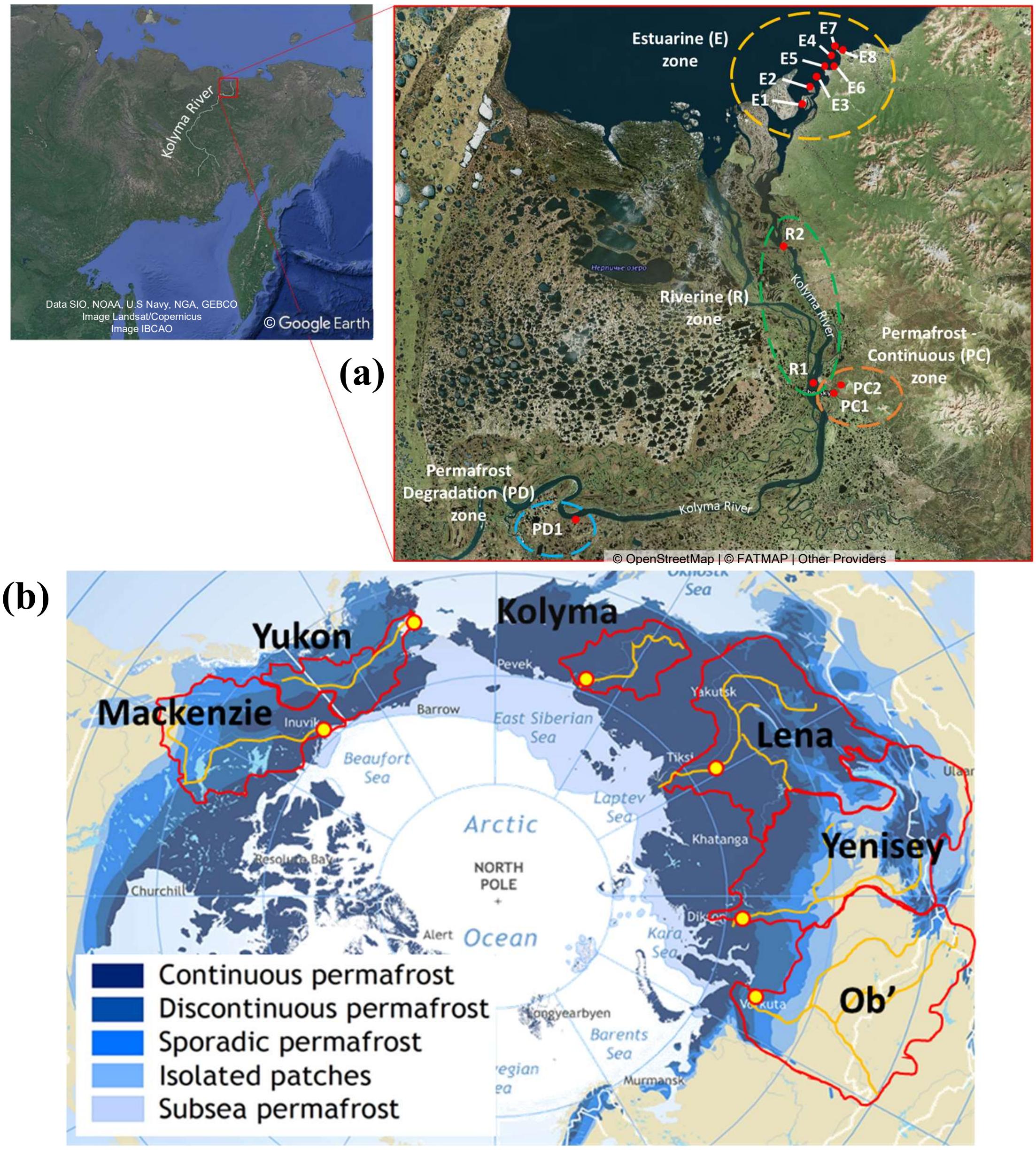
In contrast, samples PC1 and PC2 were taken from streams draining sites underlain with continuous modern permafrost with little permafrost derived DOC, if any. The sites contained functioning ecosystems of larch forests, shrub/moss and lichen understory with no exposed permafrost (Loranty *et al.*, 2018). This is representative of large areas of the Kolyma catchment as well as portions of other Russian Arctic Rivers so can be used to determine the background non-degradation signal for nitrogen species.

To determine how nitrogen species from permafrost degradation are processed within an Arctic river and a marine environment, samples were taken in the main stem of the Kolyma River, downstream of the degradation site along with samples in the estuarine zone where the Kolyma River meets the East Siberian Sea (Figure 1a). The riverine sample labelled R1 is the same site used in the ArcticGRO Kolyma samples described in 2.1.2.

2.1.2 Pan-Arctic Rivers

The Arctic Great Rivers Observatory (ArcticGRO) (https://arcticgreatrivers.org/) is an international project collecting and analysing riverine water samples using identical methods. Samples used in this study were collect in 2017 using methods described in Holmes *et al.*, (2021) from the six largest

Arctic rivers, four in Russia: Kolyma, Ob', Lena and Yenisey and two in North America: Yukon and Mackenzie (Figure 1(b)). Together, the proportion of continuous and discontinuous permafrost within these catchments is 48%, similar to the proportions across the whole pan-Arctic catchments (52%) (Tank *et al.*, 2012). Thus, these rivers represent overall pan-Arctic conditions. These catchments also cover transitions from continuous permafrost zones of the Arctic to permafrost free, capturing the variability that occurs across the pan-Arctic (Tank *et al.*, 2012). Studying the major Arctic rivers allowed comparisons of nitrogen loading and cycling between rivers to identify variations of permafrost and catchment influences. The generated datasets from this study were interpreted using discharge, concentration and other biogeochemical data from 2003 to 2018, available on the ArcticGRO website (https://arcticgreatrivers.org/data/). The overview of the production of this dataset as well as some of the associated uncertainties and variability are shown in Holmes *et al*. (2012) and Shiklomanov *et al*. (2006).



(c)

	Yukon	Mackenzie	Ob	Yenisey	Lena	Kolyma
Discharge ($km^3\ yr^{-1}$)	208	298	427	636	581	111
Catchment area ($10^6\ km^2$)	0.83	1.78	2.99	2.54	2.46	0.65
MAAT (°C)	−0.4	0.7	1.4	−1.0	−6.5	−10.1
Cont. permafrost (%)	19	13	1	31	77	99
Total forest (%)	19.7	34.4	38.6	67.3	72.1	49.9
Wetlands (%)	0.4	0.1	8.5	2.6	3.3	3.8
Water bodies (%)	7.0	10.3	2.4	2.1	1.7	1.6
Average peatland depth (cm)	135	216	201	246	293	123

Figure 1 – (a) Sample names and collection locations from sites around the lower Kolyma River and estuary. Samples collected on a research trip in autumn 2018. Satellite image 1 source: Data SIO, NOAA, U.S Navy, NGA, GEBCO | Image Landsat/Copernicus | Image IBCAO. © Google Earth. Satellite image 2 source: © OpenStreetMap | © FATMAP | Other Providers.
(b) Catchment areas (red lines) and sampling locations (red and yellow circles) of the six largest Arctic rivers (orange lines) used in the ArcticGRO III project. The extent and type of permafrost present in each catchment is also shown. Base map modified from Brown et al. (1997).
(c) Catchment characteristics of each river shown. Data taken from Amon et al. (2012), Holmes et al. (2012) and average peatland depth calculated from supplementary data in Hugelius et al. (2020).

2.2 Analysis of nitrogen species - concentrations and stable isotopes

TDN and DOC concentrations were measured using a Shimadzu TOC/TN analyser at the University of Edinburgh (Kolyma samples) and Woods Hole Research Centre (ArcticGRO samples). Inorganic nutrient concentrations were measured at the Woods Hole Research Centre using an Astoria Analyzer (ArcticGRO samples) and also calculated from mass spectrometer peak areas referenced to two internal standards with known concentrations and isotopic values (Kolyma samples). All stable isotopic analysis was carried out at the School of Geosciences, University of Edinburgh.

2.3 $\delta^{15}N$ and $\delta^{18}O$ of Nitrate (NO_3^-)

The dual isotope technique to measure nitrogen and oxygen isotopes of nitrate was carried out by the denitrifier method modified from Sigman *et al.*, (2001); Casciotti *et al.*, (2002) and McIlvin and Casciotti, (2011). It utilises denitrifying bacteria, *Pseudomonas aureofaciens,* which lack nitrous oxide (N_2O) reductase activity to convert dissolve nitrate into N_2O gas while maintaining an identical nitrogen isotopic signature to the original nitrate. The oxygen isotope signature is subject to change with water molecules so is corrected for using the method in Weigand *et al.*, (2016). Samples with low nitrate concentrations (<1µM) could not be analysed for nitrate isotopes. As a result, some samples were excluded from analysis. The analytical precision for $\delta^{15}N$-NO_3^- was ±0.4‰ and ±0.3‰ for the two reference standards IAEA-N3 and USGS-34 respectively and for $\delta^{18}O$-NO_3^- it was ±1.0‰ and ±0.8‰ respectively. This was based on >30 measurements of the international standards analysed on several different days.

2.4 $\delta^{15}N$ of TDN

This method utilises an extra step prior to the denitrifier method where the sample TDN is converted into nitrate while maintaining the TDN isotopic signature. This involves oxidation with potassium persulphate followed by digestion of the organic nitrogen to an equivalent amount of nitrate that is then prepared via the denitrifier method. This procedure was adapted from Knapp *et al.*, (2005), Thibodeau *et al.*, (2013, 2017) using internal standards to ensure that fractionation is minimal and values obtained are representative of the actual $\delta^{15}N$ of DON. $\delta^{15}N$-TDN isotopic values represent the values of both DON and DIN (nitrate + nitrite). Therefore, $\delta^{15}N$-DON is calculated using concentration weighted $\delta^{15}N$-NO_3^- and $\delta^{15}N$-TDN values and allowed the processes involved in organic and inorganic nitrogen to be compared. $\delta^{15}N$-DON could only be calculated when $\delta^{15}N$-NO_3^- values were available ([NO_3^-] > 1µM). Samples with nitrate concentrations less than 1µM were reported as $\delta^{15}N$ of TDN since $\delta^{15}N$ of DON was not calculable and using $\delta^{15}N$ of TDN allowed comparisons with other samples.

This calculation assumes that the isotopic signature of nitrate can represent that of DIN and the contribution from ammonium is negligible. This is because ammonium is unstable in peatland environments and is rapidly converted into nitrate, meaning nitrate makes up the majority of the DIN pool and ammonium concentrations are low and often below detection limits, as mentioned in Holmes *et al.*, (2012).

3 Results and Discussion

3.1 Permafrost extent and nitrogen species

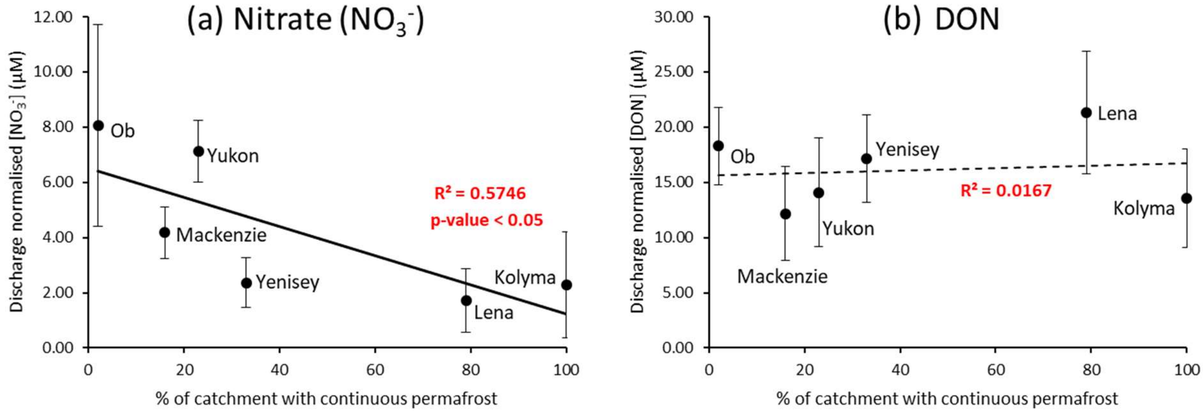


Figure 2 - Relationships between the extent of continuous permafrost within each river catchment and (a) nitrate and (b) DON discharge normalised concentrations (µM) for the period 2003 - 2018. Data from the ArcticGRO online dataset. Error bars from the discharge normalised standard deviations are quite large due to the large year-to-year variability in nitrate/DON concentrations however these do not affect the overall trends observed.

Mean ArcticGRO nitrate and DON (TDN-DIN) concentrations of all available data points in the ArcticGRO dataset from 2003 - 2018 were calculated for each of the six rivers. This produced average annual nitrate and DON concentrations (from Holmes et al., 2012). To remove the effect of unequal seasonal sampling and the large variability in hydrology in these river systems, the concentrations were normalised to the discharge of the sample collection month and plotted against percentage continuous permafrost (Figure 2). This allowed more accurate inter-river comparisons of nitrogen species concentration.

Negative correlations are present between permafrost extent and discharge normalised nitrate concentrations. The concentration trend shown is statistically significant to a 95% confidence level (p-value = 0.05) according to the Spearman's rank test. However, no statistically significant relationship exists between discharge normalised DON concentrations and permafrost extent for all rivers.

Overall, these negative linear relationships suggest that the less permafrost present in a river catchment, the more nitrate is released from the surrounding soil. Therefore, permafrost degradation may induce greater concentrations of nitrate into Arctic rivers. Similar trends have been observed in other studies (Jones *et al.*, 2005; Harms, 2013). Conversely, no significant relationship can be observed between discharge normalised DON concentrations and permafrost extent in any of the plots (Figure 2 (b)). Given that DON is the dominant form of nitrogen released from soil, the increase in nitrate concentrations but not DON suggests that cycling of organic nitrogen to inorganic forms in soils and/or upstream rivers may be promoted with decreasing permafrost extents. Figure 2 displays the variability from the extent of continuous permafrost, but not from active permafrost degradation. Local scale measurements of degradation sites from the Kolyma River were used to address if active permafrost degradation releases nitrogen and identify cycling processes involved. Seasonal trends were also used to see when each of the species become dominant and to help determine catchment-scale processes.

3.2 Local scale permafrost degradation signals

3.2.1 Concentration of nitrogen species

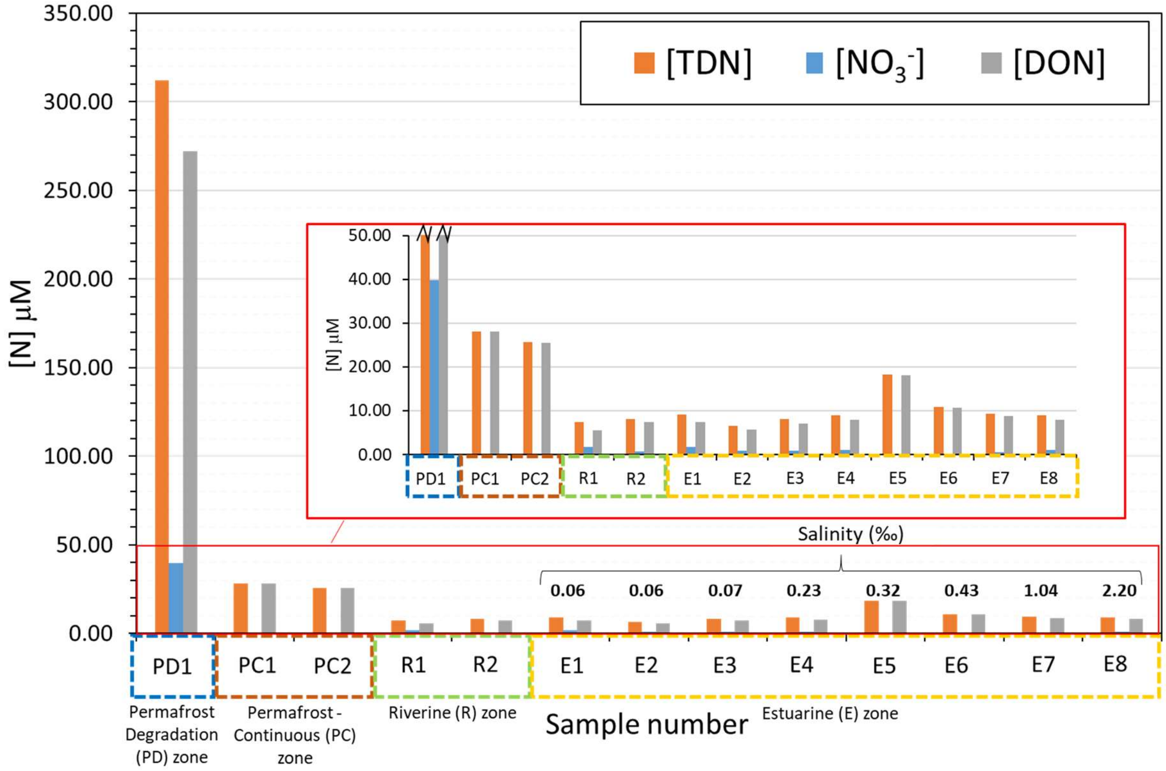


Figure 3 - Concentrations of Total Dissolved Nitrogen [TDN], Nitrate [NO_3^-] and Dissolved Organic Nitrogen [DON] in different zones of the lower Kolyma River as overviewed in Figure 1 (a). Salinity values are displayed for the estuarine samples in order of increasing salinity. The inserted panel shows the small scale differences on downstream sites.

Figure 3 shows the concentrations of different nitrogen species in zones of the Kolyma River and estuary. The concentrations of nitrate and DON represent the dissolved inorganic and the dissolved organic species of TDN respectively. Site PD1 at Duvannyi Yar, with substantial permafrost degradation, has greatly elevated concentrations of all nitrogen species in comparison to other samples. Most of the nitrogen is present as DON (312µM for DON and 40µM for nitrate). In comparison, the permafrost influenced zone (where continuous permafrost is present), has substantially lower concentrations with DON roughly 25-28µM and nitrate concentrations being almost negligible at 0.2µM. The amount of DON relative to nitrate in these sites was however much greater than the permafrost degradation site. Permafrost degradation appears to release DON and nitrate in large amounts whereas the continuous permafrost releases much less DON and very little nitrate.

In the main stem of the river, DON concentrations decreased (to 6-7µM). Nitrate concentrations were greater than in the permafrost-influenced zone (1-2µM) but still an order of magnitude lower than the degradation zone. In the estuarine zone, concentrations of both DON and nitrate fluctuated slightly but remained at a similar level to the riverine samples (DON = 5-9µM, nitrate = 0.2-2µM) with no clear trend in concentration with increasing salinity. DON increased slightly in site 007 but this was anomalous in comparison with the rest of the site concentrations.

These trends suggest that within continuous permafrost zones of the Kolyma catchment, only DON is released from soil in significant amounts. DON concentrations were 169x greater than nitrate concentrations. This observation that more permafrost leads to less release of nitrate supports observations on the catchment-scale as noted in section 3.1. Our findings show that within the Yedoma permafrost degradation zone, permafrost degradation facilitates the release of large amounts of both nitrate and DON from the soil and into the dissolved phase. DON was still the dominant species, but not as much as with continuous permafrost, with a concentration 7 times greater than nitrate.

However, in the main stem of the river, the signals were quickly lost, with concentrations decreasing by 44 and 31-fold for nitrate and DON respectively. This decrease in both species was partially due to a dilution effect but could also be due to the diluting source having a lower proportion of nitrate than DON. Such a possibility is consistent with continuous permafrost occupying the vast majority of the catchment with smaller inputs of DON and with lower DON: nitrate ratios. DON concentrations may be 10-times higher than nitrate concentrations in the main stem due to nitrate being more readily removed than DON. However, there was no clear change in concentrations downriver, suggesting processing of the nitrogen pool may be small but cycling processes are difficult to determine using only concentration data.

3.2.2 Nitrogen Isotopic signatures

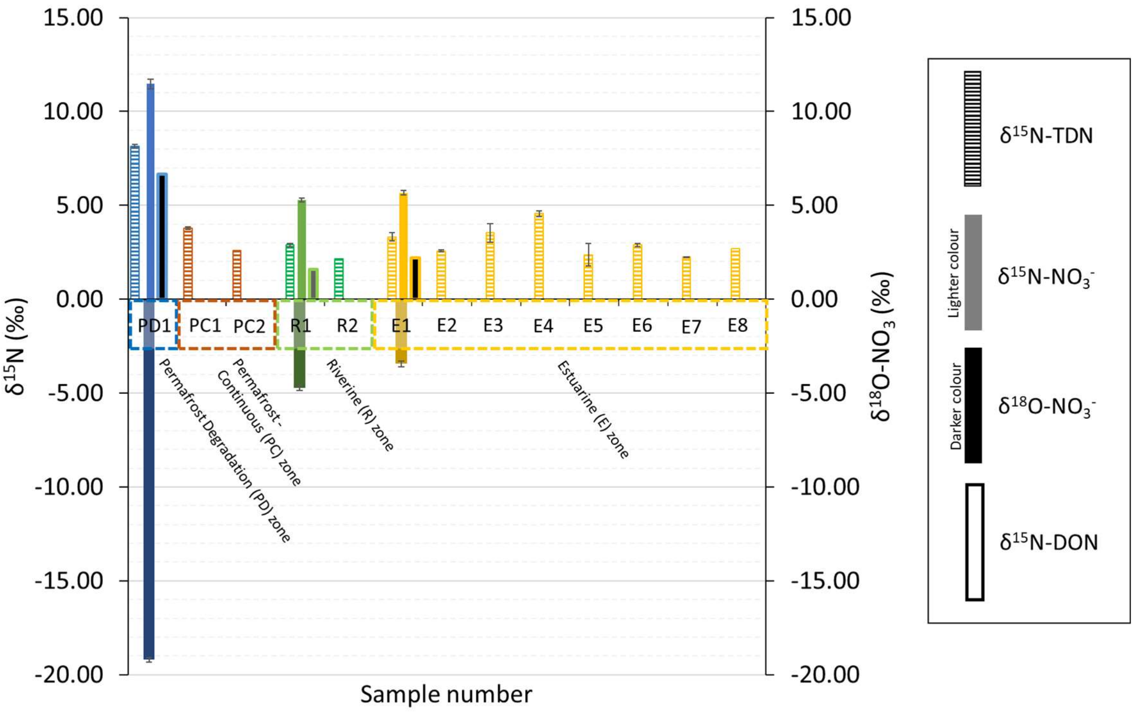


Figure 4 - Nitrogen isotopes of TDN, Nitrate (NO_3^-) and DON in different zones of the lower Kolyma River as overviewed in Figure 1(a). Oxygen isotopes ($\delta^{18}O$) of nitrate are also shown on the negative scale below the nitrogen isotope values. Only three sites (PD1, R1 & R2) were able to have nitrogen isotopes of nitrate (and therefore also of DON) analysed as most nitrate concentrations were <1μM. However, since nitrate concentrations were very small in comparison to DON (see Figure 3) – especially for the permafrost influenced site, then it can be assumed that the nitrogen isotopic signature of DON is roughly equal to the signature of TDN ($\delta^{15}N$-DON ≈ $\delta^{15}N$-TDN). The permafrost-influenced sample was analysed across four repeat runs allowing a robust standard deviation to be calculated.

Figure 4 shows the stable isotopic signatures of different nitrogen species in zones along the Kolyma River. At the permafrost degradation site, nitrogen isotopes of all species were enriched in ^{15}N ($\delta^{15}N-NO_3^-$ = 12‰, $\delta^{15}N$-DON = 7‰) and $\delta^{18}O-NO_3^-$ values were very negative at -19‰. In comparison, the permafrost influenced sites had lower isotopic values for DON (3 to 4‰).

The signals observed in the permafrost degradation site were rapidly lost in the main stem of the river and into the estuary. In the river, $\delta^{15}N-NO_3^-$ was ~5‰ and $\delta^{15}N$-DON was 2 to 5‰, while

$\delta^{18}O-NO_3^-$ was around -5‰. At the start of the estuary, $\delta^{18}O-NO_3^-$ increased to -3‰. With consideration of the errors associated with the measurement, there were no clear trends observed for $\delta^{15}N$ moving downstream (similar to the concentration data) and into the estuary, suggesting minimal alterations to dominant processing cycles of nitrogen in the main river stem.

In summary, a unique signal representing inputs from degrading Yedoma permafrost was detected using concentrations and isotopic signatures of nitrogen species (Figure 3 and Figure 4). From the site at Duvannyi Yar, extensive permafrost degradation brings water to the Kolyma River with very high DON concentrations (272µM) and high $\delta^{15}N$-DON (6.7‰). In addition, nitrate concentrations were high (40µM) with very high $\delta^{15}N-NO_3^-$ (11.5 ± 0.26‰) but very low $\delta^{18}O-NO_3^-$ (-19.2 ± 0.37‰).

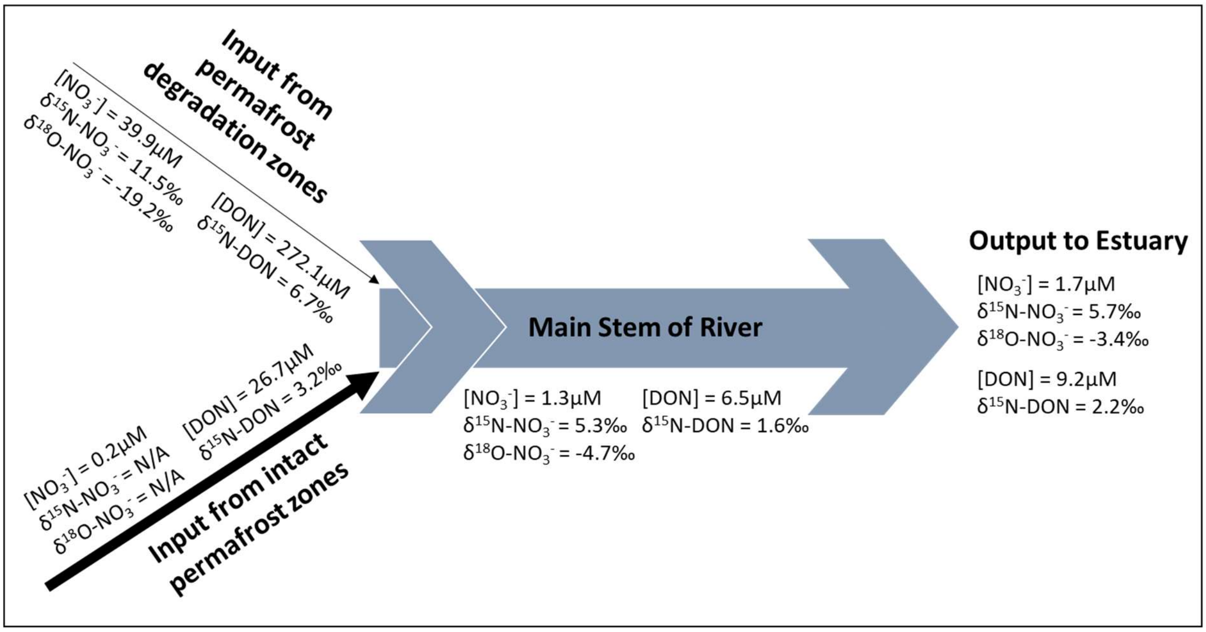


Figure 5 – Summary of concentration and isotopic signals of nitrate and DON species in the Kolyma system. Data displayed are average values of all samples in each zone of the river

3.2.3 Explanation of signals observed and likely processing

During degradation, permafrost releases large amounts of organic matter and organic nitrogen (DON) from the soil and ice (272µM in this study, Figure 5). This undergoes rapid mineralization, firstly to highly reactive ammonium then to nitrate via nitrification (Voigt *et al.*, 2017). The lighter isotope of nitrogen is preferred for these reactions through kinetic fractionation (Mariotti *et al.*, 1981), however the first step of this reaction (ammonification, DON converted to ammonium), is associated with a small fractionation factor (Swart *et al.*, 2008) so cannot fully explain the high isotopic signature of the residual DON pool (6.7‰). Nitrification produces high concentrations of nitrate (40µM), however the waterlogged and anaerobic conditions in the soil, combined with the lack of vascular plants for competition (Repo *et al.*, 2009), produces good conditions for denitrifying bacteria to convert the readily available nitrate to atmospheric N_2 via denitrification. This reaction produces much stronger kinetic fractionation than nitrification (Swart *et al.*, 2008) so this partial denitrification, where not all nitrate is denitrified, results in the residual nitrate pool becoming isotopically heavy with a high $\delta^{15}N-NO_3^-$ signal of 11.5‰. DON also shows this high denitrification signal suggesting exchange of denitrified nitrogen between the nitrate and DON pools through the assimilation of partially denitrified heavy nitrate and the production of heavy DON by remineralisation. Even though ^{14}N is preferred to form DON, a highly invigorated nitrogen cycle with continuous nitrogen exchange between pools explains the unusually heavy $\delta^{15}N$ values in both DON and nitrate pools.

Additionally, the fact that DON is not isotopically heavier than nitrate is also expected as the primary source of DON is from decaying organic matter preserved in the permafrost and this process releases organic matter with a low $\delta^{15}N$ to start with that forms DON also with a lower $\delta^{15}N$ (Sipler and Bronk, 2015). This is supplemented with a smaller contribution from DON formed from the recycled heavy nitrate. Therefore, nitrogen processing in the permafrost degradation zone not only involves active release of DON by heterotrophic remineralisation with anaerobic processes such as denitrification, but also exchange between nitrogen pools. Oxygen isotopes of nitrate provide further evidence for this recycling.

During denitrification, fractionation of nitrogen and oxygen is 1:1; therefore, oxygen isotopes should behave similarly to nitrogen isotopes and become isotopically heavy (high signal) in the residual nitrate pool (Sigman *et al.*, 2009). This is not observed however, as $\delta^{18}O\text{-}NO_3^-$ in the permafrost degradation stream had a very negative (low) signal (-19.2‰). Therefore, denitrification alone cannot explain the oxygen isotopic signatures. The $\delta^{18}O\text{-}NO_3^-$ signal 'resets' to the value of ambient water and dissolved oxygen when it is recycled (Buchwald and Casciotti, 2010) while the fixed nitrogen is internally cycled, retaining its isotopic signatures (Sigman *et al.*, 2009). The observed $\delta^{18}O\text{-}NO_3^-$ signal in the permafrost degradation zone is very close to the value of $\delta^{18}O\text{-}H_2O$ of Kolyma River water for this time of year (-20‰) (Yi *et al.*, 2012). However, this stream water was draining straight from the ancient ice wedges and had not been in contact with the main stem 'modern' water. The $\delta^{18}O\text{-}H_2O$ of ice wedges was much lower than present day river $\delta^{18}O\text{-}H_2O$: -33.3‰ (Vonk *et al.*, 2013) due to different environmental conditions during the formation period of this permafrost (Hubberten *et al.*, 2004; Vonk *et al.*, 2013). Given that the denitrification signal was largely reduced in $\delta^{18}O\text{-}NO_3^-$ suggests that the partially denitrified nitrate was almost completely recycled through the assimilation-ammonification-nitrification cycle during permafrost degradation. This vigorous nitrogen cycling and exchange between nitrogen pools should occur in the degradation site soil before reaching the river. Collectively, the dual nitrogen and oxygen isotopic signals of nitrate and nitrogen isotopes of DON provide evidence for a range of nitrogen recycling process active in the degradation zone. This produced unusually heavy $\delta^{15}N$ values in both DON and nitrate pools and a $\delta^{18}O\text{-}NO_3^-$ signal representing both the recycling and denitrification processes. These isotopic signals show a unique signature where inputs from Yedoma permafrost degradation enter the main stem of the river. Processing in the main stem can then alter these signals, explaining the signal observed at the river mouth.

Organic matter from this permafrost site is very biolabile and ancient permafrost DOC is the most biolabile source of DOC in riverine Arctic systems due to lack of processing and survival of bacteria (Vonk *et al.*, 2013). Up to 50% of permafrost DOC can be lost in less than seven days in the Kolyma River (Spencer *et al.*, 2015). This time period is equal to water residence times between headwater streams in degradation zones and the river mouth (3 days) (Vonk *et al.*, 2013). However, DON may behave differently to DOC in terms of cycling. Unlike DOC (where a large proportion of the carbon is oxidised and lost as CO_2) (O'Donnell *et al.*, 2016), DON will mostly be converted into nitrate during degradation. This nitrate will likely continue to be recycled along with DON degradation in the river.

Therefore, it is expected that the high $\delta^{15}N$ values (for both DON and nitrate) from the degradation site would be retained through recycling and even if some nitrogen was lost as N_2 or N_2O or to PON (which sinks out) via assimilation the residual dissolved pool would remain isotopically heavy. However, since these DON signals were not clearly observed downstream this suggests that the contributions of these permafrost degradation streams were relatively small compared to other DON sources in the main stem of the river (Drake *et al.*, 2018) probably receiving waters from continuous permafrost, resulting in nitrogen signals from permafrost degradation being quickly lost. Dilution with main stem water containing lower concentrations and lower $\delta^{15}N$ values is a major contributor to the changes observed.

The main stem isotopic signatures represent the average catchment characteristics (a combination of all permafrost influenced and degradation sites) and since the $\delta^{15}N$-TDN were much more similar (the same within error) to the permafrost influenced site, it can be assumed that these conditions represent the majority of the Kolyma catchment as it has near 100% continuous permafrost coverage. However, within that TDN input, permafrost influenced sites supply mostly DON but very little nitrate (Figure 2 and Figure 3). From the permafrost zone to the main stem, DON concentrations decreased and nitrate concentrations increased slightly (even with dilution effects). The isotopic signature of the main stem nitrate was also significantly heavier than that of permafrost and main stem DON. The concentration trends suggest that recycling of DON to nitrate was occurring in the river and, when combined with the isotopic trends, some of the isotopically heavy nitrogen from DON and nitrate originating in the degradation site may have contributed to these recycling processes. This allows the heavy nitrogen signal from the degrading Yedoma permafrost to be transferred and retained in the main stem nitrate. This was assisted by the negligible diluting nitrate inputs from much of the permafrost-covered catchment. Importantly, this also suggests that a significant nitrate pool in the main stem is produced from DON recycling rather than from direct nitrate inputs to the river.

However, $\delta^{18}O$-NO_3^- values in the main stem were higher than the degradation site (-3.4 to -4.7‰). These values were much greater than would be expected from nitrogen recycling and nitrate/DON exchange occurring in the main stem. Determining the cause for these high signals is difficult due to a multitude of possible factors influencing the isotopic signatures. Co-occurrence of partial nitrate uptake and nitrification in the main stem which decouples the nitrogen and oxygen isotopes (Sigman *et al.*, 2009) may be occurring but would only account for a $\delta^{18}O$-NO_3^- increase of around 5‰ (Wankel *et al.*, 2007). External sources such as atmospheric deposition and surface runoff with minimal interaction with catchment soils (e.g. snowmelt or high riverine discharge during sampling due to localised rainfall) may also bring high $\delta^{18}O$-NO_3^- and lower $\delta^{15}N$-DON values into the main stem (Heikoop *et al.* (2015), Thibodeau *et al.* (2017)). However, the amount of atmospheric $\delta^{18}O$-NO_3^- signal that reaches the main stem may be low as studies have shown that nearly all snowpack nitrate is assimilated or remineralised before being released into the river, thus losing nearly all the high $\delta^{18}O$-NO_3^- signal (Tye and Heaton, 2007).

Overall, determining the cause of the high $\delta^{18}O$-NO_3^- values and lower $\delta^{15}N$-DON in the main stem relative to the permafrost zone cannot be constrained with this study, but is likely to be some combination of atmospheric, microbial and recycling signals with co-occurrence of uptake, nitrification and possible denitrification. All of these may change seasonally which is explained in greater depth in section 3.3.

In summary, a unique signature representing inputs from degrading Yedoma permafrost was identified in the lower Kolyma River catchment indicating anaerobic degradation, denitrification, and vigorous nitrogen cycling within permafrost soils undergoing degradation. Dilution of the DON degradation signal occurs in the main stem but the DON (from the degradation site as well as the surrounding catchment) also undergoes mineralisation to nitrate, transferring the isotopic degradation signature to the nitrate. Therefore, increases in the nitrogen release from Yedoma permafrost soils, irrespective of the species, is most likely to be reflected in riverine nitrate concentrations. However, signals are unlikely to be strongly observed around the mouth of rivers unless very spatially extensive degradation zones are present in the catchment providing large enough fluxes of nitrogen species liberated from permafrost. This would allow the degradation signal to persist through the background catchment-wide nitrogen signal from modern surface soils.

The permafrost degradation occurring at this Kolyma site is only one type of degradation mechanism that can occur. It involves erosion of ice rich permafrost (Yedoma) found mainly in the Lena and Kolyma catchments but not in other Russian Arctic river catchments such as the Ob' and Yenisey (Wild *et al.*, 2019) (some is also present in the Yukon catchment). This type of degradation produces a greater export in the form of POC than DOC (Wild *et al.*, 2019), as seen in the Kolyma and Lena. This preferred release of POC (thus PON) from Yedoma permafrost could partially explain why a stronger degradation signal was not observed downstream in the Kolyma River. Other degradation mechanisms such as top-down active layer deepening occur widely across the Ob' and Yenisey catchments and produce significantly more degradation sourced DOC than POC (Wild *et al.*, 2019), and possibly more DON than PON. With this type of degradation mechanisms, the depth of peat would likely play a more important role in interactions with different soil horizons and the associated release of different dissolved species.

Large seasonality of DOC permafrost contribution exists in Arctic rivers (Wild *et al.*, 2019). Permafrost derived DOC had a greater contribution to total DOC flux in all four rivers in late autumn and winter compared to spring and summer when modern DOC sources dominate export. A similar mechanism may also operate for DON where the sources in spring and summer are not derived as strongly from permafrost but from surface soils that experience minimal nitrogen processing. Therefore, permafrost signals and associated processes should be considered on spatial (inter-catchment) and temporal scales.

3.3 Seasonal nitrogen species trends in rivers

3.3.1 Time series concentration and discharge trends

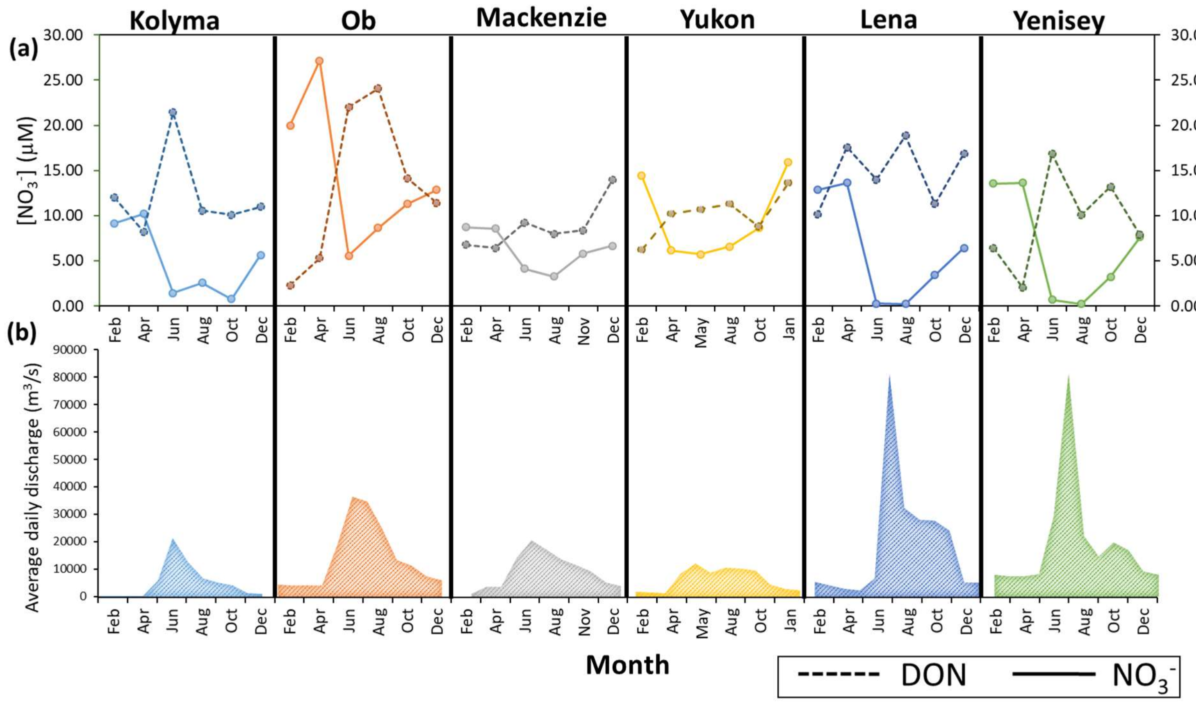


Figure 6 - Seasonal concentrations (a) for nitrate and DON in the six Arctic GRO rivers between 2003 and 2018. Discharge trends for each river are also shown in (b). Note, sample concentration values were taken six times throughout the year, every second month. The daily discharges for each month were averaged to produce the average daily discharge value for each month, 12 per year. Data obtained from the ArcticGRO online database.

Figure 6(b) shows that all six rivers follow a similar seasonal discharge trend typical of northern high-latitude rivers. Low flow is present in winter months, where groundwater is the primary source of water. During spring, snowmelt causes rapid increases in discharge (the spring freshet) peaking in late May to June. Peaks are greatest in the Lena and Yenisey. After the freshet, discharge decreases throughout summer, occurring more rapidly in the Lena and Yenisey, while in other rivers, peak discharge extends throughout summer, most apparent in the Yukon River.

All rivers in general show increases in DON concentrations [DON] in summer months during peak discharge and this concentration increase is highest in the Ob' followed by the Yenisey and Kolyma and lowest in the Lena, Mackenzie and Yukon where only small seasonal changes occur in [DON]. Nitrate concentrations [NO_3^-] in most rivers show opposite seasonal trends to [DON] (Figure 6 (a)) with the Ob' showing the greatest seasonal change of all rivers in both nitrate and DON. The Lena and Yenisey show nitrate concentrations decreasing to almost zero in the summer months during peak discharge.

In general, Figure 6 confirms that DON is the dominant form of nitrogen released from these soils and transported in these rivers, due to its high concentration during the high discharge periods of the spring freshet. This DON source is likely derived from surface runoff through organic rich top soil (Harms, 2013). Following the local scale Kolyma section, seasonal stable isotopes trends are used next to detect (1) permafrost degradation signals and (2) any in-stream processing of nitrogen.

3.3.2 Time series nitrogen isotopic trends

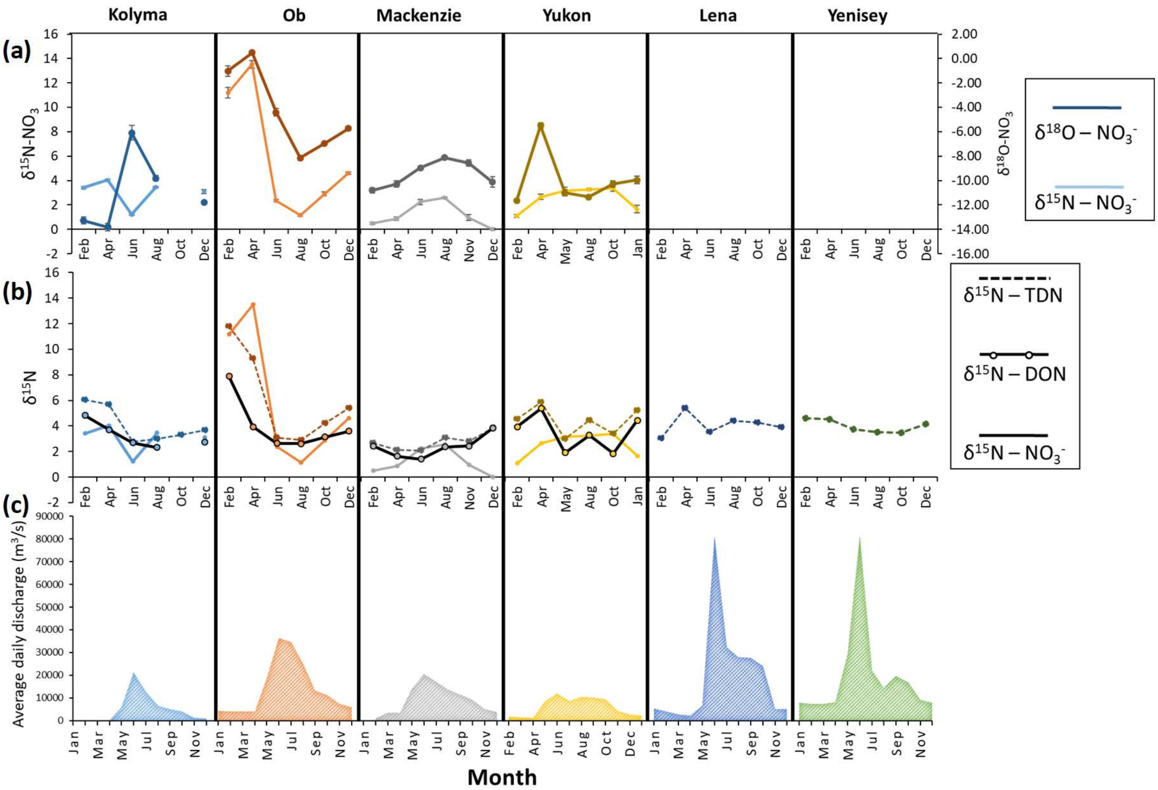


Figure 7 - Seasonal nitrogen (and oxygen) isotopic trends for all six Arctic GRO rivers. Nitrate isotopes as part of the dual isotope technique ($\delta^{15}N$ and $\delta^{18}O$) are shown on (a). Nitrogen isotopes of TDN, nitrate and DON, note the one scale for all three, are shown on (b). Seasonal discharges are also shown on (c). Only $\delta^{15}N$ values of TDN were plotted for the Lena and Yenisey since nitrate concentrations were very low for dual isotopic analysis of nitrate, hence $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values were not obtained. However, since nitrate concentrations were very small in comparison to DON (see Figure 6) then it can be assumed that the nitrogen isotopic signature of DON is approximately equal to the signature of TDN ($\delta^{15}N\text{-}DON \approx \delta^{15}N\text{-}TDN$)

Figure 7 presents a time series isotopic analysis of the Arctic rivers. The sampling sites were located at the mouths of the rivers (Figure 1), therefore they integrate signals of various source of nitrogen and nitrogen cycling processes in the catchment. From Figure 6 and Figure 7, strong seasonal variations affect nearly all the trends of nitrogen species in each river, but the trends suggest that discharge was not the greatest influencer on the isotopic signatures. Summer values of $\delta^{15}N$ of nitrate, DON and TDN are around 2 to 4‰, similar to the Kolyma River main stem in summer, indicating a mixed nitrogen source dominated by surface nitrogen sources diluting signals from continuous permafrost and permafrost degradation signals (Figure 7). These results are consistent with previous studies of DOC in Arctic rivers (Wild *et al.*, 2019). Permafrost derived DOC has a greater contribution to total DOC flux in all four rivers in late autumn and winter compared to spring and summer when modern DOC sources dominate export. A similar mechanism may also operate for DON where the sources in spring and summer are not derived as strongly from permafrost but from surface soils that experience minimum nitrogen processing (Harms, 2013).

$\delta^{15}N\text{-}NO_3^-$ and $\delta^{15}N$-DON values of the Kolyma and Ob' in late winter and early spring are high before becoming lower in spring/summer and returning to high values at the end of the year (Figure 7) (this is also seen in the Yukon to a lesser extent). It is notable that the Kolyma and Ob' have the highest and lowest continuous permafrost extent respectively among the large Arctic rivers. We evaluate the seasonal trend further in the Ob' River (with comparison to the Kolyma), which has the largest seasonal isotopic shift out of all the rivers (Figure 7).

3.3.3 Relating seasonal trends to nitrate sources, permafrost degradation and nitrogen cycling mechanisms

The Ob’ has the greatest seasonal isotopic shifts with very heavy winter δ^{15}N-NO_3^- values of 12 to 14‰ occurring over winter and early spring but decreasing to 2‰ in summer and a change from 8 to 2.5‰ for δ^{15}N-DON. The δ^{18}O-NO_3^- trend for the Ob’ River follows a similar pattern to the δ^{15}N-NO_3^- (i.e. they are coupled). However, for the Kolyma, the two isotopes are decoupled and show strong opposing trends, though this trend could be influenced by the anomalously high δ^{18}O-NO_3^- value in June and may not represent true conditions.

The peak δ^{15}N-NO_3^- values in the Ob’ river are similar to the signal for denitrification in high-latitude permafrost regions (Harms, 2013) and the isotopic and nitrate concentration peak in winter could be further evidence of extensive denitrification sources. Despite low concentrations of DON during the winter months, its isotopic signature was similar to the Kolyma degradation site, however the higher values of δ^{15}N-NO_3^- suggests that different processes are occurring in each river and that the signal cannot be compared to the possible permafrost degradation signal observed in the Kolyma (section 3.2.3). The stronger denitrification signal may be more visible in the main stem of the Ob’ unlike in the Kolyma due to a much lower extent of continuous permafrost within the catchment (permafrost present as discontinuous or sporadic under the large peatland of Western Siberian Lowlands (Wild *et al.*, 2019)). The lack of permafrost in the Ob’ catchment may also allow some groundwater encroachment of the mineral horizon in some places within the catchment. Here DON can be adsorbed and mineralised to nitrate (Harms, 2013). Denitrification of this remineralised nitrate due to the waterlogging of the soil in these large wetlands would also lead to the high isotopic signatures observed. It is important to note that these denitrification processes occur without permafrost degradation influence in the Ob’ whereas the denitrification signal observed in the Kolyma Yedoma degradation site was likely due to the permafrost degradation. Denitrification signals are much more influential in the Ob’ than the Kolyma where the permafrost extent is very low. The high nitrate concentrations show that a substantial amount of denitrified nitrate is added to the rivers and the Ob’ River is displaying a source-dominated signal, with instream processes possibly less influential.

The coupling of δ^{15}N-NO_3^- and δ^{15}N-DON throughout the year suggests the same source for both nitrogen species. However, some DON may also be oxidised into nitrate in the main stem and allow the heavy δ^{15}N signal to be transferred from the DON to the nitrate. This would also reduce the DON concentrations as observed.

The observed variability of nitrate isotopes in the Ob’ River can be approximated to changes between two dominant sources as outlined in Figure 8. The heavier winter δ^{15}N-NO_3^- values in the Ob’ represent groundwater dominated sources and the high δ^{18}O-NO_3^- values are largely coupled to the δ^{15}N-NO_3^- (Figure 7). This is further evidence for denitrification in the consistently wet conditions of the Ob’ catchment, preventing significant recycling of the denitrified nitrate and resetting of the δ^{18}O-NO_3^- to δ^{18}O-H_2O. (Frey and McClelland, 2009). Additionally, the lack of permafrost allows more percolation of groundwater in winter and a greater input of a denitrified signal through deeper lateral subsurface flow. The lower δ^{15}N-NO_3^- summer values were consistent with minimally processed atmospheric nitrogen sources, with little denitrified nitrate present, delivered through surface runoff during the spring freshet to the river. However, the lower δ^{18}O-NO_3^- values in the summer do not correspond to an influence of an isotopically high atmospheric or snowmelt nitrate source. This could be due to the main stem summer signal being a mix of different sources and recycling occurring (as described previously for the local scale Kolyma catchment). The $\delta^{18}O-NO_3^-$ values are lower and closer to the $\delta^{18}O-H_2O$ values of the Ob' (14.85‰) (Yi *et al.*, 2012), than seen in the Kolyma, suggesting some degree of nitrate recycling that can cause $\delta^{18}O-NO_3^-$ values to be reset to water values. These values are likely mixed with surface runoff signals from snowmelt (bringing higher $\delta^{18}O-NO_3^-$ signals) and near surface runoff through topsoil, masking the smaller input of denitrification signals from groundwater.

A regression line between the two likely different sources in the Ob' (Figure 8) shows the dominant source changing throughout the year and main-stem water showing mixing between them. Overall, it is likely that the groundwater derived signal is present throughout the year as part of a mixed signal but the seasonal variation of dominant sources influences its visibility in the main stem. Surface spring/summer flows dominate and mask the groundwater signal during summer whereas in winter the subsurface flow is dominant and allows the groundwater and associated denitrified signal to be more clearly observed

The Kolyma seasonal trend is similar to the Ob' except the magnitude of isotopic and concentration change was less (Figure 7). $\delta^{18}O-NO_3^-$ was decoupled from the $\delta^{15}N-NO_3^-$ in the Kolyma, unlike the coupling in the Ob. The continuous permafrost coverage preventing catchment-wide denitrification in the Kolyma along with the observed conversion of DON to nitrate and subsequent recycling could explain the decoupling throughout the year. This decoupling also suggests that nitrate uptake is low and the small contribution of nitrate due to the high continuous permafrost extent is likely to drive nitrate limitation in this river, despite DON remineralisation (Figure 2). This similar but suppressed trend suggests that the denitrification signal is less influential and was diluted, similar to local-scale observations (section 3.2). The greater coverage of permafrost in the Kolyma catchment compared to the Ob' may reduce the seasonal change in nitrogen species signals, especially nitrate (as observed in Figure 2) by restricting flow-paths to minimal contact with mineral horizons and reducing groundwater flow. This can also explain the observed mixing line and the surface source dominance throughout the year shown in Figure 8.

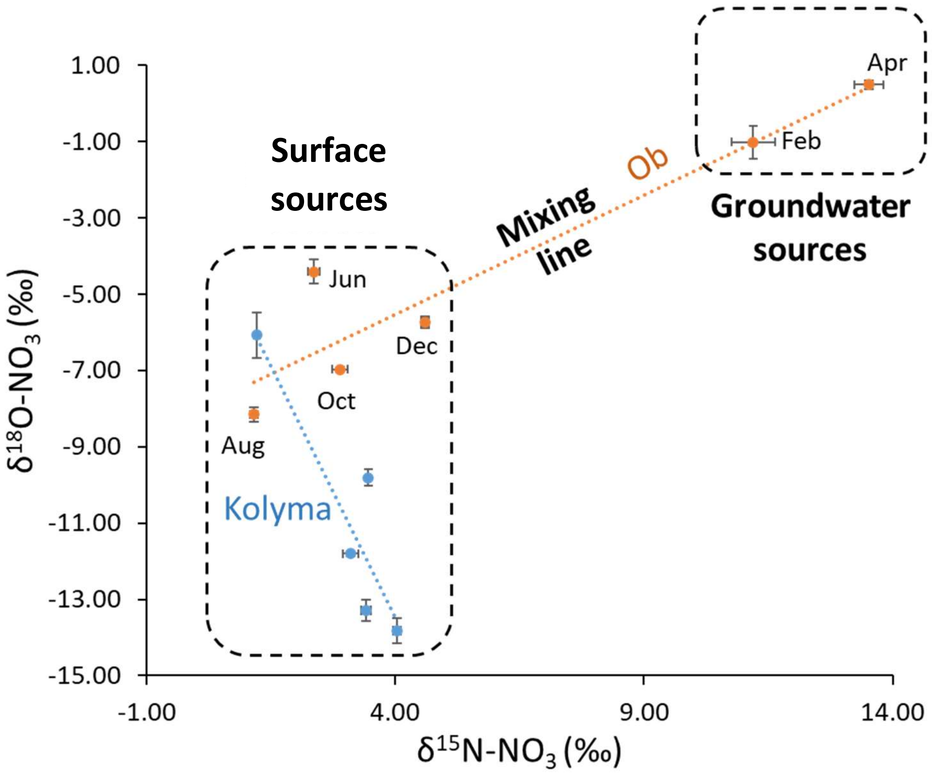


Figure 8 – Likely different sources of nitrate throughout the year in the Ob' and Kolyma catchments inferred by relationships between δ^{15}N-NO_3^- and δ^{18}O-NO_3^-. A mixing line can be plotted as a regression line between the two sources. The location on the plot that each sample occurs can indicate the dominant nitrate sources at that time and from that, the processes occurring can be inferred.

The local scale permafrost degradation signals observed from the Yedoma permafrost degradation in the Kolyma may be visible in the seasonal trends due to similar main stem DON and nitrate signals in the early season, possibly assisted by the lack of other nitrate inputs and DON recycling to nitrate. However, it is not possible to observe any permafrost degradation signals in the Ob' catchment or to compare trends with previous local scale findings due to the dominance of the groundwater derived denitrification signal and different catchment conditions.

3.3.4 Explanations for times series trends in other Arctic rivers

The Mackenzie and Yukon show δ^{15}N-NO_3^- trends peaking in the summer months (Figure 7). This was an opposite trend to the nitrate concentration, and more closely follows the discharge trends. The Yukon had the most prolonged δ^{15}N-NO_3^- peak out of all the rivers. Little change in δ^{15}N-DON occurred for the Mackenzie while for the Yukon it showed variability all year with no clear trends, δ^{18}O-NO_3^- was strongly coupled to δ^{15}N-NO_3^- for the Mackenzie but was uncoupled for the Yukon.

In the Mackenzie River, the source signal in the summer months is dominated by runoff, carrying a large DON signal. However, since DON isotopes and concentrations are decoupled from nitrate isotopes and concentrations, the factors influencing both nitrogen species are different. Nitrate is influenced mainly by instream processes (Harms, 2013) due to assimilation or uptake of nitrate by phytoplankton in summer. The smaller isotopic shift between seasons could also signify assimilation rather than denitrification (Struck, 2012). This process would be assisted by the large area of lakes in the Mackenzie catchment where water residence times are increased allowing extensive primary productivity (Janjua and Tallman, 2015).

The Yukon followed similar trends to the Mackenzie (for $\delta^{15}N$, [NO_3^-], [DON]) suggesting uptake in the summer months was also a dominant nitrogen cycling process. Similarly, there is extensive lake cover in the Yukon catchment (Brabets *et al.*, 2000). However, $\delta^{18}O$-NO_3^- and $\delta^{15}N$-NO_3^- were uncoupled and variable, potentially reflecting different sources of water throughout the year and the extended discharge period providing water involved in nitrate processing with different $\delta^{18}O$-H_2O values. These $\delta^{18}O$-H_2O trends can be observed in the ArcticGRO database (Holmes *et al.,* 2021)

It was difficult to determine any dominant processes within the Lena and Yenisey due to the lack of nitrate isotopic data and the little seasonal change in $\delta^{15}N$-TDN (DON). However, a unique aspect of these rivers is the very high freshet discharge and the associated high DON concentrations but very low nitrate concentrations. The fact that these large changes in runoff can occur without a change in isotopic DON could suggest that recent topsoil derived organic matter was the dominant source of nitrogen throughout the year, similar to observations for carbon (Wild *et al.*, 2019).

3.4 Implications of findings and possible future changes

Permafrost degradation will have different impacts on riverine nitrogen geochemistry in different catchments across the Arctic. With future permafrost degradation, through both active layer deepening and erosional degradation, the seasonal trends may change from the Kolyma style more towards the Ob' style since the Ob' represents a catchment with very little permafrost present. Greater shifts in concentrations and $\delta^{15}N$ isotopic signals between seasons would be expected with high $\delta^{15}N$ signals in the winter and early spring through denitrification of waterlogged soil but a rapid shift in $\delta^{15}N$ with runoff conditions. However, this would depend on other catchment conditions as well as the style and rate of degradation.

As degradation released DON was observed to be converted to nitrate in the main stem of the Kolyma and likely in other rivers, this would increase the amount of bioavailable nitrogen (nitrate is more bioavailable for assimilation than DON) and possibly fuel increased productivity. As observed in the study, this conversion would have the greatest impact in catchments with few other nitrate inputs, e.g. from high continuous permafrost coverage, such as the Kolyma. However, if active layer deepening induces the widespread reduction of continuous permafrost extent in favour of discontinuous coverage, this may allow nitrogen input processes similar to those described for the Ob' to dominate over this main stem mineralisation of nitrate for the long term.

This study demonstrates that nitrate concentrations may increase the most relative to other nitrogen species and would carry with it a high isotopic signature from denitrification processes. This increase of nitrate is supported by other studies such as Walvoord and Striegl (2007) but not by Frey *et al.* (2007) who predict an increase in DON not nitrate. There is ongoing debate over the dominant species likely to be observed.

Irrespective of N species released and the degradation mechanism, nitrogen fluxes are likely to increase with permafrost degradation causing significant impact to the coastal zones. Any increases in nitrogen loading to coastal Arctic areas will have large impacts on productivity since these zones are heavily nitrogen limited (Thibodeau *et al.*, 2017). Currently, productivity peaks over a short period in summer when light is not limiting. However, permafrost degradation and greater nitrogen fluxes may increase the magnitude of these productivity peaks inducing possible algal blooms. Yet, light limitation will still control productivity later in the year. Overall, the cycling of these nitrogen species in coastal zones is essential to understand further to make robust predictions of future change.

4 Conclusions

Overall, catchment permafrost coverage seems to control main stem nitrate concentrations but not DON, with large extents of continuous permafrost leading to low concentrations of nitrate in Arctic rivers. In local Kolyma degradation sites, Yedoma permafrost degradation was characterised by high DON and nitrate concentrations, high $\delta^{15}N$-DON and $\delta^{15}N-NO_3^-$ and very low $\delta^{18}O-NO_3^-$. These signatures indicate rapid recycling and exchange between nitrogen pools resulting in the entire system becoming isotopically heavy for nitrogen. Upon release to the main river stem, this signature is greatly diluted but evidence for recycling of degradation derived DON to nitrate, transferring the heavy isotopic signature to nitrate, was observed. This DON recycling could be the main source of nitrate in catchments with extensive permafrost coverage and few nitrate inputs. However, these input signals from Yedoma degradation are unlikely to be observed strongly at the river mouth unless degradation zones are more spatially extensive.

$\delta^{15}N$ of nitrate, TDN and DON during summer and spring freshets generally exhibit values around 2 to 4‰, DON dominates the nitrogen export within these rivers, in the form of fresh DON derived from surface runoff through modern, organic rich topsoil. However, Arctic rivers all have different nitrogen dynamics based on their catchment characteristics. The Ob' catchment, with its lowest extent of permafrost coverage and extensive peatland area demonstrates a strong denitrification signal, however this cannot be linked to the degradation induced denitrification signal observed in the Kolyma. The Ob' isotopic signal is strongly seasonal and influenced by the changing soil flow paths that arise throughout the year. The Kolyma had a similar seasonal trend but with reduced magnitude and showed evidence of differing processes occurring compared to the Ob' but were similar to local scale observations. A diluted denitrification signal, DON recycling to nitrate and low nitrate uptake were all possibly assisted by the lack of other nitrate inputs and high permafrost coverage. In other Arctic river catchments, different factors can mask any fresh permafrost degradation signals. Lacustrine nitrogen assimilation and uptake are dominant in the Mackenzie and seasonal changes in water sources are important for the Yukon catchment while large freshet discharges in the Lena and Yenisey likely inundate the catchments with runoff-derived nitrogen.

It is possible that with future decreases in catchment permafrost coverage, seasonal nitrogen dynamics in Arctic rivers could begin to resemble that of the Ob' catchment. In general, increased fluxes of nitrogen are expected as a result of degradation which would have impacts on coastal environments and ecosystems, as well as in rivers with nitrogen limitation. However, the extent of this is unclear at present. Further studies are required to explore more local scale and coastal nitrogen cycling and the impacts of permafrost degradation on riverine and coastal environments.

This study shows how nitrogen isotopes can be used to integrate catchment wide processes in Arctic rivers as well as showcasing small scale nitrogen dynamics within permafrost degradation zones. Utilising this technique across further sites in the Arctic will help to further our understanding of current processes and future changes in Arctic nitrogen cycling.

5 Data Availability

Data will be made available on a public repository upon final publication.

6 Author Contributions

AF carried out laboratory work and wrote the manuscript. RSG designed of the study and helped with the interpretation of the data. RET assisted with laboratory work. Both RSG and RET contributed to the writing of the manuscript. JR and RGMS collected samples from the Kolyma and provided further information on the sites in the lower Kolyma catchment. RMH manages the online Arctic GRO dataset used for this project made available the ArcticGRO samples. CM led and coordinated the CAO, ARISE project. All authors provided comments on the manuscript.

7 Conflict of Interest Statement

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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10 References

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