



# Article Carbon and Nutrient Stoichiometric Relationships in the Soil–Plant Systems of Disturbed Boreal Forest Peatlands within Athabasca Oil Sands Region, Canada

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Abstract: Peatlands store carbon (C), nitrogen (N), and phosphorus (P), and the stoichiometric relationship among them may be modified by ecosystem disturbances, with major implications for boreal peatland ecosystem functions. To understand the potential impact of landscape fragmentation on peatland nutrient stoichiometry, we characterize the stoichiometric ratios of C, N and P in the soil-plant systems of disturbed boreal forest peatlands and also assessed relationships among site conditions, nutrient availability, stoichiometric ratios (C:N:P) and C storage in four sites that represent the forms of disturbed peatlands in the Athabasca oil sands region. Our results showed that nutrient stoichiometric balance differed across and within these peatlands, among plants, peat, and groundwater. Ratios of C:N and C:P in peat is a function of nutrient and moisture conditions, increasing from nutrient-rich (C:N = 28; C:P = 86) to nutrient-poor fens (C:N = 82; C:P = 1061), and were lower in moist hollows relative to drier hummock microforms. In groundwater, the drier nutrient-rich fen had higher N:P ratios relative to the nutrient-poor fen, reflecting interactions between dominant hydrologic conditions and stoichiometric relationships. The N:P ratio of plants was more similar to those of peat than groundwater pools, especially in the most recently disturbed nutrient-poor fen, where plant C:N:P ratios were greater compared to older disturbed sites in the region. These findings suggest that disturbances that modify moisture and nutrient regimes could potentially upset the C:N:P stoichiometric balance of boreal forest peatlands. It also provides valuable insights and essential baseline data to inform our understanding of how peatland C:N:P stoichiometry would respond to disturbance and restoration interventions in a boreal forest region at the tipping point of environmental change.

Keywords: boreal forest; peatland; C:N:P stoichiometry; disturbance; restoration; Athabasca oil sands region

## 1. Introduction

Peatlands are major land units in the northern boreal forest region on Canada. These peatlands support vital ecological functions, which include peat accumulation, nutrient sequestration, and the provision of unique habitats for biodiversity conservation [1–3]. The ability of peatlands to sustain these ecological functions can be attributed to the persistence of anoxic conditions, which slows the rate of litter decomposition, consequently reducing the mineralization rate of organically bound nutrients in the partially decomposed litter [4–6]. The resulting nutrient conditions support the assemblage of diverse plant communities, ranging from fast growing vascular species (e.g., sedges) in nutrient-rich fens to the dominant *Sphagnum* spp. in nutrient-poor fens [7]. Peatland ecological studies have shown that aside from hydrologic conditions, the availability of nutrients is a major control on the capacity of peatlands to accumulate carbon (C) [8,9]. The organic matter that



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). forms peat constitutes primary macronutrients such as nitrogen (N), phosphorus (P) and potassium (K), which are essential for plant C fixation (productivity) and development of physiological characteristics such as the ability to withstand period stress [10]. The relative concentrations (ratios) of N and P in organic matter regulate the rate of microbial-mediated C oxidation during decomposition and mineralization processes [11–13]. Hence, a shift in the ratio of macronutrient concentrations within the soil–plant system may modify C

cycling dynamics in peatlands. Ecosystem disturbances that lead to increased availability of essential nutrients can modify the ratios of macronutrient concentrations within the soil-plant system through the interaction of peatland vegetation with reactive forms of nutrients available in the environment. For instance, peatlands in the Athabasca oil sands region (AOSR) of Canada are threatened by the cumulative impacts of oil sands development such as landscape fragmentation and modification of peatland hydrology following drainage of development sites [14]. The region has been described as one of the major hotspots of peatland disturbance due to the large footprint of oil sands extraction [15,16]. Studies from this region indicate that the construction of semi-permanent roads and well pads on peatlands leads to a change in site hydrology, oxidation of peat, and subsequent release of mineralised nutrients into the groundwater of surrounding peatlands [17,18]. Atmospheric N deposition within the vicinity of active mine sites presents another source of exogenous nutrient input to peatlands in this region, with a reported average of about 4 kg ha<sup>-1</sup> year<sup>-1</sup> of reactive forms of N (NO<sub>3</sub>–N and NH<sub>4</sub>–N), relative to 1 kg ha<sup>-1</sup> year<sup>-1</sup> background level recorded in typically N-limited boreal forest sites [19-21]. These exogenous nutrient inputs could modify the stoichiometric balance of C, N and P in peatland vegetation through increase in primary productivity and nutrient uptake, subsequently altering the litter chemistry and biogeochemical functioning of boreal peatlands near industrial development sites [22,23].

Changes in macronutrient balances within peatlands affect C cycling and storage by altering the C:N:P ratios in plant litter [24,25]. As such, the uncertainties surrounding the future response of peatland C stock to variable inputs of nutrients from exogenous sources highlight the need to characterize the stoichiometric ratio of C, N and P in the soil–plant system of disturbed peatlands located in a region at the tipping point of major ecosystem change. No recent study has characterized the stoichiometric ratio of macronutrients in disturbed peatlands within the vicinity of oil sands developments. However, in the near future, such research data will be essential to inform a mechanistic understanding of how peatland ecological functions, especially C storage, would respond to the cumulative impact of anthropogenic and natural disturbance regimes.

To address these knowledge gaps, the objectives of this study were to: (1) evaluate the chemical characteristics of shallow groundwater across the disturbed peatlands; (2) characterize the patterns of elemental concentrations and nutrient stoichiometric ratios in the soil–plant systems within microforms (hummock and hollows) across sites; and (3) assess relationships between nutrient ratios in plants and potential sources of labile nutrients (i.e., groundwater and peat) relative to site conditions. Consistent with established peatland stoichiometry literature, we hypothesized that irrespective of the degree of disturbance, the presence of microtopographic gradients will control soil C stock and nutrient storage in peatlands [26]. Given the potential for mineral controls (sorption of Fe/Al or Ca) on P mobility [27,28], we hypothesized an increase in N:P ratios within the soil-water system along the gradient of nutrient-poor to nutrient-rich sites, which may be apparent in plant tissue as an increase in P limitation (i.e., N:P >16:1). It was also hypothesized that the patterns of stoichiometric ratios in peatlands would reflect the degree of disturbance across sites.

#### 2. Materials and Methods

#### 2.1. Description of Study Sites

Field research was conducted in four peatland sites that represent the various forms of disturbed peatlands in this region, leading to some degree of variation in hydrology



and water chemistry. The peatlands include a rich, saline and poor fens located within the AOSR near Fort McMurray, AB CA (Figure 1).

**Figure 1.** Location of the study sites (dark circles) relative to active industrial development hub in the Athabasca Oil Sands Region, near Fort McMurray, Alberta, Canada (inset map). The rich fen site is adjacent to industrial development centers to the North whereas the JACOS fen is located within an in-situ disturbance lease.

The nutrient-rich fen site (Rich fen) is located within the larger Poplar Creek Fen, ~7 km northwest of the active oil sands development hub, near Fort McMurray, CA (56°56' N,  $111^{\circ}33'$  W). The site sits next to a pipeline right-of-way, that was decommissioned over 12 years ago, leading to a slight modification in site hydrology. A previous study on the site reported that the vegetation cover is dominated by Larix laricina (larch), Betula glandulosa (dwarf birch), Equisetum fluviatile (swamp horsetail), Smilacena trifolia (three-leaved Soloman's-seal), Carex spp. and moss including Polytrichum spp., Tomenthypnum spp. and Sphagnum spp. [17]. The hyper-saline fen (Saline fen) is least impacted site, located approximately 40 km south of the industrial hub ( $56^{\circ}34'$  N,  $111^{\circ}16'$  W). The site is characterized by a sharp transition from the nutrient-rich saline fen to a nutrient-poor treed fen. Detailed descriptions have been previously reported [28–30]. Peat and vegetation samples from this study site were collected in the rich-poor fen transition zone under dominant vascular species cover, such as Triglochin maritima (Seaside arrowgrass), and Juncus balticus in the Saline portion, Ledum rhododendrum (Labrador tea), Rubus chamaemorus (cloudberry), and *Vaccinium oxycoccos* (cranberry) in the poor fen portion. Some of bryophytes found on the site include Sphagnum fuscum, S. capillifolium and Cladonia mitis (green reindeer lichen) (A. Borkenhagen, Unpublished). First nutrient-poor fen (Poor fen) is situated on a local topographic high (Stony Mountain ~740 masl), about 62 km south of the industrial hub (56°22' N, 111°14' W). The hydrology of this site was impacted by a road construction that occurred over 30 years ago. Vegetation cover within the fen is dominated by Sphagnum spp. (e.g., S. capillifolium, S. agustifolium and S. magellanicum). Additionally, present in abundance are sedges (e.g., Carex aquatilis and C. limosa) and ericaceous shrubs (Betula glandulosa, Oxy*coccus microcarpus, Chamaedaphne calyculata,* and *Andromeda polifolia*), with a discontinuous tree cover that is dominated by stunted *Picea mariana* and some *Larix laricina* [31,32].

The most recent industry-impacted poor fen is within an in-situ oil sands development lease operated by Japan Canada Oil Sands Company (JACOS). The site is located in Hangingstone, about 50 km south of Fort McMurray (56°19′ N, 111°39′ W) and was disturbed through the construction of a semi-permanent road in 2001, which bisected the fen and restricted water flow along the natural hydrologic gradient [17,18]. Given the hydrological disturbance and tendency for N and P input to this poor fen from peat oxidation, the site was specifically selected before the commencement of restoration work to serve as baseline for future assessment of restoration effects on the nutrient status of peatland soil and dominant plants. The fen's vegetation cover comprises mosses (e.g., *Sphagnum fuscum*), lichen (e.g., *Cladonia stellaris*) and ericaceous shrubs (e.g., *Rhododendron groenlandicum* and *Vaccininium vitis-idaea*). A detailed description of the site is presented in [18].

#### 2.2. Sample Collection and Analysis

Sampling for this study was conducted in August 2015, just prior to when some peatland plants were about to transition from active growth to the senescence phase. Twelve sampling locations with two microforms (peatlands often comprise undulating patterns of two microtopographic positions: hummocks-which are elevated, relatively dry, densely vegetated patches, and hollows-which are lower, sparsely vegetated wet depressions [26] were randomly selected within each fen. Where present, the living surface moss layer was removed, and peat was sampled within a  $1 \times 1$  m area using a knife to cut into a depth of 0 to 10 cm from the surface in each of the two microforms in all of the 12 sampling locations (n = 24). Vegetation samples were collected randomly at six of the sampling locations at each site. For mosses, capitula of the living moss layer were collected from the hummock and hollow species, whereas photosynthetically active leaves of three dominant vascular plants (e.g., Vaccininium vitis-idaea, Chamaedaphne calyculata and/or Rhododendron groenlandicum) were randomly collected at three of the sampling locations in each fen. In the lab, peat samples from each sampling point were homogenized in the original sample bags before removing two subsamples (~5 g dry weight) for bio-available nutrient extractions.

One of the peat subsamples was shaken for one hour in a solution of 50 mL distilled-deionized water for the determination of soluble reactive P (SRP), whereas the other peat subsample was shaken in a solution of 50 mL 2M KCl for nitrate ( $NO_3^-$ ) and ammonium ( $NH_4^+$ ) extractions [33]. The extracts were gravity filtered through Whatman No. 42 ashless filter paper and frozen until analysis. Analysis for determination of SRP,  $NO_3^-$ -N and  $NH_4^+$ -N concentrations were completed using colorimetric techniques (Bran Luebbe AA3, Seal Analytical, Seattle, WA, USA, Methods G- 102-93 ( $NH_4^+$ -N), G-109-94 ( $NO_3^-$ -N +  $NO_2^-$ -N), and G-103-93 ( $PO_4^{3-}$ -P (SRP)). Total inorganic N (TIN) was estimated as the sum of  $NO_3^-$ -N and  $NH_4^+$ -N.

Subsamples of peat and vegetation slated for elemental analyses were oven-dried at 60 °C until a constant weight, and ground to a fine powder (60-mesh sieve). Concentrations of C and N were determined by dry combustion on an elemental analyzer (CHNS Analyzer-EA 1108, Carlo Erba, Milan, Italy). Total Iron (Fe), P, and K were determined on an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES: Optima 8000, Perkin Elmer LLC, Norwalk, CT, USA), after digestion in concentrated sulphuric acid and hydrogen peroxide with selenium and lithium sulphate catalysts [34]. Digested samples were filtered to < 0.45 µm before analysis. The approach by Koerselman and Meuleman [35] was applied to assess whether plants are classified as either limited by N (mass ratio N:P < 14:1), P (N:P > 16:1), or co-limited by N:P and some other element (e.g., K, when 14:1 < N:P < 16:1). The ratio of total Fe to total P (Fe:P) concentrations in peat was used as an indicator of mineral influences on the overall peat P pool across sites.

Samples for groundwater chemistry (pH, conductivity, major ions and nutrients) were collected from 12 shallow (100 cm depth) PVC wells used for monitoring water table depth

in the sampling plots within each study site. The wells were purged 24–72 h prior to sampling, and samples collected were filtered in the field through a 0.45  $\mu$ m filter, attached to a hand operated FlipMate filtration system (Delta Scientific Laboratory Products Ltd., Canada). The filtrates were frozen until analyses for bioavailable nutrient pools in the groundwater (i.e., SRP, NO<sub>3</sub><sup>-</sup>-N and NH<sub>4</sub><sup>+</sup>-N) using the colorimetric techniques stated above. Major ions (anions, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and cations, Ca<sup>2+</sup>, Na<sup>+,</sup> Mg<sup>2+</sup>, K<sup>+</sup>) were analyzed using ion chromatography (DIONEX ICS 3000, IonPac AS18 and CS16 analytical columns).

#### 2.3. Statistical Analysis

All statistical analyses were performed with R [36]. The analyzed variables were tested for normality prior to any parametric tests, and when necessary, appropriate transformations (log transformation) were implemented for all required data before parametric analysis. The variability in soil–plant stoichiometric relationships among four sites was analyzed using linear mixed effects (lme) model in package "nlme" [37], which included site, microform and interaction between them. Pairwise comparison of significant effects was carried out by Tukey's Honestly Significant Differences tests ("TukeyHSD" R Development Core Team, 2013), considered significant at p < 0.05. A standard principal component analysis (PCA) was employed on logarithmically transformed peat and vegetation chemical data (total C, N, P, K and Fe), using singular value decomposition scaled to have unit variance ("prcomp" function) [36].

## 3. Results

## 3.1. Chemical Characteristics of Shallow Groundwater

The average growing season water table depth varied among the fens, with deeper water table positions found in the Saline and Rich fens, whereas the JACOS and Poor fens had shallower water table depths (Table 1). Groundwater chemistry showed a gradient in the concentration of major ions (e.g.,  $SO_4^{2-}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ) among the sites, with the Poor fen at the lower concentrations margin, Rich fen at the intermediate and Saline at the upper margin (Table 1). The high concentrations of Cl<sup>-</sup> and Na<sup>+</sup> observed in Saline fen groundwater were reflected in the electrical conductivity, which was significantly (p < 0.001) higher than those of the other fens. The inorganic N:P ratio (i.e., TIN: SRP) of groundwater also showed an increasing gradient from the Poor fen to the Rich fen. Consequently, relative to all the sites, the N:P ratio of the groundwater pool at the JACOS fen was the lowest, given the high P concentration in groundwater at this site (Table 1; Figure 2). Across all the sites, NH<sub>4</sub><sup>+</sup> was the dominant form of inorganic N in groundwater, whereas NO<sub>3</sub><sup>-</sup>-N was available in very low concentration, especially in the Saline fen. The concentration of TIN was significantly higher (p < 0.05) in the Saline fen than the other fens.

**Table 1.** Mean (standard deviation) of physicochemical characteristics of shallow groundwater across the range of natural fen types in the Athabasca Oil Sand Region.

Variables	Saline Fen	<b>Rich Fen</b>	Poor Fen	JACOS
WTD (cm)	-27 (21)	-36 (33)	-7 (6.1)	-18 (11)
pH	6.3 (0.9)	6.9 (0.4)	4.9 (0.3)	3.5 (0.1)
EC ( $\mu$ S/cm)	12,789 (7265)	474 (161)	23 (8)	180 (20)
$NH_4$ -N (µg L <sup>-1</sup> )	497 (3890)	288 (232)	161 (137)	440 (254)
$NO_3$ -N (µg L <sup>-1</sup> )	14 (8)	150 (160)	45 (74)	75 (31)
TIN ( $\mu g L^{-1}$ )	511 (410)	438 (282)	199 (171)	515 (285)
SRP ( $\mu g L^{-1}$ )	21.5 (16.2)	8.18 (5.1)	96.2 (122.0)	126 (77)
N: P ratio (mass/mass)	22	67	8	9
$K^{+}$ (mg L <sup>-1</sup> )	8.1 (12.4)	1.1 (0.7)	0.6 (0.6)	1.0 (0.1)
$Ca^{2+}$ (mg L <sup>-1</sup> )	156.6 (142.9)	28.5 (8.9)	8.2 (10.5)	7.2 (1.4)
$Mg^{2+}$ (mg L <sup>-1</sup> )	77.9 (71.2)	11.9 (4.6)	2.0 (3.7)	1.8 (0.1)
$Na^{2+}(mg L^{-1})$	5471.7 (8683.2)	7.7 (2.5)	2.0 (2.6)	3.8 (0.7)
$SO_4^{2-}$ (mg L <sup>-1</sup> )	95.2 (155.0)	12.6 (11.8)	4.2 (10.4)	6.4 (7.8)
$Cl^{-}$ (mg $L^{-1}$ )	5671.0 (7636.0)	2.4 (1.5)	0.7 (1.8)	6.7 (3.4)

WTD: Water table depth; EC: Electrical Conductivity; TIN: Total Inorganic N; SRP: Soluble Reactive Phosphorus.



**Figure 2.** Relationships between nutrient limitation patterns in major plant functional types (mosses white bars and shrubs in grey bars) and N:P ratios of nutrient reservoirs (peat solution in brick bars and groundwater in dotted bars) among all the study sites, following the approach of Koerselman and Meuleman (1996).

## 3.2. Elemental Concentration and Stoichiometric Ratios in Soil–Plant System

Inorganic fractions of N in peat were dominated by  $NH_4^+$ , typically comprising 80–90% of TIN (Table 2) and differed significantly (p < 0.01) among the sites. In sites with deeper water table positions (i.e., Rich and Saline fens), concentrations of inorganic forms of N ( $NO_3^-$  and  $NH_4^+$ ) were greater (p < 0.01) in drier hummocks than in hollows. Whereas in the wetter sites (Poor fen and JACOS), only  $NH_4^+$ -N was significantly higher (p < 0.01) in hollows, whereas  $NO_3^-$ -N was not significantly different (p > 0.05) between microforms. Total inorganic N comprised a very small fraction (<0.5%) of the total N (TN) pool in peat. Similarly, the bio-available P fraction (i.e., SRP) constituted a very small proportion of the total P (TP) pool stored in the peat (<1% in all sites). A greater percentage of the bio-available N and P fraction was estimated for hummocks, especially in the Poor and JACOS fen sites with higher water table.

**Table 2.** Mean (standard deviation) of elemental composition and nutrient ratios in peat and vegetation samples across the range of fen types and within site microforms.

PEAT CHEMISTRY	SALINE FEN		RICH	RICH FEN		R FEN	JACOS FEN	
	Hummock	Hollow	Hummock	Hollow	Hummock	Hollow	Hummock	Hollow
Ext. NO <sub>3</sub> -N (µg/g)	2.25 (0.74)	2.04 (0.73)	1.64 (0.87)	1.50 (0.57)	1.54 (0.19)	1.39 (0.18)	0.83 (0.17)	0.82 (0.08)
Ext. NH <sub>4</sub> -N ( $\mu$ g/g)	14.04 (3.65)	9.73 (1.87)	17.91 (4.51)	14.76 (3.98)	16.71 (2.34)	20.58 (4.64)	10.55 (3.44)	12.11 (3.19)
TIN $(\mu g/g)$	16.29 (3.45)	11.76 (1.87)	19.56 (4.42)	16.26 (3.94)	18.25 (2.36)	21.96 (4.61)	11.78 (3.27)	13.02 (3.22)
SRP $(\mu g/g)$	2.51 (0.86)	2.26 (0.86)	1.43 (0.31)	0.88 (0.20)	3.63 (1.32)	2.13 (0.70)	3.24 (1.35)	3.74 (2.84)
C (mg/g)	420.31 (17.0)	401.03 (5.4)	399.04 (11.3)	386.41 (12.0)	418.37 (4.0)	410.14 (4.2)	434.62 (2.1)	431.91 (1.9)
N (mg/g)	18.27 (2.93)	25.22 (2.58)	10.48 (0.52)	11.56 (1.18)	7.34 (0.58)	9.96 (0.82)	4.89 (0.27)	6.95 (0.87)
P(mg/g)	5.57 (0.69)	6.42 (0.69)	0.79 (0.06)	0.90 (0.13)	0.92 (0.17)	0.85 (0.08)	0.40 (0.03)	0.55 (0.08)
K (mg/g)	1.75 (0.12)	1.66 (0.14)	4.48 (0.41)	3.25 (0.40)	5.36 (1.12)	2.70 (0.37)	2.62 (0.22)	2.58 (0.36)
Fe $(mg/g)$	0.55 (0.07)	0.79 (0.09)	2.95 (0.55)	2.13 (0.38)	1.0 (0.11)	0.71(0.12)	0.82 (0.06)	0.85 (0.07)
C:N Ratio	34 (6.5)	22 (6.7)	39 (2.5)	37 (4.4)	61 (4.4)	44 (3.4)	92 (5.3)	72 (7.6)
C:P Ratio	96 (15)	75 (12)	537 (40)	528 (73)	616 (99)	539 (61)	1172 (89)	950 (111)
N:P Ratio	3 (2.2)	4 (2.4)	14 (3.6)	13 (2.6)	8 (2.5)	11 (2.7)	13 (2.4)	13 (2.9)
Fe:P Ratio	0.1 (0.03)	0.1(0.05)	4 (2.8)	3 (1.0)	1 (1.1)	1 (0.3)	2 (0.7)	2 (0.9)

PEAT		SALINE FEN		RICH FEN		POOR FEN			JACOS FEN			
ISTRY	Hummoc	k H	ollow	Humn	nock	Hollow	Humr	nock	Hollow	Humn	nock	Hollow
	VEGETATION CHEMISTRY											
	Hu- moss	Ho-moss	Vascular	Hu- moss	Ho-moss	Vascular	Hu- moss	Ho-moss	Vascular	Hu- moss	Ho-moss	Vascular
C (mg/g)	428 (6.6)	427 (2.8)	484 (25)	445 (2.0)	442 (5.4)	504 (26)	449 (0.8)	447 (1.7)	515 (30)	453 (3.6)	448 (1.0)	538 (25)
N (mg/g)	8.7(0.6)	10 (0.8)	11 (1.0)	9.8 (1.1)	11 (1.2)	13 (1.5)	9.7 (0.4)	9.2 (0.7)	13 (0.8)	9.2 (0.3)	12 (1.2)	12 (1.2)
P (mg/g)	5.6 (0.7)	5.6 (1.3)	6.0 (0.9)	6.4 (0.2)	3.9 (1.5)	3.9 (1.3)	5.4 (0.5)	4.1 (0.9)	5.1 (1.5)	0.6 (0.1)	1.0 (0.1)	1.3 (0.1)
K (mg/g)	9.3 (1.8)	8.4 (0.7)	13 (5.4)	28 (2.2)	24 (4.9)	31 (9.9)	24 (8.2)	30 (2.8)	43 (16)	13 (1.6)	14 (1.4)	13 (0.9)
C:N Ratio	50 (4.0)	42 (3.8)	43 (3.5)	47 (5.6)	43 (4.0)	39 (5.7)	46 (1.8)	49 (3.8)	41 (2.6)	50 (1.9)	38 (4.0)	46 (4.1)
C:P Ratio	79 (9.2)	84 (17)	86 (17)	70 (2.7)	200 (18)	174 (37)	85 (7.7)	118 (23)	131 (24)	771(109)	468 (33)	432 (14)
N:P Ratio	2 (0.5)	2 (0.9)	2 (0.5)	2 (0.2)	2 (0.6)	5 (4.2)	2 (0.2)	2 (0.5)	3 (2.4)	16 (3.4)	12 (0.7)	10 (0.9)

Table 2. Cont.

Peat C content was higher in the drier hummock microform relative to the hollow peat in all the sites (Table 2). In contrast, the total N content of peat was significantly higher (p < 0.001) in the hollows than hummocks across all sites. Consequently, the C:N ratio of peat increased along the microtopographic gradient, with significantly lower ratios (p < 0.001; Table 3) estimated for hollows in all the sites. Similarly, the total P content of peat was higher (p < 0.05) in hollows than hummocks across all sites, especially in Saline fen (p < 0.01). Thus, the N:P ratio of Saline fen peat was significantly lower (p < 0.001; Table 3) than those of all the other fens (Figure 2). The Fe:P ratio estimated for Saline fen peat was an order of magnitude lower than the ratios of the other fens (Table 2). Using the product of the mean bulk density measurements for surface peat (0–10 cm depth) from our sites and the mean concentration of total C, N and P at the same depth, the amount of C, N, and P stored per unit area across the study sites was estimated (Table 4).

Material	Ratio	Factor	F-Statistic	<i>p</i> -Value
	N:P	Site Microtopography Microtopography x Site	$\begin{array}{l} F_{3,23}=28.462\\ F_{1,47}=1.6483\\ F_{3,47}=0.2038 \end{array}$	<0.001 0.21 0.89
Peat	C:N	Site Microtopography Microtopography x Site	$\begin{array}{l} F_{3,23} = 38.1015 \\ F_{1,47} = 11.1928 \\ F_{3,47} = 1.0532 \end{array}$	<0.001 <0.001 0.37
	Site F <sub>3</sub> C:P Microtopography F Microtopography x Site F	$\begin{array}{l} F_{3,23}=52.2549\\ F_{1,47}=3.7309\\ F_{3,47}=1.2575 \end{array}$	<0.001 0.06 0.30	
	N:P	Site Microtopography/PFT Microtopography/PFT x Site	$F_{3, 8} = 48.3075$ $F_{2, 11} = 0.1131$ $F_{6, 11} = 2.8909$	<0.001 0.89 0.03
Vegetation	C:N	Site Microtopography/PFT Microtopography/PFT x Site	$\begin{array}{l} F_{3,8}=0.299\\ F_{2,11}=3.1754\\ F_{6,11}=0.7895 \end{array}$	0.83 0.06 0.59
	C:P	Site Microtopography/PFT Microtopography/PFT x Site	$F_{3,8} = 27.9797$ $F_{2,11} = 0.2276$ $F_{6,11} = 6.6905$	0.01 0.81 0.14

Table 3. Results from the linear mixed effect models for Stoichiometric ratios of peat and vegetation.

	Bulk Density	Carbon and Nutr	ient Concentration (0–10 cm)	s in Upper Peat	Carbon and Nutrients Stored in Upper Peat (0–10 cm)			
Sites	(0–10 cm) g/cm <sup>3</sup>	С	Ν	Р	C Stock	N Stock	P Stock	
	8		(g/kg)			(kg/ha)		
SALINE Fen	0.125 (0.01) <sup>1,2</sup>	411.1 (46)	21.6 (10)	6.0 (2.0)	51,382.2 (5773)	2700.8 (1280)	747.3 (304)	
<b>RICH Fen</b>	0.060 (0.03) <sup>3</sup>	393.3 (40)	11.0 (3)	0.8 (0.3)	23,595.1 (2399)	658.6 (178)	50.3 (20)	
POOR Fen	0.033 (0.03) 3,4,5	413.8 (15)	8.7 (3)	0.9 (0.4)	13,550.7 (482)	283.7 (92)	29.1 (14)	
JACOS Fen	0.028 (0.01) <sup>3</sup>	433.3 (7)	5.9 (2)	0.5 (0.2)	12,131.4 (193)	165.6 (68)	13.2 (6)	

**Table 4.** Mean bulk density, carbon, and nutrients concentrations (standard deviation) used in estimating potential C and nutrients (N and P) stock among the range of peatland in the Athabasca Oil Sands Region.

<sup>1,2</sup> [29,38], <sup>3</sup> [39], <sup>4,5</sup> [32,40].

In the living tissue of plants, C content of vascular species increased significantly (p < 0.05) along the poor-rich fen gradient and were higher (p < 0.001) than those of bryophytes (Table 2). There was no significant difference (p > 0.05; Table 3) between the C and N content of hummock and hollow bryophyte species in all the sites. In contrast, the N contents of vascular species were significantly higher than (p < 0.001) than those of bryophyte species, especially the hummock moss species. Hence, the C:N ratios of mosses, especially the hummock species, were higher than ratios estimated for vascular species. Relative to the other sites, the P content of living plant tissues in the JACOS fen was low (p < 0.001). Consequently, the N:P ratios of both bryophytes and vascular plants in JACOS were significantly higher (p < 0.001; Table 3) than ratios estimated for these plants from the other sites. Following the characterization of homeostasis [41], vegetation C:N across sites in both vascular and bryophyte living tissues appear homeostatic, but this is not the case for N:P and C:P (Figure 3).

A principal component analysis (PC) revealed clear separation in the chemical composition of plants between the JACOS fen (the recently impacted poor fen) and the other older impacted Poor fen (Figure 4a). The difference between JACOS fen and the other Poor fen is found almost entirely along the PC1 axis, dominated by variation in total Fe (r = -0.65) and P (r = -0.45) concentrations. In contrast, the JACOS fen was not distinct from the other sites in PC space of peat chemical data (Figure 4b), showing overlap with both the Poor and Rich fens. Instead, the Saline fen was distinct from the three other fens, separated by PC1 values, which are closely associated with total N (r = -0.61) and P (r = -0.62) concentrations.



Figure 3. Cont.



**Figure 3.** Resource and organism stoichiometry in (**A**) C:N, (**B**) N:P, and (**C**) C:P (all as g g<sup>-1</sup>) across the four study sites (saline fen, SF; rich fen, RF; poor fen, PF; and Jacos fen, JF). C:N, N:P, and C:P ratios display a homeostatic trend across the four sites as per the approach of Sterner and Elser (2002), given that the strengthen of the relationship was not significant (p > 0.05 throughout). Points and error bars are the mean and one standard deviation of 24 peat and 9 vegetation samples per site.



Figure 4. Cont.



**Figure 4.** Principal components analysis of major element concentrations in (**A**) all living vegetation tissues across both plant functional types and (**B**) all peat material across both microforms across all four fen sites, shown with 68% probability ellipses for each site.

## 4. Discussions

## 4.1. Shallow Groundwater Chemistry and Nutrient Availability

Our groundwater chemistry results support existing peatland biogeochemistry literature [18,42], which suggests that nutrient availability in peatlands is strongly influenced by site geochemistry and hydrology through groundwater-surface water interactions (water table fluctuation). With a higher degree of water table fluctuation in the nutrient-rich fens, we observed greater mineral contributions to the groundwater, as indicated by higher concentrations of  $Ca^{2+}$  and  $Mg^{2+}$ , as well as greater mineral influences on the availability of nutrients, especially P. Consistent with previous fen water chemistry studies in central Alberta and other northern peatlands [43–45], our results show that  $Ca^{2+}$  and  $SO_4^{2-}$  are the predominant peatland cation and anion, respectively, and decrease from the rich to poor fen types (Table 1). An exception to this trend is observed in the Saline fen, which shows the predominance of Na<sup>+</sup> and Cl<sup>-</sup> as the major cation and anion, respectively. A previous hydrogeochemistry study in this fen suggests that the accumulation of Na<sup>+</sup> and Cl<sup>-</sup> salts in Saline originates from the erosional edge of the underlain Cretaceous Grand Rapids Formation [46].

Generally, the elemental composition of fen groundwater affects the availability of nutrients through chemical sorption [47]. For instance, our results show that relative to the nutrient-rich fens, concentrations of SRP were larger in groundwater and soils of the nutrient-poor fens, especially the JACOS fen. Lower concentrations of SRP observed in the Rich fen can be attributed to the high content of mineral elements (e.g.,  $Ca^{2+}$  and  $Fe^{3+}$ ), which binds with mineralized P, limiting the availability and mobility of SRP. Further, there is a tendency for exacerbated adsorption of P to redox sensitive minerals (e.g., Fe oxides) in the Rich and Saline fen sites, given deeper water table depths and the higher efficiency of P adsorption under aerobic conditions [48]. Thus, the higher concentration of SRP observed in JACOS and Poor fens with shallow water tables (Table 2) is likely because mineralized P is less readily chelated in low cation peat with limited P sorption potentials [49].

## 4.2. Stoichiometric Ratios of C to Macronutrients in the Soil–Plant System among Fens

Our results shows that the C:N and C:P ratios of peat and vegetation vary along a geochemical gradient, increasing from the Saline fen to the poor JACOS fen, and also along a microtopographic gradient (decreasing from hummocks to hollows), with the exception of the C:P ratios of mosses, which were mostly higher in hollow species. The higher C:N ratios observed in hummock peat and vegetation suggest that the aerobic conditions found in hummocks support more efficient mineralization of C and N relative to hollows [50,51]. With the exception of the highest C:N ratio observed in peat from JACOS (92:1 and 72:1 for hummocks and hollows, respectively), the C:N and C: P ratios estimated at our Poor fen site are within the range reported by [52] for bryophyte dominated ombrotrophic peatland in eastern Canada. Similarly, the C:N and C: P ratios of sedge peat from Saline fen were within the range estimated for sedge peats in Minnesota [49] (Table 5) and in the southern Boreal region of Alberta [45]. These findings suggest that irrespective of past disturbance regimes, there is a consistent relationship between vegetation community that comprise the peat litter and the C to macronutrients ratios of peat. Thus, it is apparent that the difference in stoichiometric ratios among the peatlands in our study reflect the gradients of water chemistry, hydrologic condition, and vegetation assemblages in these sites.

**Table 5.** Nutrient stoichiometry of the studied peatlands in the Athabasca Oil Sands Region with comparable peatland sites, representing entire-core data. Ranges are shown when explicitly available in paper; otherwise; means of a single or multiple sites are given, indicated by \* or \*\*\*, respectively.

Study Reference	Study Years	Peat Stoichiometry (g $g^{-1}$ )			Study Site	
5	5	C:N	N:P	C:P		
Verhoeven et al. [4]	1987	19–59	18–37	337–2197	Ten natural and harvested fen and bog sites, The Netherlands	
Bridgham et al. [49]	1991	16–38	24–32	526-913	Three natural bog and fen sites, MN, USA	
Macrae et al. [53]	2004	16–53	23–57	907–1424	Paired drained and natural open bog and poor fen in Quebec, Canada	
Wang et al. [54] *	2012	37	56	2073	Mer Bleue Bog, Eastern Canada	
Schillereff et al. [55]	2014	30-47	37–68	1129–3091	Five ombrotrophic blanket mires in a longitudinal gradient spanning the UK	
Gorham and Janssens [56]	1981-1982	57–81	31–58	2000–4727	One bog in northern Minnesota and four bogs along North American eastern coast	
Wang et al. [52] ***	1982-1985	23–33	46-60	1190–1360	~400 peat profiles across Ontario, Canada, representing bogs, fens, and swamps	
Hill et al. [57]	2010-2012	24–49	54-163	1506–2438	An ombrotrophic bog and a minerotrophic fen, northern Minnesota, USA	
Present Study	2015	22–92	3–14	75–1172	Four fens along a hydrologic gradient, AOSR	

The separation between sites within the PC space (Figure 4) provides insights as to which key elements differentiate the sites in terms of plants and peat chemical composition. With the JACOS and Saline fens being the most distinct fens in terms of plant and peat chemical compositions, the PCA results suggest that the Fe and P concentrations of plant tissue (Figure 4a) and N and P concentration of peat (Figure 4b) may be indicative of peatland biogeochemical responses to disturbance. This has important implications for the assessment of both disturbances impacts and ecosystem trajectories in natural and industry-impacted peatlands.

#### 4.3. Plant Nutrient Ratios and Carbon Storage in Peat Soils of Various Fens

The N:P ratio of dominant PFTs has been widely used as a diagnostic biometric for detecting the nature of macronutrient limitations in wetlands and other terrestrial ecosystems [58,59]. Based on the approach of [35], our results suggest that the major vegetation assemblages found in the older disturbed peatlands of the AOSR are N-limited

(N:P < 14:1; Table 2), which is consistent with previous nutrient limitation studies in natural boreal peatland of Alberta and Ontario [45,59,60]. Conversely, the plant tissue N:P ratios of mosses and vascular plants in the recently disturbed JACOS fen indicate that the plant species at this site, especially mosses, are P-limited. This result supports the hypothesis that peatland disturbance can modify the natural balance of plant tissue nutrient concentration by reversing the pattern of plant nutrient limitation relative to natural analogues (Figure 2).

Results from our study also show that the TN:TP ratios of peat (Table 2) are not reflected in either the N:P ratios in bio-available pools or plant tissues in these peatlands (Figure 2). Indeed, the total P stored in peat represents the various organic and inorganic forms of P that may be unavailable to plants [45]. This imbalance in N:P ratio between the bioavailable nutrient pools and the long-term stores in peat supports the hypothesis that the availability of P is dependent on geochemistry of the site [27,28]. Thus, a disturbance that modifies the geochemistry of peat could potentially lead to an imbalance in the ratio of essential plant nutrients.

Although the TN and TP content of peat are not reliable indicators of plant tissue nutrient conditions, they can be explored in the same way as C stock calculations [61] to estimate variability in nutrient storage among peatland types, to enable us to quantify the impact of various forms of disturbance (e.g., wildfire) on peatland's C and nutrient stock. The estimates of C storage obtained for our study sites are within the range reported for northern peatlands [62], where there is still a dearth of information on N and P stocks. With the highest and lowest stocks of C and nutrients observed in the Saline and the Poor fens, respectively, our estimate also confirms that more C and nutrients are stored in the upper peat layer of nutrient-rich fens than their nutrient-poor counterparts (Table 4).

#### 4.4. Potential Impact of Disturbance on Stoichiometry and Carbon Storage of Boreal Fens

Peatlands in the AOSR are highly susceptible to disturbance, and subsequent exogenous input of nutrients given their proximity to an industrial development hub [19]. Evidence from the productivity of *Sphagnum fuscum* and biogeochemical response of soil processes to exogenous nutrient inputs suggest that the impact of such disturbance on the structure and function of peatlands will be more pronounced in poor fens and ombrotrophic bogs due to the inherent nutrient poor conditions and dependency on precipitation chemistry [21]. Our findings are in agreement with this, as the C to nutrient ratio of acrotelm peat from the poor fen sites exceeded the critical level for mineralization of organic matter [63]. Thus, any potential shift in C:nutrient ratios of these nutrient poor fens in response to exogenous nutrient addition will stimulate organic matter mineralization and subsequent decline in C storage.

Studies have shown that in peatlands receiving exogenous nutrients, the imbalance between biomass production and decomposition is controlled by availability of P, moisture and soil temperature [64–66]. Our results show that in the short term, hydrological modification in JACOS was associated with increases in bio-available P, especially within hollow microforms. Thus, in the absence of P limitation, long-term N addition with a stable near-surface water table could lead to an increase in peatland C storage. However, under conditions of P limitation, long-term exogenous N inputs could lead to peatland C loss [67,68].

#### 5. Conclusions and Implications for Peatland Management under Disturbance

Our study characterized stoichiometric relationships between C and nutrients (N and P) in the soil–plant systems of peatlands that represent the various degrees of disturbance in AOSR. We observed that plant chemical composition was distinct between the recently disturbed peatland and older disturbed sites, which was indicated by total elemental (especially Fe and P) content in living plant tissue. Consistent with stoichiometric relationships observed in plant tissue of boreal peatland vegetations, our results show that major peatland plant functional types in AOSR are N-limited, except for the recently disturbed site, where bryophytes, the keystone species in peatlands tend to be P-limited. Our findings

suggest that the natural N-limited conditions of boreal peatland plant communities can be modified by disturbances that alter the hydrology and nutrient regimes of peatlands, with the potential to shift the stoichiometric balance of C:N:P in the soil–plant system, especially in the short term. The implications of this stoichiometric shift on the long-term C storage will depend on dominant vegetation communities, the availability of P, and dominant water table conditions. Given the gradient of nutrient conditions between the Poor and Rich fens, it is expected that the impact of disturbances that leads to exogenous nutrient inputs could be exacerbated in nutrient-poor peatlands, which have the potential to store more C. Thus, these peatland types should be prioritized in the conservation and management of peatlands threatened by major environmental disturbances.

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