

# Chemical element concentrations and accumulation in boreal mire ecosystems in Finland

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The role of mires providing ecosystem services as element sequestration and long-term storage was determined from two major mire types, fens and bogs, in boreal Finland. A detailed analysis of 35 different chemical element concentrations, dry bulk density and age of the peat layers were used to determine the long-term element accumulation rates. Differences in several element concentrations showed a strong regional pattern. The median concentrations of non-metals such as N, S and P were 1.6 to 1.8-fold higher in fens compared to bogs. Similarly, the median heavy metal concentrations were approximately 2.2 times higher in fens. Despite the significantly lower C accumulation rates of fens, the accumulation rates of many other elements were of the same magnitude between fens and bogs. The most significant differences in the long-term accumulation rates were found within P, Al and several heavy metals (Cr, Fe, Ni, Th, U, V), which were significantly higher for fens compared to bogs. However, the accumulation rates of K and Mg were significantly lower in fens, indicating a great depletion and plant uptake. The results of this study demonstrate that intact mires contribute to multiple ecosystem service goals simultaneously, including the crucial C sequestration and storage but also other long-term element sequestration and storage including both non-metals and metals.

## Introduction

Intact mires provide several important ecosystem services such as carbon (C) sequestration and storage, nutrient and element sequestration and storage, flood and water quality regulation, dissolved organic carbon (DOC) retention and habitat provision for vegetation biodiversity and wildlife (Bonn *et al.* 2014). The role of mires as large C storages and as important contributors towards climate targets due to the continuous sequestration of CO<sub>2</sub> is widely recognized. Unlike most terrestrial ecosystems, mires act

as continuous sinks of atmospheric CO<sub>2</sub> in the global C cycle, which has led to a large C storage of approximately 436 Pg stored as peat during the Holocene (Loisel *et al.* 2014). Globally, peatlands constitute approximately 30 % of the total soil C pool in the world (Loisel *et al.* 2014), and approximately 50 % compared to 863 Pg C currently held in the atmosphere as CO<sub>2</sub> (Le Quéré *et al.* 2018).

Along with C dynamics and C storage, mires have sequestered other chemical elements and thus formed a large body of deposited elements during the Holocene. There is a relatively large

body of recent studies focusing on the element concentrations of northern peat deposits (Orru and Orru 2006, Klavins *et al.* 2009, Mezhibor *et al.* 2009, Silamikele *et al.* 2011, Biester *et al.* 2012, Stepanova *et al.* 2015, Schillereff *et al.* 2016, Veretennikova *et al.* 2021). Further, there are several environmental studies that provide a history of atmospheric pollution such as heavy metal accumulation in peat (Shotyk 1996, Jensen 1997, Shotyk *et al.* 2003, Martinez-Cortizas *et al.* 2002, Nieminen *et al.* 2002, Poikolainen *et al.* 2004, Ukonmaanaho *et al.* 2004, Syrovetsnik *et al.* 2004, Coggins *et al.* 2006, Kempter *et al.* 2017, Miszczak *et al.* 2020). Most of these atmospheric pollution results are collected from ombrotrophic bogs and represent either the surface peat layers (< 100 cm) or living *Sphagnum* mosses. However, less attention has been given to the actual element sequestration rate ( $\text{g m}^{-2} \text{yr}^{-1}$ ) and its relation to peat accumulation. Only a few studies, for example Gorham and Janssens (2005) and Pontevedra-Pombal *et al.* (2013), report both the chemical element concentrations and accumulation rates from ombrotrophic sites from eastern Canada and northwestern Spain, respectively.

Knowledge of the long-term elemental accumulation rates of mires is needed to evaluate the role of mires in providing ecosystem services such as long-term nitrogen (N) and phosphorus (P) retention compared for example to waters discharging from forestry-drained peatlands into water bodies. Evaluation is needed especially in countries with a high abundance of peat such as Finland, where 30 % of the total land area is classified as peatland (Finnish Statistical Yearbook of Forestry 2014). Overall, approximately 2/3 of the C reservoir of ecosystems in Finland is in peat (Turunen and Valpola 2020), which indicates that the other element storages and accumulation rates may be equally important. This assumption is supported, for example, by the natural ability of peat to retain heavy metals due to a large specific surface and a pore volume (Brown *et al.* 2000, Jain *et al.* 2017). In Finland, approximately 56% of the present peatland area is drained for different forms of anthropogenic land use such as peatland forestry. Therefore,

knowledge of mire ecosystem services is also needed related to the sustainable land use of mires or evaluation of peatland restoration.

Mires are predominantly northern ecosystems, especially abundant in continental boreal and sub-arctic regions, but they are also found in the tropics (Ruuhijärvi 1983, Euroala *et al.* 1984, Joosten and Clarke 2002, Yu 2011). The northern parts of Fennoscandia are characterized by mire complexes called aapa mires (patterned and nonpatterned fens) and the southern parts by raised bogs. The permafrost zone is also an important component of northern mires (Vitt *et al.* 2000, Vardy *et al.* 2000) but is marginal in northern Finland. Fens and bogs show distinct differences in the hydrology and water-flow patterns, general arrangement of minerotrophic vs. ombrotrophic vegetation, surface morphology, peat pH and stratigraphy (Pakarinen 1995, Vitt *et al.* 2000, Laitinen *et al.* 2007, Lindholm 2015). In fens, major sources of elements are supplied through surface waters from the adjacent mineral soils and by atmospheric deposition. In bogs, elements are mainly supplied by atmospheric deposition (Damman 1986, Aerts *et al.* 1992, Vitt *et al.* 2000). Differences in the general functionality of fens and bogs are also reflected in a significant difference in the long-term carbon accumulation rates (LORCA) between these mire types (Turunen *et al.* 2002). Thus, the accumulation rates of other elements can be different and more accurate estimates are needed.

The main aim of this study was to evaluate the role of boreal mires providing element sequestration as part of the ecosystem services. The specific objectives of the study were: (1) to investigate the physical properties and peat characteristics of fens and bogs; and (2) to estimate the average long-term apparent rate of elemental accumulation ( $\text{g m}^{-2} \text{yr}^{-1}$ ) of fens and bogs and its correlation with peat C accumulation. For clarity, both the terms mire and peatland are used in this study. A mire is a peatland where peat is currently being formed. A peatland is an area with or without vegetation, with a naturally accumulated peat layer at the surface, including peatlands drained for forestry, agriculture, horticulture and energy production (Joosten and Clarke 2002).

## Material and methods

### Selection of the study sites

The eight mires studied are located in the two main mire complex types of Finland, the northern aapa mire region and the southern raised bog region (Fig. 1a). The location and attributes of the study sites are shown in Table 1. These mires were selected from the Geological Survey of Finland digital database, which includes detailed and systematic field inventory results of mires studied between 1980 and 2020. Detailed information of the inventory methods is given in Lappalainen *et al.* (1984). The selected mires were originally studied and sampled from 1997–2002. The large background information of the study sites included the mire and peat types, peat thickness, degree of decomposition in von Post's (1922) 10-grade scale, subsoil quality, surface elevation and underlying topography. Existing laboratory analyses included the peat dry bulk density, water and ash content, carbon (C) and nitrogen (N) concentrations and a total of 166 radiocarbon datings from different parts of the mires (see Supplementary Information Table S1). To address the natural long-term mire development, only the undrained mires were selected from two main mire types. Also, the mires were selected so that none of the study sites was influenced by local bedrock anomalies such as the presence of black schist deposits, which are known to cause elevated chemical concentrations in the basal peat layers (Mäkilä *et al.* 2015).

### Study sites

Study sites 1–4 are large aapa mires located in the northern and middle boreal vegetation-zones (Hämet-Ahti 1981, Ruuhijärvi 1983). Most of the mire areas are treeless or sparsely treed mires (Fig. 1b–d). The most common mire types are oligo-mesotrophic flark fen, tall-sedge fen, minerotrophic low-sedge fen, low-sedge *Sphagnum papillosum* pine fen. The mean peat thickness of the sites varies from 1.1 m to 1.6 m. However, all mires also have thicker peat deposits of up to 5.4 m. Most of the peat depos-

its are weakly or moderately decomposed *Carex* or mixed *Sphagnum-Carex* peat with a mean degree of decomposition between H3.8 and H4.6 ( $H_{1-10}$ , von Post 1922). For a more detailed description of the study sites and the analysed mire profiles, see Supplementary Information section S2.

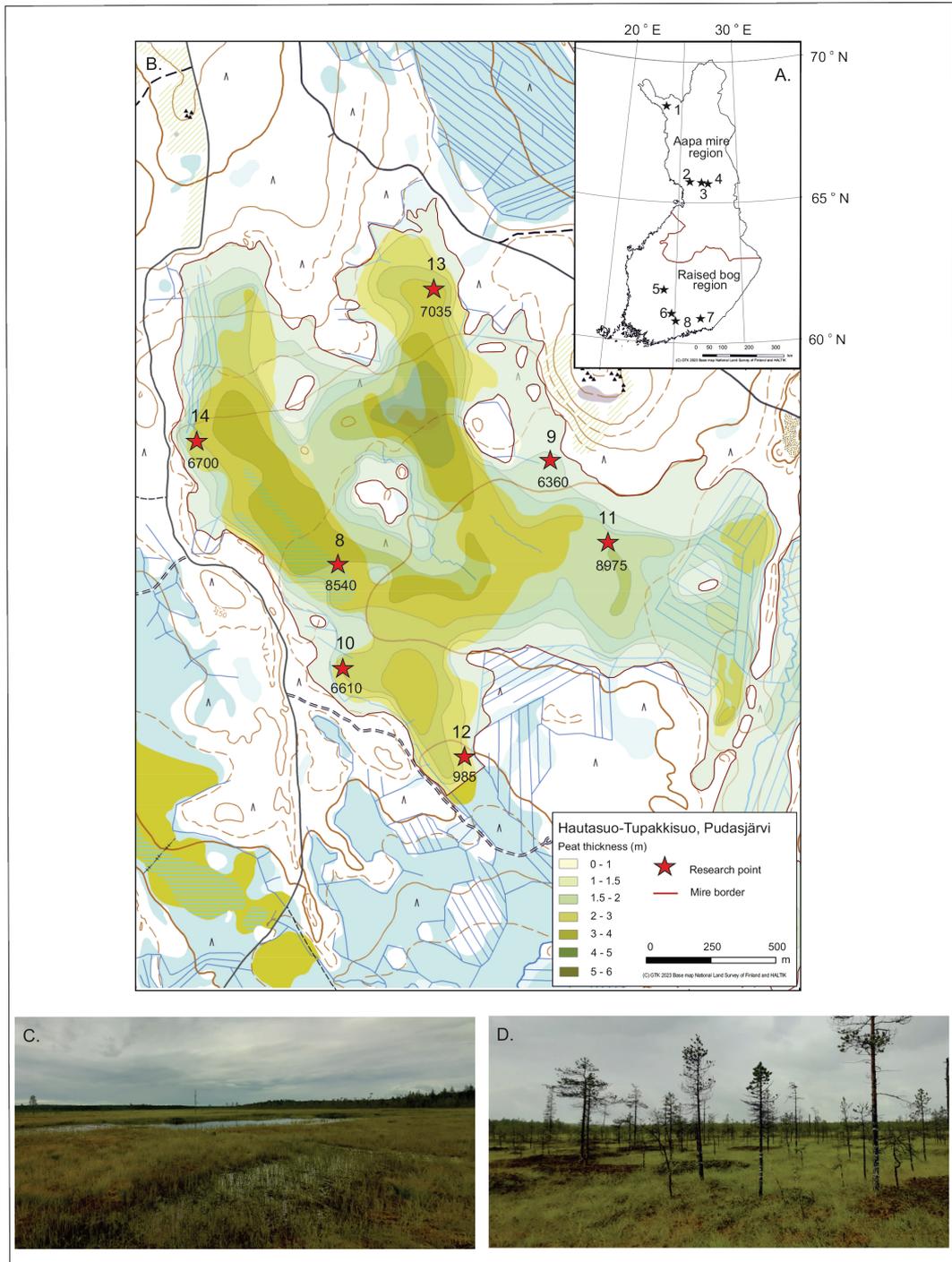
Study sites 5–8 are located in the southern and middle boreal vegetation zones (Hämet-Ahti 1981, Ruuhijärvi 1983). Most of the mire areas are sparsely treed mires such as ridge-hollow pine bog, cottongrass pine bog and *Sphagnum fuscum* pine bog. However, oligotrophic low-sedge fen and tall-sedge pine fen are also found within the mires. The mean peat thickness of the sites varies from 2.5 m to 4.8 m with the maximum thickness over 7 m in all mires. Most of the peat deposits are moderately decomposed *Sphagnum* peat with *Carex* peat at the basal layers. The mean degree of decomposition varies between H4.0 and H4.6 ( $H_{1-10}$ , von Post 1922). For a more detailed description of the study sites and the analysed mire profiles, see Supplementary Information section S2.

### Peat sampling

In 2020, 18 peat profiles were collected with a box sampler (70 × 70 × 1000 mm) and a Russian pattern side-cutting peat sampler (50 × 500 mm) for dry bulk density and element concentration analyses. In addition, ten existing peat profiles were selected from the peat archive of the Geological Survey of Finland. In the field, the mire types were verified based on the vegetation cover and surface topography (Laine *et al.* 2018). The peat type of each sample was determined (Lappalainen *et al.* 1984) and degree of decomposition was estimated with von Post's (1922) 10-grade scale, ( $H_{1-10}$ ). The 20-cm peat samples were collected in plastic bags and stored in dark and cool conditions (+4°C) approximately for a month before analysis.

### Laboratory analyses

Peat samples were analyzed by Eurofins Labtium Laboratory in Kuopio, Finland, where sam-



**Fig. 1.** (A) Eight study sites. The brown line indicates the border of northern aapa mires and southern raised bogs of Finland. (B) Hautasuo-Tupakkisuo study site with coring sites (8–14). Also, the peat thickness and the basal ages (cal. yr BP) are shown. (C) The flark fen in site 8 and (D) low-sedge *S. papillosum* pine fen in site 11.

**Table 1.** Characteristics of the study areas.

Peatland	Area ha	Mean Peat thickness m	North Lat.	East Long.	Altitude, m	Mean Temperature, °C			Annual Precipitation		
						January	July	Annual	Effective Temperature Sum, dd	Rain, mm	Mean Snow depth, 15.3. cm
1. Luovuoma	186	1.1	68°24'	23°32'	292-302	-14.9	+12.3	-2.0	550-650	457	70-80
2. Koiransuo	100	1.6	65°41'	25°58'	103-107	-9.5	+15.6	+1.7	850-950	598	50-60
3. Hautasuo-Tupakkisuo	456	1.3	65°39'	27°03'	135-154	-11.5	+15.6	+1.3	850-950	598	60-70
4. Ruosuo	475	1.2	65°39'	27°19'	168-190	-11.5	+15.6	+1.3	850-950	598	60-70
5. Silkaneva	1247	2.5	61°50'	24°10'	162-172	-7.4	+15.5	+3.3	1150-1250	714	35-45
6. Suurisuo	230	4.4	60°60'	24°48'	127-134	-6.9	+16.0	+3.8	1150-1250	590	30-40
7. Haukkasuo	281	3.4	60°49'	26°57'	55-60	-7.4	+16.9	+4.0	1250-1350	677	50-60
8. Kilpisuo	407	4.8	60°43'	25°08'	79-87	-6.2	+16.4	+4.3	1250-1350	650	30-40

For the climate at the study areas, climatological data of years 1971-2000 was used (Finnish Meteorological Institute 2021, <https://www.ilmatieteenlaitos.fi/avoin-data>). For effective temperature a +5°C threshold is used; dd is degree days (Kersalo and Pirinen, 2009).

ples were oven dried (Memmert UFE800 model) to a constant mass at 105°C and weighed. The peat samples were milled, and the ash concentration analysis made as loss-on-ignition (LOI) at 815°C (ISO 1171 method). Concentrations of 33 different elements were determined after samples were milled and then digested with HNO<sub>3</sub> acid in a microwave (US EPA 3051A) by either inductively coupled plasma mass spectroscopy (ICP-MS: Ag, As, Ba, Bi, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, Rb, Sb, Se, Sr, Th, Tl, U, V) or optical emission spectroscopy (ICP-OES: Al, B, Be, Ca, Fe, K, Mg, Mn, Na, P, S, Ti, Zn). In addition, the C and N concentrations were analyzed using a LECO CHN analyzer. The C:N ratio was calculated for each sample based on the analyses.

A total of 166 radiocarbon dates were used to calculate the calibrated dates (BP) of the peat deposits. The radiocarbon determinations were mainly carried out at the <sup>14</sup>C dating laboratory of the Geological Survey of Finland (Su). Additional samples were dated at the University of Helsinki dating laboratory (Hel) and the Poznan radiocarbon laboratory (Poz). All results were corrected for isotopic fractionation based on the <sup>13</sup>C-values given in Supplementary Information Table S1. Radiocarbon ages were converted to calendar years using CALIB REV 8.2 (Stuiver *et al.* 2022). All ages used in this article are calendar years (cal. BP).

### Calculation of accumulation rates

The dry bulk density (g cm<sup>-3</sup>) of the samples was calculated by dividing the dry peat mass by the fresh volume (cm<sup>-3</sup>), while the element density (g cm<sup>-3</sup>) was calculated by multiplying the dry bulk density by the corresponding element concentration. Areal element mass (g m<sup>-2</sup>) was determined as a function of peat depth and cumulative element mass was determined between the <sup>14</sup>C-dated horizons. The accumulated elemental mass between the <sup>14</sup>C-dated horizons was divided by the age of this horizon to give the elemental accumulation rate (g m<sup>-2</sup> yr<sup>-1</sup>). For a more detailed description of the long-term accumulation rates, see Tolonen and Turunen (1996) and Turunen *et al.* 2002.

### Data analysis

SPSS Statistics ver. 27 software was used to analyze the relationships between different measured variables. The tests of normal distribution and the homogeneity of variances were tested using the Kolmogorov-Smirnov and Levene statistical tests. To compare differences in the element accumulation between different mire types, we carried out Pearson's chi-square median test for independent medians. In the data analysis, median concentrations were preferred to emphasize the central tendency of the data to eliminate any impact of extreme values of element concentrations or radiocarbon datings of the peat sections. However, mean values also are given for all element concentrations and long-term elemental accumulation (Table 2).

## Results

### General properties of dated peat profiles

The peat layers of fens were clearly more decomposed compared to bogs. The median degree of decomposition for fens and bogs was H5.0 and H4.0, respectively (H<sub>1-10</sub>, von Post 1922). Thus, the median dry bulk density of fens (0.087 g cm<sup>-3</sup>, *n* = 156) was significantly higher compared to bogs (0.066 g cm<sup>-3</sup>, *n* = 229,  $\chi^2 = 30.52$  and *p* = 0.000). Overall, the ash concentrations for fen and bog deposits were low. The median ash concentration of fens (5.5%) was significantly higher compared to bogs (1.7%,  $\chi^2 = 106.03$  and *p* = 0.000). However, the median age of the dated peat profiles between fens and bogs were not significantly different ( $\chi^2 = 0.11$  and *p* = 0.738) even though the median age of fens was somewhat older (4720 cal. yrs BP) compared to bogs (4405 cal. yrs BP).

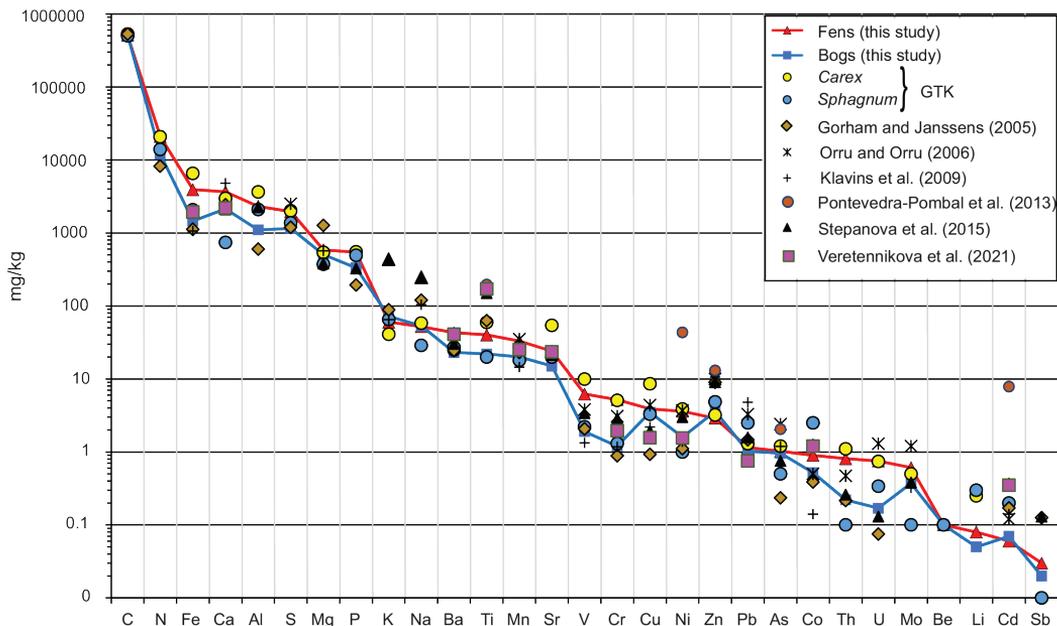
### Element concentrations

#### Non-metals

The concentration of non-metals (C, N, P, S and Se) and the statistical median differences between the two mire types are shown in Table 2

**Table 2.** The median, range and mean of the element concentrations and long-term accumulations for fens and bogs. SE = standard error of the estimate. Concentration and accumulation ratios are calculated by dividing the median value for fen by the corresponding median value for the bog. \*\* = Difference between median values is significant at the 0.01 level, \* = 0.05 level (Independent samples median test). Also, the instrument detection limit (IDL\*) for different elements is given.

Element	Fens						Bogs										
	IDL* mg kg	N	Median	Concentration range mg kg <sup>-1</sup>	Mean ± SE	N	Long-term accumulation			N	Mean ± SE	Concentration range mg kg <sup>-1</sup>	Long-term accumulation				
							Median	Mean ± SE	Accum.				Median	Mean ± SE	Conc.	Accum.	
C	500	156	508000	378000–595000	506300 ± 3390	66	13086	15733 ± 1221	229	515000	369000–606000	512000 ± 2590	78	19676	27133 ± 2109	1.0	0.7**
N	200	156	21000	5700–41600	20486 ± 498	66	606	650 ± 43	229	12000	5000–21500	12300 ± 300	78	485	588 ± 43	1.8**	1.2
Fe	50	156	3913	253–31000	4989 ± 311	66	108	144 ± 14	229	1460	125–17900	2603 ± 186	78	55	119 ± 20	2.7**	2.0**
Al	15	156	2310	163–27700	3670 ± 381	66	62	89 ± 11	229	1100	201–22300	2215 ± 193	78	46	106 ± 23	2.1**	1.3*
Ca	50	156	3663	572–12300	4528 ± 235	66	86	143 ± 18	229	2140	272–12300	2799 ± 164	78	89	135 ± 15	1.7**	1.0
S	20	156	1960	517–18400	2738 ± 223	66	54	86 ± 11	229	1150	397–10000	1487 ± 92	78	45	81 ± 17	1.7**	1.2
P	20	156	544	228–1810	653 ± 27	66	17	20 ± 2	229	334	106–1570	378 ± 14	78	13	16 ± 2	1.6**	1.3*
Mg	10	156	586	91–2690	645 ± 31	66	15	19 ± 2	229	504	71–3190	578 ± 25	78	23	33 ± 4	1.2*	0.7*
K	50	156	60	5–1710	224 ± 29	66	2	6 ± 1	229	72	23–1850	183 ± 21	78	3	15 ± 4	0.8**	0.7*
Na	50	156	52	3–317	70 ± 4	66	1	2 ± 0.3	229	53	25–126	54 ± 2	78	2	3 ± 1	1.0	0.5**
Ba	0.05	156	43	10–262	55 ± 3	66	1.3	1.6 ± 0.2	229	23	5–142	31 ± 2	78	0.9	1.4 ± 0.2	1.9**	1.4**
Ti	0.5	156	40	6–910	88 ± 11	66	1.3	2.0 ± 0.3	229	22	2–809	61 ± 8	78	0.9	3.4 ± 1.2	1.8**	1.4
Sr	1	156	24	4–71	26 ± 1	66	0.6	0.8 ± 0.1	229	15	3–83	21 ± 1	78	0.7	0.9 ± 0.1	1.6**	0.9
Mn	1	156	33	3–194	42 ± 3	66	0.9	1.3 ± 0.2	229	20	1–388	48 ± 5	78	0.6	2.5 ± 0.5	1.7**	1.5
V	0.1	156	6.2	0.8–147.0	14.7 ± 1.7	66	0.21	0.40 ± 0.07	229	1.9	0.2–53.5	5.3 ± 0.6	78	0.080	0.27 ± 0.07	3.3**	2.6**
Cr	0.5	156	5.2	0.6–63.2	8.9 ± 0.8	66	0.16	0.24 ± 0.03	229	1.2	0.3–37.0	3.1 ± 0.3	78	0.046	0.16 ± 0.04	4.3**	3.5**
Cu	0.3	156	3.9	1.1–75.4	7.2 ± 0.7	66	0.12	0.19 ± 0.03	229	3.5	0.4–64.9	6.7 ± 0.7	78	0.13	0.37 ± 0.11	1.1	0.9
Ni	0.3	156	3.6	0.8–23.6	4.8 ± 0.3	66	0.095	0.14 ± 0.01	229	1.6	0.2–24.0	2.7 ± 0.3	78	0.045	0.15 ± 0.04	2.3**	2.1**
Zn	1	156	2.9	0.5–41.6	5.6 ± 0.6	66	0.1	0.2 ± 0.04	229	3.6	0.5–149.0	9.8 ± 1.4	78	0.2	1.0 ± 0.3	0.8	0.5*
Pb	0.05	156	1.15	0.05–45.90	4.10 ± 0.54	66	0.029	0.14 ± 0.038	229	1.02	0.12–39.50	3.80 ± 0.38	78	0.045	0.33 ± 0.090	1.1	0.6
As	0.05	156	1.02	0.11–13.50	2.27 ± 0.19	66	0.022	0.073 ± 0.013	229	0.96	0.05–28.20	2.41 ± 0.26	78	0.040	0.13 ± 0.044	1.1	0.6
Co	0.05	156	0.90	0.11–9.43	1.28 ± 0.10	66	0.024	0.034 ± 0.003	229	0.52	0.06–4.81	0.83 ± 0.06	78	0.018	0.039 ± 0.008	1.7**	1.3
Th	0.02	156	0.81	0.05–27.90	1.68 ± 0.24	66	0.022	0.040 ± 0.007	229	0.22	0.01–12.90	0.95 ± 0.11	78	0.0071	0.043 ± 0.011	3.7**	3.1**
U	0.01	156	0.75	0.03–78.50	2.26 ± 0.61	66	0.017	0.048 ± 0.014	229	0.17	0.01–13.90	1.41 ± 0.19	78	0.006	0.072 ± 0.026	4.4**	2.8**
Rb	0.02	156	0.40	0.06–15.70	1.20 ± 0.18	66	0.011	0.029 ± 0.006	229	0.49	0.12–18.50	1.14 ± 0.15	78	0.024	0.083 ± 0.025	0.8*	0.5**
Mo	0.02	156	0.61	0.01–9.52	1.21 ± 0.14	66	0.014	0.039 ± 0.009	229	0.37	0.03–15.30	0.96 ± 0.14	78	0.011	0.056 ± 0.025	1.6**	1.3
Se	0.5	156	0.52	0.05–5.84	0.66 ± 0.05	66	0.013	0.019 ± 0.003	229	0.25	0.20–2.94	0.53 ± 0.04	78	0.013	0.027 ± 0.005	2.1**	1.0
Li	0.1	156	0.08	0.05–19.20	0.56 ± 0.20	66	0.021	0.11 ± 0.004	229	0.05	0.05–22.80	0.46 ± 0.13	78	0.0029	0.031 ± 0.015	1.6*	0.7
Be	0.2	156	0.10	0.10–2.86	0.28 ± 0.03	66	0.0048	0.0172 ± 0.0001	229	0.10	0.10–2.15	0.26 ± 0.02	78	0.007	0.012 ± 0.002	1.0	0.7
Sb	0.02	156	0.03	0.01–0.41	0.06 ± 0.01	66	0.0008	0.0021 ± 0.0004	229	0.02	0.01–0.61	0.07 ± 0.01	78	0.001	0.006 ± 0.001	1.5	0.8
Cd	0.01	156	0.06	0.03–0.55	0.10 ± 0.01	66	0.0017	0.0035 ± 0.0008	229	0.07	0.01–0.83	0.13 ± 0.01	78	0.0031	0.0092 ± 0.002	0.9	0.5*
Ag	0.01	156	0.02	0.01–0.14	0.02 ± 0.00	66	0.0004	0.0006 ± 0.0001	229	0.02	0.01–0.19	0.03 ± 0.00	78	0.0006	0.0017 ± 0.0004	1.0	0.7*
Tl	0.01	156	0.02	0.01–0.18	0.03 ± 0.00	66	0.0004	0.0008 ± 0.0002	229	0.01	0.01–0.30	0.03 ± 0.00	78	0.0004	0.002 ± 0.0006	2.0*	1.0



**Fig. 2.** Median concentrations for different elements in fens ( $n = 156$ ) and bogs ( $n = 229$ ) in this study. For comparison, the median concentrations of the Geological Survey of Finland database for *Sphagnum* and *Carex* peat are given ( $n = 1859$ – $2270$ , Herranen and Toivonen 2020). Also, the results of Gorham and Janssens (2005,  $n = 235$ ), Orru and Orru (2006,  $n = 684$ ), Klavins et al. (2009,  $n = n.a.$ ), Pontevedra-Pombal et al. (2013,  $n = 289$ ), Stepanova et al. (2015,  $n = 235$ ) and Veretennikova et al. (2021,  $n = 70$ ) for Canadian, Estonian, Latvian, Spanish and Russian mires are given.

and in Fig. 2. The difference in median C concentration between fens and bogs was not significant with an overall median of 51.2%. However, the median concentrations of N, P, S and Se were significantly, 1.6–2.1 -fold, higher within fens compared to bogs (Table 2). There was a weak but significant overall positive correlation between C and N concentrations ( $r = 0.38$ ,  $p < 0.01$ ), between N and S concentrations ( $r = 0.34$ ,  $p < 0.01$ , Table 3) and a moderate but significant positive correlation between P and N concentrations ( $r = 0.55$ ,  $p < 0.01$ , Table 3).

Median C:N, C:S and N:S ratios were 33:1, 360:1 and 10:1, respectively. The median C:N ratios in fens and bogs were 25:1 and 45:1, respectively. The difference in median C:N ratios between fens and bogs was significant ( $\chi^2 = 114.77$  and  $p = 0.000$ ). The variation in the C:N ratios mainly followed the variations in the N content of the peat (Table 3). Pearson's correlation coefficient between C:N ratios and N content was significant ( $r = -0.90$  and  $p = 0.000$ ). Also, the difference between median C:S ratios

in fens (255:1) and bogs (430:1) was significant ( $\chi^2 = 93.57$  and  $p = 0.000$ ). However, the median N:S ratios for fens and bogs were similar 10:1.

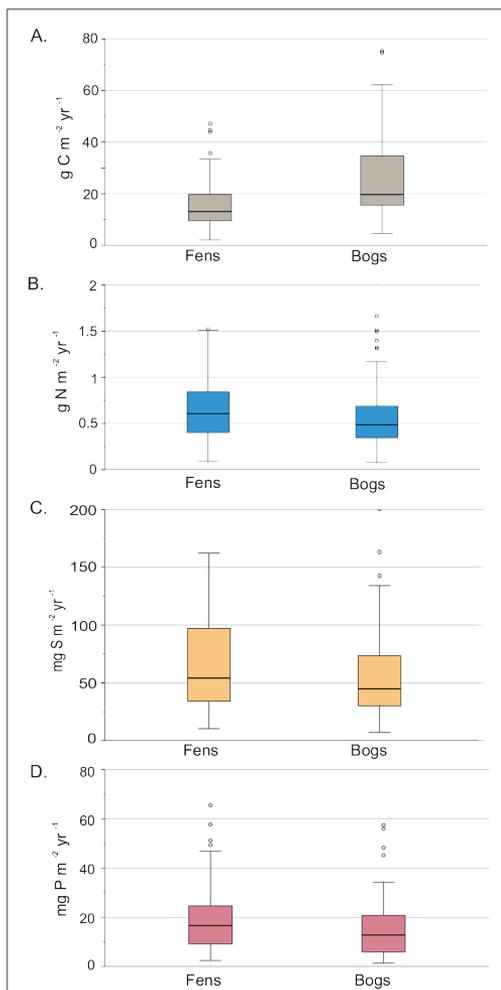
### Alkali and light metals

The concentration of alkali and light metals (Al, K, Li, Na, Rb and Ti) and the statistical median differences between the two mire types are shown in Table 2 and in Fig. 2. In fens, the median concentrations of Al, Li and Ti were 1.6–2.1 -fold higher compared to bogs. The median concentrations of Na were similar in fens and bogs. However, the median concentrations of K and Rb were significantly lower in fens compared to bogs. In descending order, median Al concentrations were over  $1000 \text{ mg kg}^{-1}$  dwt, K and Na concentrations over  $50 \text{ mg kg}^{-1}$  dwt, Ti between 20 and  $40 \text{ mg kg}^{-1}$  dwt and Rb and Li generally below  $1 \text{ mg kg}^{-1}$  dwt. Especially, Al and Ti were significantly correlated with multiple elements and ash concentration (Table 3).

**Table 3.** The Pearson correlation matrix for element concentrations, ash content (A%) and C:N ratio ( $n = 385$ ). Only significant correlations are shown. Strong correlation coefficients greater than  $\pm 0.7$  are marked in bold.

	Ag	Al	As	Ba	Be	C	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	N	Na	Ni	P	Pb	Rb	S	Sb	Se	Sr	Th	Ti	Tl	U	V	Zn	A%	C:N		
Ag	1																																				
Al	.65**	1																																			
As	.63**	.42**	1																																		
Ba	.34**	.59**	.16**	1																																	
Be	.61**	.77**	.39**	.53**	1																																
C	-.20**	-.20**				1																															
Ca	.15**	.24**	.42**	.38**	.44**	1																															
Cd	.67**	.29**	.50**	.17**	.32**	-.35**	.12**	1																													
Co	.41**	.54**	.51**	.55**	.49**	-.14**	.43**	.26**	1																												
Cr	.48**	.78**	.30**	.71**	.61**	-.33**	.26**	.26**	.63**	1																											
Cu	.75**	.76**	.68**	.60**	.63**	-.14**	.24**	.58**	.61**	.73**	1																										
Fe	.39**	.57**	.45**	.71**	.54**	-.49**	.24**	.74**	.62**	.55**	1																										
K	.51**	.36**	.37**	.16**	.28**	-.50**	.56**	.24**	.41**	.47**	.17**	1																									
Li	.58**	.74**	.44**	.42**	.67**	-.36**	.28**	.37**	.47**	.57**	.62**	.48**	.55**	1																							
Mg	.40**	.44**	.52**	.40**	.54**	-.39**	.66**	.37**	.50**	.50**	.54**	.53**	.57**	.70**	1																						
Mn	.41**	.33**	.45**	.18**	.57**	-.19**	.57**	.36**	.43**	.21**	.30**	.52**	.37**	.47**	.63**	1																					
Mo	.43**	.22**	.86**	.14**	.46**	.35**	.39**	.19**	.50**	.27**	.33**	.24**	.48**	.29**	1																						
N	.26**	.17**	.46**	.10**	.38**	.29**	-.15**	.30**	.27**	.16**	.39**	-.23**	.18**	1																							
Na	.17**	-.17**	.45**	.26**	.21**	-.17**	.11**	.52**	.18**	.47**	.32**	-.18**	1																								
Ni	.57**	.70**	.59**	.67**	.56**	-.27**	.37**	.42**	.80**	.83**	.81**	.71**	.53**	.65**	.66**	.39**	.49**	.31**	.23**	1																	
P	.42**	.68**	.20**	.66**	.49**	.18**	.15**	.37**	.62**	.47**	.56**	.11**	.31**	.12**	.15**	.55**	.48**	1																			
Pb	.27**																																				
Rb	.67**	.64**	.54**	.37**	.54**	-.46**	.16**	.54**	.45**	.61**	.71**	.41**	.85**	.81**	.70**	.39**	.43**	-.11**	.38**	.72**	.26**	.24**	1														
S	.22**	.21**	.35**	.29**																																	
Sb	.24**	-.13**	-.12**	-.32**	-.16**	-.59**	-.15**	-.12**	-.17**	.19**	-.16**																										
Se	.70**	.80**	.66**	.68**	.81**	-.16**	.35**	.45**	.63**	.76**	.90**	.61**	.36**	.63**	.55**	.40**	.35**	.23**	.77**	.56**																	
Sr	.24**	.32**	.41**	.48**	.54**	.88**	.17**	.51**	.28**	.32**	.60**	.31**	.60**	.62**	.35**	.28**	.15**	.40**	.26**	-.15**	.16**	.29**	-.15**	.43**	1												
Th	.54**	.79**	.36**	.71**	.80**	-.20**	.36**	.29**	.55**	.81**	.76**	.53**	.32**	.57**	.52**	.32**	.18**	.22**	.68**	.57**																	
Ti	.74**	.84**	.60**	.57**	.70**	-.30**	.27**	.43**	.69**	.83**	.88**	.58**	.52**	.78**	.61**	.36**	.43**	.16**	.12**	.84**	.50**																
Tl	.66**	.41**	.50**	.23**	.35**	-.40**	.15**	.77**	.39**	.41**	.58**	.27**	.71**	.52**	.48**	.39**	.40**	.22**	.54**	.20**	.51**	.73**	.30**	.37**	.46**												
U	.51**	.60**	.35**	.58**	.70**	-.16**	.34**	.29**	.43**	.62**	.73**	.36**	.35**	.49**	.51**	.22**	.12**	.12**	.57**	.42**																	
V	.39**	.64**	.26**	.70**	.51**																																
Zn	.51**	.17**	.55**																																		
A%	.52**	.67**	.38**	.55**	.61**	-.44**	.39**	.34**	.63**	.73**	.60**	.57**	.36**	.61**	.54**	.36**	.23**	.22**	.16**	.71**	.45**																
C:N	-.19**	-.39**	-.30**	-.53**	-.24**	-.19**	-.38**	-.46**	-.39**	-.29**	-.49**	.12**	-.12**	-.13**	-.25**	-.89**	.12**	-.43**	-.63**	.11**																	

Correlation is significant at the 0.01 level (2-tailed). \* Correlation is significant at the 0.05 level (2-tailed).



**Fig. 3.** (A-D) Box plot showing the long-term median rate of carbon (C), nitrogen (N), sulphur (S) and phosphorus (P) accumulation for Finnish fens and bogs. Whiskers and box bands denote quartiles.

### Alkaline earth metals

The concentration of alkaline earth metals (Ba, Be, Ca, Mg and Sr) and the statistical median differences between the two mire types are shown in Table 2 and in Fig. 2. All alkaline earth metal concentrations, excluding Be, were significantly higher in fens compared to bogs. The median concentrations of Ba and Ca were clearly 1.7–1.9 -fold higher in fens compared to bogs (Table 2). In descending order, the median Ca concentrations were over 2000  $\text{mg kg}^{-1}$  dwt, Mg: 500–600  $\text{mg kg}^{-1}$  dwt, Ba and Sr between 1 and 50  $\text{mg kg}^{-1}$  dwt and Be

below 1  $\text{mg kg}^{-1}$  dwt. The significant correlations between elements and peat ash concentration are shown in Table 3.

### Heavy metals

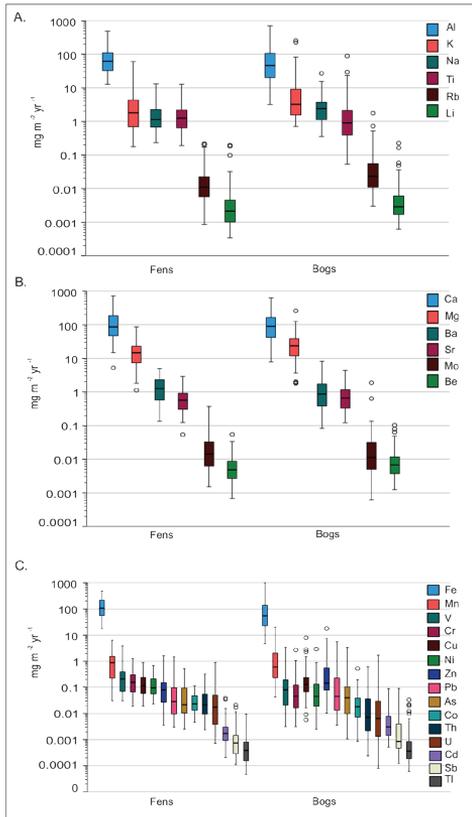
The concentration of heavy metals (As, Cd, Cu, Co, Cr, Fe, Mn, Ni, Pb, Sb, Th, U, V and Zn) and the statistical median differences between the two mire types are shown in Table 2 and in Fig. 2. Overall, the median heavy metal concentrations were approximately 2.2 times higher in fens compared to bogs. The most significant difference was with the median concentrations of Ni, Cr, Th, U and V, which were 3.3 to 4.4 times higher in fens.

The results show that concentrations of heavy metals in peat are generally low, varying from 0.02 to 33  $\text{mg kg}^{-1}$  with the exception of Fe, which had a median of 3913 and 1460  $\text{mg kg}^{-1}$  in fens and bogs, respectively (Table 2). In descending order, median Mn concentration was between 20 and 40 dwt followed by V, Cr, Cu, Ni, Zn, Pb and As generally between 1 and 10  $\text{mg kg}^{-1}$ , whereas Co, Th, U, Cd and Sb were below 1  $\text{mg kg}^{-1}$  dwt. The significant correlations between elements and peat ash concentration are shown in Table 3. Within heavy metal group, Cr, Cu and Ni were significantly correlated with multiple elements and ash concentration (Table 3).

### Element accumulation

#### Non-metal accumulation

The results of long-term non-metal accumulation and the statistical differences between the two mire types are shown in Table 2. The long-term median rate of carbon accumulation (LORCA) in fens and bogs were 13.1 ( $n = 66$ ) and 19.7  $\text{g m}^{-2} \text{yr}^{-1}$  ( $n = 78$ ), respectively (Fig. 3a). The difference in LORCA between these two mire types was significant ( $\chi^2 = 18.91$  and  $p = 0.000$ ). However, the difference in the long-term median rate of nitrogen accumulation (LORNA) between the two mire types was not significant ( $\chi^2 = 2.80$  and  $p = 0.094$ ), with



**Fig. 4.** (A) Box plot showing the long-term median rate of alkali and light metal accumulation; (B) alkaline earth metal accumulation; and (C) heavy metal accumulation for Finnish fens and bogs. Whiskers and box bands denote quartiles.

medians of 0.61 and 0.49  $\text{g m}^{-2} \text{yr}^{-1}$  in fens and bogs, respectively (Table 2, Fig. 3b). For C and N accumulation, the range of the data shows a large variation between sites and dated peat sections (Fig. 3a–b).

The range of S and P accumulation also shows a large variation between sites and dated peat sections. The difference in the long-term median rate of S accumulation between the two mire types was not significant ( $\chi^2 = 1.01$  and  $p = 0.316$ ), with medians of 54 and 45  $\text{mg m}^{-2} \text{yr}^{-1}$  in fens and bogs, respectively (Table 2, Fig. 3c). However, the difference in the long-term median rate of P accumulation between the two mire types was significant ( $\chi^2 = 5.48$  and  $p = 0.009$ ), with medians of 17 and 13  $\text{mg m}^{-2} \text{yr}^{-1}$  in fens and bogs, respectively (Table 2, Fig. 3d).

### Alkali and light metal accumulation

The results of long-term alkali and light metal accumulation (Al, K, Li, Na, Rb and Ti) and the statistical differences between the two mire types are shown in Table 2. The long-term median accumulation of Al was clearly the largest with a median of 62 and 46  $\text{mg m}^{-2} \text{yr}^{-1}$  in fens and bogs, respectively (Table 2, Fig. 4a). In descending order, the long-term median accumulation of Al was followed by K and Na and Ti, between 1 and 10  $\text{mg m}^{-2} \text{yr}^{-1}$  dwt and Rb and Li below 1  $\text{mg kg}^{-1}$  dwt (Fig. 4a, Table 2). Within alkali and light metal accumulation, the long-term median rate of Al accumulation was significantly higher in fens compared to bogs. However, the long-term elemental accumulation rates of K, Na and Rb were significantly lower in fens compared to bogs. The difference in median accumulation of Li between the two mire types was not significant (Table 2).

### Alkaline earth metal accumulation

The results of long-term alkaline earth metal accumulation (Ba, Be, Ca, Mg and Sr) and the statistical differences between the two mire types are shown in Table 2. In fens and bogs, the long-term median rate of Ca accumulation was similar, varying between 80 and 90  $\text{mg m}^{-2} \text{yr}^{-1}$ , whereas the Mg accumulation rate varied between 15 and 25  $\text{mg m}^{-2} \text{yr}^{-1}$ . The long-term median rates of Ba and Sr accumulation were around 1  $\text{mg m}^{-2} \text{yr}^{-1}$ , whereas the Be accumulation rate was only between 4 and 7  $\mu\text{g m}^{-2} \text{yr}^{-1}$  (Fig. 4b, Table 2). Within alkaline earth metal accumulation, the long-term median rate of Ba accumulation was significantly higher in fens compared to bogs. However, the corresponding accumulation rate of Mg was significantly lower for fens (Table 2). For Be, Ca and Sr, the difference in median accumulation rates between the two mire types was not significant.

### Heavy metal accumulation

The results of long-term heavy metal accumulation (As, Cd, Cu, Co, Cr, Fe, Mn, Ni, Pb, Sb,

Th, Tl, U, V and Zn) and the statistical differences between the two mire types are shown in Table 2. The long-term median accumulation of Fe was clearly the largest with a median of 108 and 55 mg m<sup>-2</sup> yr<sup>-1</sup> in fens and bogs, respectively (Table 2, Fig. 4c). In fens, the second largest group of heavy metal accumulation included Mn, V, Cr and Cu, Zn and Ni with long-term accumulation ranging between 0.1 and 1 mg m<sup>-2</sup> yr<sup>-1</sup>. In bogs, the second largest group included Mn, Zn and Cu with the long-term median rates ranging between 0.1 and 1 mg m<sup>-2</sup> yr<sup>-1</sup>. Otherwise, the long-term median rate of heavy metal accumulation was below 0.1 mg m<sup>-2</sup> yr<sup>-1</sup> dwt (Fig. 4c, Table 2). Within heavy metal accumulation, the long-term median rate of Cr, Fe, Ni, Th, U and V accumulation was significantly higher for fens compared to bogs. However, the long-term elemental accumulation rates of Cd and Zn were significantly higher for bogs (Table 2).

## Discussion

### Element concentrations

An analysis of 35 chemical elements in fens and bogs in Finland shows that both the concentrations and accumulation rates vary greatly between and within the mire types. Overall, the median concentrations of different chemical elements were low and agree well with the results of a large Geological Survey of Finland database collected from Finnish peatlands (Fig. 2, Heranen and Toivonen 2020). The median concentration values found in this study were also of the same magnitude compared to mires from Estonia and western Siberia (Fig. 2, Orru and Orru 2006, Stepanova *et al.* 2015, Veretennikova *et al.* 2021) but somewhat higher compared to the bogs of Latvia (Klavins *et al.* 2009, Silamikele *et al.* 2011) and bogs of eastern Canada (Gorham and Janssens 2005). Compared with our study, the similarities with Estonian and West Siberian mires may largely be explained by the fact that the dataset of Estonian and Siberian mires were collected from different types of mires including ombro-oligotrophic bogs and minerotrophic fens (Orru and Orru 2006, Stepanova *et al.* 2015, Veretennikova *et al.* 2021). In our data, the profiles

of the bogs include a variety of different types of mires ranging from ombrotrophic to oligotrophic mires including occasionally *Carex-Sphagnum* deposits in deeper basal peat layers. In fens, the peat deposits are *Carex* or *Sphagnum-Carex* dominated. In our study, the variety in the peat type quality and overall differences between the fens and bogs could be seen in their mean C:N ratios, which were 25:1 and 45:1 for the fens and bogs, respectively. Compared to our study, similar C:N ratios have been reported for fen and bog peat layers (Kuhry and Vitt 1996, Ohlson and Okland 1998, Stepanova *et al.* 2015, Veretennikova *et al.* 2021). However, the results of Klavins *et al.* (2009) and Gorham and Janssens (2005) represent only the nutrient poor ombrotrophic *Sphagnum* moss peat deposits. For example, Gorham and Janssens (2005) report a mean C:N ratio 65:1 for the five studied ombrotrophic bogs. In comparison, the mean C:N ratio for our six ombrotrophic study sites, excluding all but *Sphagnum* deposits, was similar 58:1.

Although, there is a lot of variation within individual elements and between fens and bogs, the concentrations of C, the most abundant element, were relatively homogenous with a median of 51.2%. More variation was found in N concentrations, where the median concentration of *Carex* dominated fen sites (2.1%) was 1.8-fold higher compared to the *Sphagnum* dominated bogs sites (1.2%). The concentrations of these two main peat elements were similar to other results across northern peatlands (Gorham and Janssens 2005, Loisel *et al.* 2014, Turunen and Valpola 2020). Overall, the median concentrations of fens were 1.8-fold compared to bogs. Within non-metal concentrations, the median concentrations of N, S, P and Se were 1.6 to 2.1-fold higher in fens compared to bogs. Within metal concentrations, the median concentrations of Al, Fe, Cr, Ni, Se, Th, Ti, U and V were 2.0 to 4.4-fold higher in fens than in bogs. This element group includes various heavy metals. Overall, a large group of heavy metals (Co, Cr, Fe, Mn, Ni, Sb, Th, U and V) had 1.5 to 4.4-fold higher median concentrations in fens compared to bogs. For bogs, only two elements (K and Rb) had significantly higher concentration values compared to fens.

In this study, the mires were selected so that none of the study sites was influenced by known

local bedrock anomalies such as the presence of black schist deposits. Also, the possible atmospheric pollution on the study sites is assumed to be marginal since there is no history of mining or metallurgy in nearby areas. Reasons for the higher elemental concentrations in fens can be found in the general functionality of these mire types. The properties of bog-fen gradients differ significantly in the hydrology and water-flow patterns, and thus in the sources of elements. In fens, the effect of bedrock and soil type on the average peat element concentrations can be distinct when the major sources of elements are supplied through surface waters from the adjacent mineral soils. In bogs, the elements are mainly supplied by atmospheric deposition (Damman 1986, Aerts *et al.* 1992). These fundamental differences are reflected in mire pH, vegetation, peat stratigraphy and in the level of median elemental concentrations in peat deposits. This is in accordance with several studies indicating that mainly climate but also the geomorphological and hydrological conditions and local geology are the main factors controlling the chemical composition of mires (Christanis *et al.* 1998, Gorham and Janssens 2005, Orru and Orru 2006, De Vos *et al.* 2006, Klavins *et al.* 2009, Silamikele *et al.* 2011, Mäkilä *et al.* 2015). Overall, the bog-fen gradient is primarily related to water chemical variables such as pH. Thus, the important relationship of pH with ombrotrophic bogs (pH < 4), oligotrophic fens (pH ~4), mesotrophic fens (pH ~5) and eutrophic fens (pH > 6) is well acknowledged (e.g. Pakarinen 1995, Sjörs and Gunnarsson 2002, Laitinen *et al.* 2007, Tahvanainen *et al.* 2002, 2003, Tahvanainen 2004, Wheeler & Proctor 2000, Lindholm 2015).

Overall, local geological conditions can have a significant impact on peat elemental concentrations. In northern and eastern Finland, where the presence of black schist bedrock is relatively common (Arkimaa *et al.* 2000), higher concentrations of S and several heavy metals such as As, Co, Cr, Fe, Ni, Pb, V and Zn are found in the basal peat layers (Parviainen *et al.* 2014, Mäkilä *et al.* 2015). However, the elevated concentrations in peat are usually found directly over the geological deposits and not detected in other parts of the mire basin. Also, eutrophic fens with

the calcareous schist terrain in northern Finland have had even 5-10 times higher Mg, Ca and Fe concentrations compared to mires not affected by calcareous bedrock (Virtanen 1993). In coastal sites, a substantial increase among B, Mg, and Na concentrations are found where windblown sea spray is an important factor regionally (Damman 1986, Gorham and Janssens 2005).

## Element accumulation

In this study, the C accumulation results of fens and bogs can be considered representative for the boreal peat deposits. The range of median LORCA (13–20 g m<sup>2</sup> yr<sup>-1</sup>) and the height increment (0.30–0.73 mm yr<sup>-1</sup>) estimates were in the same magnitude as many other published LORCA data for boreal and subarctic mires (Gorham 1991, Tolonen and Turunen 1996, Clymo *et al.* 1998, Turunen *et al.* 2001, 2002, Gorham and Janssens 2005, Loisel *et al.* 2014). The highest C accumulation rates were found for ombrotrophic bog sites with a median LORCA of 25.5 g m<sup>2</sup> yr<sup>-1</sup>. Further, the fen and bog profiles are comparable throughout their development history since the median ages of these two major mire types were similar and close to the average age of Finnish peat deposits (4200 cal. yrs, Turunen *et al.* 2002). This is an important factor, since the age of the peat deposits is one of the major predictors of C accumulation with the highest values found in young mires (Tolonen and Turunen 1996). Also, the median long-term accumulation rates of N (0.54 g m<sup>-2</sup> yr<sup>-1</sup>), S (49 mg m<sup>-2</sup> yr<sup>-1</sup>) and P (15 mg m<sup>-2</sup> yr<sup>-1</sup>) were in the same magnitude with other results reported for northern mires (Malmer and Holm 1984, Malmer *et al.* 1997, Malmer and Wallen 1999, Gorham and Janssens 2005, Karjalainen *et al.* 2016). Overall, these non-metals are the most significant element storages of mires and at the same time, the key nutrients for biological uptake by living vegetation. In this study, significant correlations were found between long-term C and all other non-metal accumulation rates, especially with N, during the Holocene (Table 4).

While the median LORCA estimates found in this study were within the normal range, they

**Table 4.** The Pearson correlation matrix for element accumulation and C:N ratio ( $n = 144$ ). Only significant correlations are shown. Strong correlation coefficients greater than  $\pm 0.7$  are marked in bold.

	Ag	Al	As	Ba	Be	C	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	N	Na	Ni	P	Pb	Rb	S	Sb	Se	Sr	Th	Ti	Ti	U	V	Zn	C:N				
Ag	1																																					
Al	<b>.80**</b>	1																																				
As	<b>.85**</b>	<b>.85**</b>	1																																			
Ba	<b>.60**</b>	<b>.72**</b>	<b>.53**</b>	1																																		
Be	<b>.64**</b>	<b>.74**</b>	<b>.51**</b>	<b>.60**</b>	1																																	
C	<b>.51**</b>	<b>.25**</b>	<b>.35**</b>	<b>.37**</b>	<b>.38**</b>	1																																
Ca	<b>.45**</b>	<b>.38**</b>	<b>.46**</b>	<b>.46**</b>	<b>.56**</b>	<b>.57**</b>	1																															
Cd	<b>.87**</b>	<b>.53**</b>	<b>.63**</b>	<b>.49**</b>	<b>.50**</b>	<b>.68**</b>	<b>.49**</b>	1																														
Co	<b>.79**</b>	<b>.91**</b>	<b>.89**</b>	<b>.71**</b>	<b>.64**</b>	<b>.36**</b>	<b>.49**</b>	<b>.57**</b>	1																													
Cr	<b>.68**</b>	<b>.88**</b>	<b>.74**</b>	<b>.83**</b>	<b>.57**</b>	<b>.25**</b>	<b>.38**</b>	<b>.48**</b>	<b>.86**</b>	1																												
Cu	<b>.88**</b>	<b>.92**</b>	<b>.94**</b>	<b>.68**</b>	<b>.57**</b>	<b>.35**</b>	<b>.36**</b>	<b>.66**</b>	<b>.90**</b>	<b>.84**</b>	1																											
Fe	<b>.66**</b>	<b>.83**</b>	<b>.72**</b>	<b>.85**</b>	<b>.69**</b>	<b>.34**</b>	<b>.55**</b>	<b>.49**</b>	<b>.88**</b>	<b>.85**</b>	<b>.77**</b>	1																										
K	<b>.77**</b>	<b>.55**</b>	<b>.64**</b>	<b>.42**</b>	<b>.48**</b>	<b>.65**</b>	<b>.45**</b>	<b>.80**</b>	<b>.59**</b>	<b>.52**</b>	<b>.63**</b>	<b>.48**</b>	1																									
Li	<b>.74**</b>	<b>.89**</b>	<b>.83**</b>	<b>.51**</b>	<b>.67**</b>	<b>.20**</b>	<b>.35**</b>	<b>.50**</b>	<b>.81**</b>	<b>.73**</b>	<b>.82**</b>	<b>.70**</b>	<b>.56**</b>	1																								
Mg	<b>.77**</b>	<b>.66**</b>	<b>.75**</b>	<b>.53**</b>	<b>.61**</b>	<b>.75**</b>	<b>.70**</b>	<b>.74**</b>	<b>.72**</b>	<b>.62**</b>	<b>.72**</b>	<b>.65**</b>	<b>.78**</b>	<b>.70**</b>	1																							
Mn	<b>.72**</b>	<b>.54**</b>	<b>.51**</b>	<b>.43**</b>	<b>.73**</b>	<b>.57**</b>	<b>.64**</b>	<b>.75**</b>	<b>.57**</b>	<b>.43**</b>	<b>.51**</b>	<b>.58**</b>	<b>.72**</b>	<b>.56**</b>	<b>.73**</b>	1																						
Mo	<b>.78**</b>	<b>.79**</b>	<b>.97**</b>	<b>.47**</b>	<b>.39**</b>	<b>.31**</b>	<b>.46**</b>	<b>.55**</b>	<b>.84**</b>	<b>.70**</b>	<b>.89**</b>	<b>.65**</b>	<b>.59**</b>	<b>.77**</b>	<b>.72**</b>	<b>.43**</b>	1																					
N	<b>.55**</b>	<b>.46**</b>	<b>.53**</b>	<b>.64**</b>	<b>.41**</b>	<b>.75**</b>	<b>.70**</b>	<b>.59**</b>	<b>.59**</b>	<b>.55**</b>	<b>.50**</b>	<b>.63**</b>	<b>.53**</b>	<b>.30**</b>	<b>.66**</b>	<b>.49**</b>	<b>.50**</b>	1																				
Na	<b>.48**</b>	<b>.25**</b>	<b>.40**</b>	<b>.25**</b>	<b>.33**</b>	<b>.83**</b>	<b>.62**</b>	<b>.61**</b>	<b>.32**</b>	<b>.26**</b>	<b>.35**</b>	<b>.29**</b>	<b>.76**</b>	<b>.26**</b>	<b>.76**</b>	<b>.55**</b>	<b>.39**</b>	<b>.61**</b>	1																			
Ni	<b>.84**</b>	<b>.91**</b>	<b>.92**</b>	<b>.72**</b>	<b>.57**</b>	<b>.36**</b>	<b>.44**</b>	<b>.62**</b>	<b>.95**</b>	<b>.91**</b>	<b>.94**</b>	<b>.83**</b>	<b>.67**</b>	<b>.84**</b>	<b>.78**</b>	<b>.55**</b>	<b>.89**</b>	<b>.58**</b>	<b>.37**</b>	1																		
P	<b>.43**</b>	<b>.46**</b>	<b>.29**</b>	<b>.69**</b>	<b>.53**</b>	<b>.49**</b>	<b>.51**</b>	<b>.50**</b>	<b>.42**</b>	<b>.55**</b>	<b>.34**</b>	<b>.60**</b>	<b>.41**</b>	<b>.20**</b>	<b>.71**</b>	<b>.40**</b>	<b>.41**</b>	<b>.1</b>																				
Pb	<b>.48**</b>	<b>.21**</b>	<b>.23**</b>	<b>.62**</b>	<b>.62**</b>	<b>.33**</b>	<b>.76**</b>					<b>.58**</b>				<b>.43**</b>	<b>.46**</b>																					
Rb	<b>.89**</b>	<b>.81**</b>	<b>.88**</b>	<b>.54**</b>	<b>.57**</b>	<b>.50**</b>	<b>.41**</b>	<b>.77**</b>	<b>.81**</b>	<b>.73**</b>	<b>.87**</b>	<b>.66**</b>	<b>.89**</b>	<b>.85**</b>	<b>.84**</b>	<b>.66**</b>	<b>.83**</b>	<b>.50**</b>	<b>.58**</b>	<b>.89**</b>	<b>.34**</b>	<b>.38**</b>	1															
S	<b>.74**</b>	<b>.70**</b>	<b>.83**</b>	<b>.57**</b>	<b>.38**</b>	<b>.44**</b>	<b>.54**</b>	<b>.62**</b>	<b>.83**</b>	<b>.71**</b>	<b>.81**</b>	<b>.66**</b>	<b>.62**</b>	<b>.64**</b>	<b>.72**</b>	<b>.44**</b>	<b>.85**</b>	<b>.62**</b>	<b>.45**</b>	<b>.85**</b>	<b>.29**</b>	<b>.20**</b>	<b>.77**</b>	1														
Sb	<b>.47**</b>	<b>.22**</b>	<b>.24**</b>	<b>.63**</b>	<b>.33**</b>	<b>.76**</b>						<b>.56**</b>			<b>.37**</b>	<b>.50**</b>		<b>.43**</b>	<b>.45**</b>	<b>.47**</b>	<b>.98**</b>	<b>.35**</b>	<b>.19**</b>	1														
Se	<b>.81**</b>	<b>.84**</b>	<b>.82**</b>	<b>.66**</b>	<b>.69**</b>	<b>.39**</b>	<b>.47**</b>	<b>.62**</b>	<b>.82**</b>	<b>.74**</b>	<b>.87**</b>	<b>.74**</b>	<b>.57**</b>	<b>.76**</b>	<b>.71**</b>	<b>.55**</b>	<b>.77**</b>	<b>.50**</b>	<b>.38**</b>	<b>.82**</b>	<b>.39**</b>	<b>.17**</b>	<b>.76**</b>	<b>.69**</b>	<b>.20**</b>	1												
Sr	<b>.50**</b>	<b>.49**</b>	<b>.47**</b>	<b>.62**</b>	<b>.71**</b>	<b>.59**</b>	<b>.92**</b>	<b>.49**</b>	<b>.58**</b>	<b>.48**</b>	<b>.45**</b>	<b>.68**</b>	<b>.42**</b>	<b>.39**</b>	<b>.70**</b>	<b>.66**</b>	<b>.43**</b>	<b>.72**</b>	<b>.56**</b>	<b>.50**</b>	<b>.60**</b>	<b>.28**</b>	<b>.42**</b>	<b>.52**</b>	<b>.28**</b>	<b>.56**</b>	1											
Th	<b>.70**</b>	<b>.91**</b>	<b>.72**</b>	<b>.78**</b>	<b>.18**</b>	<b>.39**</b>	<b>.46**</b>	<b>.82**</b>	<b>.85**</b>	<b>.84**</b>	<b>.79**</b>	<b>.43**</b>	<b>.79**</b>	<b>.57**</b>	<b>.49**</b>	<b>.64**</b>	<b>.40**</b>	<b>.18**</b>	<b>.80**</b>	<b>.43**</b>	<b>.67**</b>	<b>.59**</b>	<b>.83**</b>	<b>.52**</b>	1													
Ti	<b>.85**</b>	<b>.95**</b>	<b>.94**</b>	<b>.63**</b>	<b>.60**</b>	<b>.28**</b>	<b>.36**</b>	<b>.59**</b>	<b>.91**</b>	<b>.84**</b>	<b>.96**</b>	<b>.76**</b>	<b>.62**</b>	<b>.91**</b>	<b>.72**</b>	<b>.50**</b>	<b>.91**</b>	<b>.44**</b>	<b>.31**</b>	<b>.95**</b>	<b>.29**</b>	<b>.89**</b>	<b>.81**</b>	<b>.85**</b>	<b>.42**</b>	<b>.84**</b>	1											
Tl	<b>.88**</b>	<b>.61**</b>	<b>.73**</b>	<b>.44**</b>	<b>.47**</b>	<b>.60**</b>	<b>.44**</b>	<b>.92**</b>	<b>.64**</b>	<b>.54**</b>	<b>.72**</b>	<b>.51**</b>	<b>.90**</b>	<b>.62**</b>	<b>.77**</b>	<b>.66**</b>	<b>.53**</b>	<b>.63**</b>	<b>.71**</b>	<b>.38**</b>	<b>.60**</b>	<b>.89**</b>	<b>.69**</b>	<b>.58**</b>	<b>.63**</b>	<b>.41**</b>	<b>.48**</b>	<b>.619**</b>	1									
U	<b>.78**</b>	<b>.89**</b>	<b>.84**</b>	<b>.64**</b>	<b>.66**</b>	<b>.21**</b>	<b>.39**</b>	<b>.51**</b>	<b>.83**</b>	<b>.78**</b>	<b>.90**</b>	<b>.71**</b>	<b>.51**</b>	<b>.81**</b>	<b>.63**</b>	<b>.46**</b>	<b>.81**</b>	<b>.38**</b>	<b>.25**</b>	<b>.85**</b>	<b>.27**</b>	<b>.76**</b>	<b>.72**</b>	<b>.86**</b>	<b>.46**</b>	<b>.90**</b>	<b>.92**</b>	<b>.58**</b>	1									
V	<b>.55**</b>	<b>.74**</b>	<b>.55**</b>	<b>.81**</b>	<b>.52**</b>	<b>.19**</b>	<b>.27**</b>	<b>.40**</b>	<b>.67**</b>	<b>.85**</b>	<b>.71**</b>	<b>.74**</b>	<b>.32**</b>	<b>.48**</b>	<b>.38**</b>	<b>.30**</b>	<b>.48**</b>	<b>.47**</b>	<b>.14**</b>	<b>.67**</b>	<b>.63**</b>	<b>.48**</b>	<b>.50**</b>	<b>.40**</b>	<b>.65**</b>	<b>.40**</b>	<b>.80**</b>	<b>.66**</b>	<b>.37**</b>	<b>.64**</b>	1							
Zn	<b>.89**</b>	<b>.64**</b>	<b>.81**</b>	<b>.43**</b>	<b>.41**</b>	<b>.58**</b>	<b>.37**</b>	<b>.88**</b>	<b>.68**</b>	<b>.57**</b>	<b>.78**</b>	<b>.50**</b>	<b>.87**</b>	<b>.66**</b>	<b>.78**</b>	<b>.65**</b>	<b>.76**</b>	<b>.50**</b>	<b>.58**</b>	<b>.78**</b>	<b>.31**</b>	<b>.58**</b>	<b>.93**</b>	<b>.74**</b>	<b>.57**</b>	<b>.66**</b>	<b>.33**</b>	<b>.49**</b>	<b>.76**</b>	<b>.94**</b>	<b>.62**</b>	<b>.38**</b>	1					
C:N	<b>.19**</b>	<b>.28**</b>	<b>.28**</b>	<b>.39**</b>	<b>.19**</b>	<b>.26**</b>	<b>.19**</b>	<b>.26**</b>	<b>.19**</b>	<b>.26**</b>	<b>.19**</b>	<b>.23**</b>	<b>.28**</b>	<b>.19**</b>	<b>.23**</b>	<b>.30**</b>	<b>.25**</b>	<b>.19**</b>	<b>.25**</b>	<b>.30**</b>	<b>.25**</b>	<b>.19**</b>	<b>.23**</b>	<b>.21**</b>	<b>.20**</b>	<b>.25**</b>	<b>.25**</b>	<b>.25**</b>	<b>.25**</b>	<b>.25**</b>	<b>.25**</b>	<b>.25**</b>	<b>.25**</b>	<b>.25**</b>	<b>.25**</b>	<b>.25**</b>		

\*\* Correlation is significant at the 0.01 level (2-tailed). \* Correlation is significant at the 0.05 level (2-tailed).

were approximately 10% lower compared to the large dataset results of Turunen *et al.* (2002) for undrained fens and bogs of Finland and thus it is possible that other accumulation values are underestimated accordingly since significant correlations were found between long-term C and other non-metal accumulation rates. These lower C sink values are likely linked to a slightly weaker balance between C input and decay of the studied mires during their development history since the other peat properties, such as the mean dry bulk density, C and ash concentrations were close to those obtained for other peat deposits in Finland or other boreal region (Gorham 1991, Kuhry and Vitt 1996, Vitt *et al.* 2000, Turunen *et al.* 2001, 2002, Gorham and Janssens 2005, Loisel *et al.* 2014). In this study, the median dry bulk density of 0.073 g cm<sup>-3</sup> was similar to Turunen *et al.* (2002), representing peat columns near the mean depth of different mire types in Finland. Also, the median C concentration was 51.0%, close to the mean C concentration of 52.3% from the Geological Survey of Finland (Turunen and Valpola 2020). It is notable that mire fires can slow the progress of vertical peat accumulation and result in great C losses and lower LORCA values (Kuhry 1994, Pitkänen *et al.* 1999). However, no evidence of significant C losses due to fires could be found in this study.

The results of the <sup>14</sup>C-dated peat sections show that the net C accumulation has varied largely between and within mires during the Holocene. This is natural since the mire development is regulated by internal and external factors such as climate and local conditions (Ohlson and Okland 1998, Piilo *et al.* 2020) and thus the balance between C input and decay can change considerably during the mire development history. The LORCA and other elemental sequestration rates address the median accumulation over different phases of vegetation and hydrological conditions of northern mires. The use of aerobic surface peat layers as indicators of element accumulation can be misleading because these weakly decomposed surface peat layers are still undergoing a rapid C cycle and losing elements such as C, K, N and P by aerobic decay, leaching and plant uptake (Gorham and Janssens 2005). Overall, most of the organic matter is decomposed in the acrotelm, and approximately

only 10% of the litter mass reaches the deeper, permanently water-saturated anoxic catotelm. In the deep peat layers, decomposition proceeds at perhaps 1% of the rate in the acrotelm (Clymo *et al.* 1998, Frolking *et al.* 2002). Thus, the catotelm is the only real layer of long-term element accumulation.

Overall, the comparison of surface and deeper peat layers is complicated since the elemental enrichment ratios can vary significantly depending, for example, on mire nutrient status, pH, the redox reactions and peat decomposition processes. In the oxidized surface layer, several elements such as Fe, Mg, N and S play important roles in plant biomass production, peat decomposition and redox reactions and thus the element ratios can vary (Clymo *et al.* 1998, Moore *et al.* 2004, Hänsch and Mendel 2009, Veretennikova *et al.* 2021). In this study, the results indicate a great depletion and plant uptake of Mg and K since their accumulation rates were significantly lower in fens compared to bogs. These elements are among crucial macronutrients (e.g. Ca, Mg, N, P, K and S) which, along with micronutrients (e.g. Cu, Zn, Mn, Fe and Ni), are essential for higher plant uptake and play a critical role in metabolic processes such as photosynthesis, respiration and N assimilation (Hänsch and Mendel 2009, Maathuis 2009). In the oxic-anoxic transition zone, the mobility of several elements such as Ca, K, Mg and Zn is an additional factor to be considered (Damman *et al.* 1992, Pakarinen *et al.* 1983, Syrovetskii *et al.* 2004, Biester *et al.* 2012). In undrained mires, the depth of this transition zone depends on the hydrology and thus the redox potential of the oxic surface layer can fluctuate seasonally (Niedermeier and Robinson 2007, Kane *et al.* 2019). Also, the peat decomposition processes during the mire development history have a strong influence on several element concentrations. Elements such as N and organically bound Cl and Br are found to be linearly enriched through peat decomposition and associated mass loss (Biester *et al.* 2012). Overall, the deeper anaerobic peat layers are characterized by low temperatures, a very low hydraulic conductivity and decreased redox potential, which constrains the decomposition processes (Beckwith *et al.* 2003, Beer *et al.* 2008, Mobilian and Craft 2021).

The results of this study show that northern mires are characterized by a significant long-term accumulation of non-metals, mainly C and N. The total elemental storage of Finnish peatlands can be estimated as 5346 Tg, which includes 5080 Tg as C, 167 Tg as N and 99 Tg as other chemical elements. Despite the relatively low accumulation rates of other chemical elements, the total size of this storage is significant based on the long-term peat accumulation and elemental retention. In this study, the fundamental differences between fens and bogs are reflected not only in significant differences in elemental concentrations of peat but also in accumulation rates. Despite the significantly lower C accumulation rates of fens, the accumulation rates of many other elements were of the same magnitude between fens and bogs. The most significant differences in the long-term accumulation rates were found within P, Al and several heavy metals (Cr, Fe, Ni, Th, U, V), which were significantly higher for fens compared to bogs. However, the accumulation rates of K and Mg were significantly lower in fens indicating a great depletion and plant uptake as essential macronutrients for higher plants. Overall, the long-term C and N sinks were followed by Fe, Ca, Al, S, P and Mg with median accumulation ranging between 10 and 110 mg m<sup>-2</sup> yr<sup>-1</sup>. The relatively high concentrations and accumulation rates of Al, Fe, Ca and Mg in peat are in accordance with the general abundance of these same elements in the earth. Al, Fe, Ca and Mg are the four most abundance metals in earth's crust (De Vos *et al.* 2006 and references within). In the heavy metal group, the overall retention and long-term median rate of heavy metal accumulation followed the sequence Fe > Mn > Cu > V > Zn > Cr > Ni > As > Pb > Co > Th > U > Cd > Sb, which is close to the general binding sequence order found in several studies (Aldrich and Feng 2000, De la Rosa *et al.* 2003, Tipping *et al.* 2003).

Generally, the low accumulation rates of heavy metals were expected since the studied mires are in a natural state, there is no anthropogenic land use, hydrological disturbance or major atmospheric pollution sources nearby. Although these accumulation rates were low, below 1 mg m<sup>-2</sup> yr<sup>-1</sup>, the natural ability of peat

to retain heavy metals is high due to a large specific surface and a pore volume (Brown *et al.* 2000, Jain *et al.* 2017). The sorption capacity is dependent on the peat type and pH. In weakly decomposed *Sphagnum* peat for example, the important properties of the peat material include the porous structure with high water retention capacity, low pH and nutrient content. These properties alone create a high liquid-retention capacity. Mires act as environmental filters and purifiers once they sieve and accumulate large amounts of elements within the catchment. For example, the results of Pontevedra-Pombal *et al.* (2013) demonstrate the elevated concentrations and accumulation rates of Ni, Zn, As, and Cd in peat due to prehistoric and historic anthropogenic deposition. Within heavy metals, it has also been found that increased concentrations of Ca enhanced the sorption of certain heavy metals in peat, such as Pb, Cd, Cu and Zn (Wolf *et al.* 1977). Brown (1993) found a strong correlation between the total exchangeable Ca, Mg, and Fe on the peats and their sorption capacity for heavy metals. In this study, an overall moderate positive correlation was found between Ca and heavy metal accumulation rates.

In this study, the mercury (Hg) concentrations were not investigated. Main reason for this was that the drying temperature for the archive peat samples was 105°C and the same temperature was also used for the collected new samples. It is possible that the high temperature could affect the Hg concentrations due to the possible presence of volatile Hg species. The results of Roos-Barraclough *et al.* (2002) indicate that the effects of Hg loss may remain marginal if using lower drying temperatures of 60–90°C. However, high levels of Hg have been found in surface peat layers due to anthropogenic sources (e.g. Grigal 2003, Roos-Barraclough *et al.* 2003). Hg is a complex and volatile toxic global pollutant that is widely dispersed through the atmosphere from natural sources such as volcanoes but largely from anthropogenic emissions such as coal combustion, smelting, and waste incineration to remote pristine areas (Grigal 2003). Hg sequestration in peatlands has ranged from historical rates of approximately 3 µg m<sup>-2</sup> to near-surface accumulation rates up to 90 µg m<sup>-2</sup> (Roos-Barra-

clough *et al.* 2003, Grigal 2003 and references within).

Intact mires ecosystems contribute to multiple ecosystem service goals simultaneously. Mires provide crucial C sequestration and storage, dissolved organic carbon (DOC) retention and other non-metal and metal sequestration and long-term storage. The downside of this functional interdependence is that failure to achieve one goal will likely undermine others in a negative mutually reinforcing cycle. Ongoing loss of mire area due to anthropogenic use leads to a failure to halt the net C loss of the organic soils, reduces options for climate mitigation, and the mire ecosystem integrity and connectivity thus causing further loss of ecosystems, species and genetic diversity and ecosystem service (Diaz *et al.* 2020). For example, different forms of anthropogenic land use of peatlands will generally increase the annual C and nutrient loss from peatlands. Recently published nutrient export studies indicate that forestry-drained peatlands contribute to water quality much more than previously estimated (Nieminen *et al.* 2017, 2018). The discharge of total N and P concentrations were over two times higher in 60 year old drainage areas compared to natural sites (Nieminen *et al.* 2017). Wise use of peatlands is only effective if they are based on an understanding of the processes within the catchments that underpin mire ecosystems and biodiversity and the distinct threats to them, such as drainage, logging and tillage practices (e.g. Tickner *et al.* 2020).

## Conclusions

The main conclusions of this work were: (1) A detailed analysis of 35 different chemical element concentrations showed that the geochemical characteristics of fens and bogs differ from one another, which is caused by the geographic location of the sites, variations in the mire type surface topography, hydrology, vegetation and thus the C:N ratio and stratigraphy of the peat deposits. Overall, the median concentrations of non-metals and heavy metals were significantly higher in fens compared to bogs. (2) Despite the significantly lower C accumulation rates of fens, the accumulation rates of many

other elements were of the same magnitude between fens and bogs. The most significant differences in the long-term accumulation rates were found within P, Al and several heavy metals (Cr, Fe, Ni, Th, U, V), which were significantly higher for fens compared to bogs. (3) Rates of element accumulation vary greatly between and within the mire types depending on the spatial and temporal patterns of element distribution within peat sections. (4) Functional mire hydrology is crucial for peat growth and chemical element sequestration. The results of this study demonstrate that mires contribute to multiple ecosystem service goals simultaneously, including the C sequestration and storage but also other long-term element sequestration and storage including both non-metals and metals. In future studies, the knowledge of mires providing present day element sequestration can be improved by measuring the water chemistry of the peatland catchments, where both elemental inputs and outputs are measured and compared to actual accumulation rates found in peat layers. Also, more comprehensive spatial research would reveal a better picture of the overall behavior of major, minor and trace elements related to the hydrology within large mire complex types.

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