

Water chemistry gradient in a degraded bog area

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Abstract Surface and ground water was sampled in a degraded bog area 36 times during 1993–2003 at Five representative points: point E (natural area with *Sphagnum* as the main vegetal cover), point W (boundary between the natural and degraded areas), point W' (area installed with vinyl sheeting), point WW (area where *Sasa* thrives), and point NC (area with naturally formed ditches). Analysis of variance (ANOVA) was conducted for parameters measured in surface water and ground water at 0.5, 1.0, 1.5, and 2.0 m depths. "Sampling point" (i.e. locations along the degradation gradient) accounted for most of the variation in surface and ground water chemistry. It accounted for 30–80% of the total variation in pH, electrical conductivity, ammonia, dissolved nitrogen, major cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), alkalinity and dissolved organic carbon. "Year" accounted for more variation in nitrate, nitrite, chloride, and sulfate than the sampling point did, but the variation in dissolved reactive phosphorus and dissolved phosphorus concentrations was not based on any of the calculated variables.

Keywords Bog; land-use change; plant diversity; water chemistry; water level

Introduction

Water chemistry is one of the most important aspects of wetland ecosystems due to its strong correlation with vegetation types (Vitt *et al.*, 1995; Hotes *et al.*, 2001) and its important role in maintaining the original diversity of wetland plant species. This role is more pronounced in bogs, which are rain-fed peaty wetlands. Local species thrive under a bog's acidic, nutrient-poor conditions and are highly sensitive to any changes in the chemical conditions at the mire surface (Bragg and Tallis, 2001). However, adjoining land-use changes such as drainage development for agriculture have great impact on its hydrology and hydrochemistry. Sarobetsu Mire is a case in point. Such changes have been occurring on the western side of the mire, where its ecosystem is gradually losing its natural state due to the development of agricultural land. This has led to invasion by the non-native species of dwarf bamboo (*Sasa palmata*) that prefer dry conditions (Inoue *et al.*, 1992) in place of the native *Sphagnum* spp. This paper addresses the changes in water chemistry in this degraded bog that have resulted from human disturbances in the surrounding areas and discusses the mechanisms behind the observed degradation.

Material and methods

Site description

Sarobetsu Mire, a coastal bog in northern Hokkaido, measures 23,000 ha. The peat thickness ranges from 5 to 7 m. Most of the surface is less than 10 m a.s.l., the figure being 6 m at the central mire area. The mire is topographically very flat, with a gentle slope of about 1/3,000 toward the Sarobetsu River. The vegetation of the bog is characterized by moss cover of *Sphagnum papillosum*, *Sphagnum riparium*, and *Drepanocladus exannulatus*. The vegetation in the shrub layer is predominantly *Rubus chamaemorus*,

doi: 10.2166/wst.2006.039

Scirpus wichurae, *Drosera anglica*, *Hemerocallis middendorffii* and *Myrica gale*. Sedges of *Phragmites communis* and *Carex lasiocarpa* var. *occultans* are also present. Agricultural development in Sarobetsu Mire started in anti-hunger projects after World War II. At first, immigrant farmers gave up their attempts to cultivate the land, due to frequent flooding. During 1961–1969, the Hokkaido Development Bureau constructed a main shortcut channel to prevent flooding by lowering the water level. This construction succeeded in changing the hydrological conditions of the area and increased the productivity of the farmland. However, the emergence of invasive *Sasa* spp. endangered the unique habitat preserved in the raised bog. This threat brought attention to the importance of conserving the remaining wetland. In 1974, 7,000 ha of this area were designated as Rishiri Rebun Sarobetsu National Park, including the study area.

Sampling points and field methods

To examine the broadest possible range of mire degradation, five sampling points (Figure 1: E, W, W', WW and NC) were chosen. Point E is on the eastern side of the mire, where the water level is still high and the natural bog vegetation is preserved. The ground surface is covered by *Sphagnum nemoreum* Scop. and *S. papillosum* Lindb. Point W, approximately 180 m west of point E, represents the *Sasa* front, i.e. the boundary between the natural and degraded areas. The ground cover is predominantly *Sphagnum*, as well as *Oxycoccus quadripetalus*, and *Carex middendorffii*. Point W' is 150 m west of point W. This is where 0.3-mm-thick and 1.3-m-width vinyl sheeting was installed in 1991 to raise the water level and re-establish the bog vegetation. The leaf area index (LAI) of *Sasa* in this area is 0.6, slightly higher than at point W, where the LAI is 0.5. Point WW is the area with a high distribution of *Sasa*: the LAI value is 1.8, the highest among all sampling points. The only natural plant observed on the ground surface is *Ilex crenata* var. *paludosa*. The water level is also very low, and surface water is not present. Point NC is the area where a naturally formed gully system (natural channel) drains from the mire into the Sarobetsu River. The *Sasa* distribution is also high here, and the LAI value is 1.3, with no *Sphagnum* moss or other bog vegetation present.

Water samples were collected during 1993–2003. Using a polyvinyl jug that was rinsed before each sampling, surface water samples were collected directly from 30-cm-diameter PVC pipes that had been installed for the experiment. Groundwater was collected from 7.5-cm-diameter PVC pipes by suction after initially purging the water at the start of each sampling, to obtain fresh water samples. Each point had four pipes, and

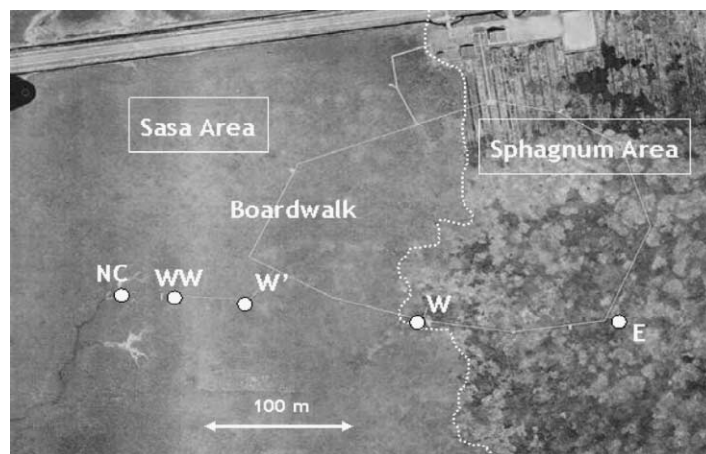


Figure 1 Sampling points (aerial view)

each pipe had 5.0-mm-diameter holes punched around the circumference at various depths relative to the mire surface: 0.5, 1.0, 1.5 or 2.0 m. Between sampling periods the PVC pipes were capped to avoid contamination. The water levels at points E, W, W' and WW were monitored bi-hourly by water level logger during 1993–1997 and during November 2002 –November 2003.

Analytical and statistical methods

Water samples were chilled immediately to 5 °C after sampling to minimize microbial reactions. Within 2 days, samples were filtrated through a 0.45- μm membrane filter. Chemical analyses were conducted according to analytical methods recommended in [Water Analysis \(2000\)](#). The following were analyzed: pH, electrical conductivity (EC), alkalinity 4.3 Bx (50 ml of each sample was titrated with 0.02 mol l⁻¹ sulphuric acid, with pH = 4.3 as the endpoint), dissolved organic carbon (DOC) measured by combustion-infrared spectrometric method (Shimadzu TOC-5000), and major inorganic ions (Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻) measured by ion chromatography with ECD (Hewlett-Packard IC-7000RP). Phosphorus content was measured by spectrophotometry (measured in the form of molybdenum blue) after persulfate digestion, where ammonia (NH₄⁺-N) was determined by spectrophotometry (phenate method), nitrite (NO₂⁻-N) was determined by spectrophotometry (Griss reagent), nitrate (NO₃⁻-N) was measured by ion chromatography with ECD, and dissolved nitrogen (DN) was measured by spectrophotometry (phenol method) after persulfate digestion. For data analysis, precipitation data are the average daily precipitation. For better comparison of meteorological data, data for July through November were calculated together with data from other months as well as separately, because they were available for each monitored year. Three statistics of water level were used for the analysis; mean water level (WL_{mean}), water level range (WL_{mm}) and water level standard deviation (WL_{sd}). WL_{sd} and WL_{mm} were used to indicate the fluctuation of water levels. Surface water and groundwater chemical data were compared in terms of sampling point, year, month and depth. Surface water samples were compared in terms of sampling point, year and month. Analyses of variance (ANOVA) were performed using the Data Analysis add-in of Microsoft Excel. Results are reported in percent of the sum of variance components for all factors.

Results and discussion

Variation in water level

The average annual precipitation in this area is 1,049 mm ([Takahashi, 1988](#)), which corresponds to 2.87 mm average daily precipitation. Generally, the precipitation was higher during spring to autumn, and in 1993 and 2003 it was slightly less than in other years ([Table 1](#)). However, the water levels during the period from May through November were slightly lower than during the entire year, as can be seen from the 2003 data, especially at point E. This was because the winter snowfall did not flow directly out from the mire, but remained in the mire and kept the water levels high. According to [Takahashi \(1988\)](#), the average depth of snow cover during winter (January and February) is about 1 m. Water levels generally responded quickly to precipitation events over 10 mm and when periods of little or no precipitation exceeded two weeks, water levels

Table 1 Average daily precipitation (mm)

	1993	1994	1995	1996	1997	2003
July–November	2.16	3.09	3.63	3.55	3.90	2.67
Entire year	n.a.	2.66	3.89	2.66	3.20	n.a.

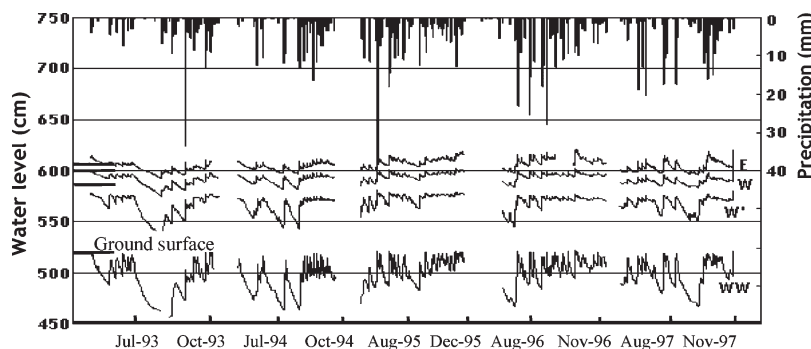
Table 2 Summary of water level variations (in cm)

	E	W	W'	WW
Ground surface level	606.6	600.9	586.7	519.0
WL _{mean} (May–Nov 2003)	−4.4	−8.4	−18.5	−21.5
WL _{mm} (May–Nov 2003)	18.3	16.5	41.8	43.9
WL _{sd} (May–Nov 2003)	4.4	3.4	11.0	12.5
WL _{mean} (1993–1997)	−1.3	−9.0	−18.9	−21.5
WL _{mm} (1993–1997)	28.1	27.7	44.0	65.0
WL _{sd} (1993–1997)	5.1	4.8	8.8	14.3
WL _{mean} (1993–1997 & 2003)	−1.4	−8.9	−17.7	−21.2
WL _{mm} (1993–1997 & 2003)	28.1	27.7	47.0	65.0
WL _{sd} (1993–1997 & 2003)	5.5	4.6	9.2	13.7

fell noticeably (Figure 2). The responses of water levels at the four monitored points to each precipitation event showed greater instability in the westward direction. WL_{sd} and WL_{mm} were smaller at points E and W than at points W' and WW. The maximum difference between the highest and the lowest water level was 65 cm at point WW, and only 28 cm at points E and W. The small WL_{sd} and WL_{mm} indicate that the water level in the eastern part of the mire is more stable and has less fluctuation than that of the western part. The variable WL_{mean} shows a similar trend: it decreased gradually at point W', and the lowest value was at point WW, at 21.5 cm in depth. The patterns of WL_{sd}, WL_{mm} and WL_{mean} for these four sampling points show a degradation gradient toward the western part of the mire. This result shows that the soil in the degraded area has poor water retentivity. These observations are consistent with the fact that *Sphagnum*, which usually acts as a huge sponge in a natural bog, is absent. The low water retentivity of the soil is considered to be the result of the low water level, which exposes the bare peat after the loss of *Sphagnum* cover.

Water chemistry gradient

Water chemical analysis is summarized in Figure 3. In general, there is an ombrotrophic-minerotrophic gradient as one moves from east to west. Moreover, water chemistry characteristics of point NC and, to a lesser extent, point WW are noticeably different from those of the other sampling points. In terms of water temperature, there is no evidence of different patterns from surface to 2 m depth between all sampling points. The insulating ability of a natural bog ecosystem (Vitt *et al.*, 1995) is not evident. At all sampling points the temperature at the surface is higher than that of the groundwater, gradually decreasing in the depth direction. The surface water pH of all five sampling

**Figure 2** Water level fluctuations (cm) and precipitation data (mm) for the 1993–1997 sampling period.

Due to space limitations, water level data for 2003 are not shown in the graph. Precipitation and water level data for 1993–2003 is summarized in Tables 1 and 2

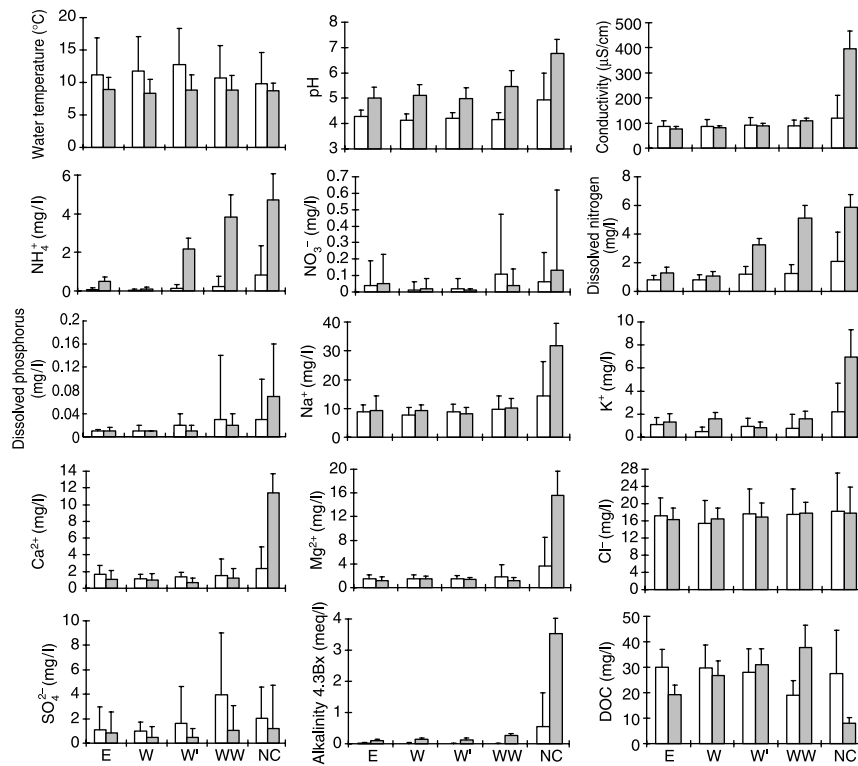


Figure 3 Chemical properties of water during the 1993–2003 sampling period. Means are given, with their standard deviations. Only data for surface water (□) and groundwater at 2-m depth (■) are presented and summarized, in light of the relatively consistent pattern of the chemical properties with respect to depth (Tables 3 and 4)

Table 3 Analysis of variance for the parameters measured in surface water and groundwater at 0.5, 1.0, 1.5, and 2.0 m depth. Significance level * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$; ns, not significant $P > 0.05$. "Point" indicates sampling point, and it also applies to point-depth and point-year

Variable	% Total variation						
	Point	Year	Point-depth	Depth	Month	Point-year	Error
Water temperature	0.4ns	11.2**	10.4ns	7.7ns	71.6***	2.3ns	4.4
pH	52.0***	7.6***	18.1***	18.1***	2.6*	2.5***	9.1
EC	68.8***	9.2***	11.7***	2.0*	4.1**	1.3***	2.8
NH ₄ ⁺ -N	46.9***	5.3***	16.3***	18.3***	1.7ns	-0.9***	12.4
NO ₂ ⁻ -N	2.9**	30.4***	1.1ns	0.0ns	5.5***	18.6***	41.4
NO ₃ ⁻ -N	2.2*	69.0***	1.2ns	0.2ns	11.4***	7.0***	9.2
DN	51.3***	3.3*	14.2***	17.7***	1.9ns	-0.2***	11.8
DRP	16.1***	5.6***	6.0***	1.1ns	1.9ns	13.1***	56.3
DP	13.0***	3.2*	2.9***	0.3ns	1.1ns	11.4***	68.1
Na ⁺	60.3***	15.2***	7.3***	1.3ns	3.3*	-5.3***	17.9
K ⁺	53.5***	9.5***	8.1***	2.8**	8.2***	0.0***	17.9
Ca ²⁺	64.7***	11.7***	11.9***	1.0ns	3.7**	-1.1***	8.1
Mg ²⁺	66.8***	8.6***	11.1***	1.3ns	2.9*	-0.9***	10.1
Cl ⁻	2.8**	54.3***	1.5ns	1.1ns	15.4***	11.7***	13.0
SO ₄ ²⁻	3.5***	44.1***	4.2***	5.1***	8.1***	3.0***	32.0
4.3 Bx	76.1***	6.8***	9.4***	2.9**	2.7*	-0.5***	2.6
DOC	31.7***	7.4***	32.2***	2.2*	4.5**	2.4***	19.6

Table 4 Analysis of variance for the parameters measured in surface water

Variable	% Total variation				
	Point	Year	Point-year	Month	Error
Water temperature	3.9ns	–	–	92.8***	3.3
pH	26.3***	11.0ns	26.4***	4.8ns	31.5
EC	6.5ns	23.0***	50.6***	14.7*	5.2
NH ₄ ⁺ -N	15.6***	8.7ns	43.1***	4.3ns	28.2
NO ₂ ⁻ -N	2.8ns	34.3***	37.3***	6.2ns	19.5
NO ₃ ⁻ -N	3.5ns	65.1***	–	21.0**	10.5
DN	20.4***	11.3ns	28.3***	5.0ns	35.0
DRP	5.2ns	4.9ns	77.0***	3.2ns	9.8
DP	3.9ns	9.1ns	31.6ns	3.5ns	52.0
Na ⁺	12.9**	38.1***	36.2ns	12.8***	0.0
K ⁺	17.6***	12.1*	41.9***	10.9ns	17.4
Ca ²⁺	5.8ns	32.5***	50.2***	–	11.4
Mg ²⁺	11.4*	26.4***	58.6***	–	3.6
Cl ⁻	2.5ns	61.1***	–	32.4***	3.9
SO ₄ ²⁻	12.8**	36.1***	9.2**	10.3ns	31.5
4.3 Bx	18.0***	14.0ns	65.1***	3.7ns	0.0
DOC	17.1**	14.88ns	29.5**	20.9**	17.7

Note: For some parameters (water temperature, nitrate, calcium, magnesium, and chloride) ANOVA were not performed for all variables, due to their close correlations.

points studied was still low (pH 4.13 to 4.28), but it was slightly higher at point NC (pH 4.94). The surface water pH at point NC showed greater variation (SD = 1.05) than those at the other points, perhaps due to precipitation events, since during the periods of little or no precipitation, pH rose to 7 (data not shown). This shows that the bog is no longer a natural bog. The pH at 2-m depth was higher than at the surface, and it gradually increased from point E toward point NC. Sampling point accounts for 52% of the variation in the surface water and groundwater but only 26.3% of the variation in surface water alone. Alkalinity and conductivity showed trends similar to those of pH, with point NC having higher values for these at the surface than any other point, and alkalinity and EC gradually increased from point E toward point NC for samples at the 2-m depth.

The high alkalinity at point NC may be a result of the high pH value, because if the pH increases beyond 6, then carbonic acid dissociates into hydrogen ions (H⁺) and bicarbonate ions (HCO₃⁻). Therefore the carbonate–bicarbonate buffering system typical of surface waters replaces the humic substances' contribution to the buffering system at pH values less than 5 (Gorham *et al.*, 1984).

Nitrite concentrations were usually below the detection limit, while the highest values for nitrate concentration were at point WW at the surface (0.11 mg/l) and at point NC at the 2-m depth (0.13 mg/l). Sampling point alone accounts for less than 3% of the total variation in nitrite and nitrate in surface water and at all sampling depths. For nitrate, the variation for yearly difference is more evident than that for other variations, accounting for 65% ($P < 0.001$) of the variation in surface water and 69% ($P < 0.001$) of the variation for all sampling depths, showing that there was instability in nitrate concentration during the sampling period (1993–2003). Monthly variation was slightly pronounced at the surface, accounting for 21% of total variation. DRP concentrations were usually below the detection limit, and the concentration of other nutrient forms (NH₄⁺-N, DN, and DP) both at the surface and at the 2-m depth showed consistent increases according to degradation gradient, from point E toward point NC. NH₄⁺-N and DN concentrations started to increase at point W' (2.18 mg/l for NH₄⁺-N and 3.24 mg/l for DN at 2-m depth), and DP concentration showed noticeable increase at point WW, especially at the surface

with the value of 0.03 mg/l, similar to that at point NC. Sampling point accounts for 47% and 51% of the variation in NH_4^+ -N and DN concentrations, respectively, at all sampling depths. Moving water at the natural channel and unstable water levels of point WW seemed to be responsible for the high nutrient content, since moving water is able to supply much more nutrient by desorption from peat soil, even if the concentrations at any one time are fairly low. In terms of phosphorus content, however, the degradation gradient alone accounts for 16% of DRP concentration and 13% of DP concentration. The errors for these two parameters are 56% and 68%, perhaps due to their low concentrations, which may make the parameters prone to quick response to each environmental event and to measurement error caused by disturbed samples.

In terms of major cation contents, Na^+ was the dominant ion and K^+ had the lowest content of any ion, which is similar to the case of other coastal mires in Hokkaido (Hotes *et al.*, 2001). The cation concentrations are consistent with the EC values, with only point NC showing great differences from the other sampling points. Both surface water and groundwater at 2-m depth showed considerably higher concentrations at point NC than at other points, and the concentration at 2 m depth was higher than that at the surface. There were slight differences in major cation contents among the other four sampling points, either in surface water or in groundwater, but these differences did not show a degradation gradient toward the western side. Ca^{2+} and Mg^{2+} showed a steady concentration decrease with depth, which was also seen at 0.5, 1.0, and 1.5 m depths, although there were slight exceptions at point W (data not presented). In addition to being caused by evaporative effects, the higher concentration at the surface was probably caused by cation exchanges with the peat, since high Na^+ input from rain led to high concentrations of other cations, including Ca^{2+} and Mg^{2+} . The four points (E to WW) showed a tendency for Ca^{2+} and Mg^{2+} concentrations to decrease with depth and for Na^+ and K^+ concentrations to increase with depth. This shows that the cation exchange capacity of the peat at the surface is higher than that below the surface, which is also consistent with the fact that the surface water has lower pH than the ground, since less humification of organic content at lower pH enables the soil to have a higher capacity to absorb exchangeable ions. In contrast, point NC, which had higher pH than other points, showed less cation exchangeability, and the ions contained in the water there were not much reduced. The source of variations in surface and ground water for all major cations was mostly sampling point, which accounted for between 54% (for K^+) and 67% (for Mg^{2+}) of variation. However, point-year interaction was the most important source for almost all major cation variations in surface water, except for Na^+ , and the difference between years was more easily seen than for other variations.

DOC concentration showed a degradation gradient for both surface water and groundwater. Surface DOC concentration decreased from point E toward point WW, whereas at 2-m depth the DOC concentration increased in the westward direction. Point NC showed irregularity in DOC concentration at both depths, with highest DOC concentration (27.52 mg/l) being at the surface and the lowest (7.94 mg/l) being at the 2-m depth. That irregularity at point NC may be attributable to the presence of gullies that provide and transport particulate organic matter from eroded peat soil. This also explains the high variation in DOC concentration at the surface ($\text{SD} = 16.91$), since the leaching of eroded peat soils depends on each precipitation event. The low DOC concentration at the 2-m depth suggests that there was high microbial activity, which converted the organic matter into inorganic form; this conversion also occurred to nutrients. Point-depth interaction accounted for 32.2% of the variation in surface and ground water DOC concentrations, and sampling point accounted for 31.7% of such variation. As for Cl^- content, its overall range within the mire is small, ranging from 15.48 mg/l to 18.28 mg/l. There is no

obvious difference in Cl^- concentration between sampling points and depth, showing that the main source of water is from precipitation and that the mire has not experienced seawater inundation. Sulfate concentration showed significant difference among the sampling points. The concentrations at point WW and NC were higher than at other points, all of the concentrations having a pattern in which the concentration decreased with depth. However, difference between years was the most significant source for variation in Cl^- and in SO_4^{2-} , accounting for 61% and 36% of the variation for surface water and 54% and 44% of the variation for all sampling depths.

Mire degradation and water chemistry changes

In the degraded area (points WW and NC) the soil has poor water retentivity. Much of this may be due to the low levels of organic matter present. Organic matter from dead plants creates protective mulch that reduces soil erosion and water evaporation and acts as a sponge to absorb water in the soil. Many authors have shown that hydrologic parameters control the chemical and biotic processes in wetland ecosystems, and that those parameters may be the most important factors in wetland ecosystem development, regulating natural processes. A stable and high water level will keep the soil from drying (as seen at points E and W), and when soil and peat layer becomes dry, it is prone to erosion and decomposition. Decomposition of peat soil affects the surface water and groundwater chemistry, particularly after leaching when the decomposed soil is washed by rainwater, which yields a high concentration of DOC (such as that observed at point NC, at the surface). The decline of water level in the mire will make inflow from surrounding areas possible. This inflow can transport mineral-rich soil and sediment, which can cause changes in water chemistry. According to Bragg and Tallis (2001), in response to adjoining land-use changes, many species of typical blanket mire vegetation (including *Sphagnum*) had declined substantially in abundance or had become extinct during a 28-year period. Once bare peat is exposed, it is prone to the adverse affects of natural weather events, which is followed by erosion of the peat. After bare peat is exposed, the next degradation stage will occur, ranging from the development of gully systems to the large-scale removal of the peat blanket. Considering the fact that development in the land surrounding Sarobetsu Mire started in 1961, about 40 years ago, it is considered that the gully systems found in the vicinity of point NC have resulted from degradation. Without concerted efforts to conserve the mire, the gullies will spread. Gully systems result from fundamental changes in the hydrology of the peat mass, where the lateral transport of excess water towards the peat margins through the permeable acrotelm is replaced, in part or in whole, by transport over the bog surface. This change in flow direction may lead to the changes in water chemistry, since the surface flow at the eroded peat surface will transport nutrients and minerals that are incorporated into the suspended sediments.

Conclusions

- Land-use changes in surrounding areas are affecting the hydrological regime of Sarobetsu Mire. The lowered water level is causing hydrochemistry changes and is allowing nutrient and mineral loading from adjacent agricultural areas. Groundwater chemistry at all sampling points shows the influence of mineral-rich groundwater inflow through the mire basin, which yields an ombrotrophic-minerotrophic gradient seen in degradation on the western side of the mire.
- ANOVA analysis showed that the water chemistry parameters which most closely correlate to the degradation gradient are pH, EC, $\text{NH}_4^+\text{-N}$, DN, Na^+ , K^+ , Ca^{2+} , Mg^{2+} , 4.3 Bx, and DOC concentrations, and sampling points accounted for 30–80% of total

variation. NO_3^- -N, NO_2^- -N, Cl^- , and SO_4^{2-} were more closely related to year than to other variation, and the variation in DRP and DP concentrations was not based on any of the calculated variables.

- The restoration of water chemistry for the conservation of the mire needs to address all aspects that govern the hydrological regime, such as topographical and morphological mire surface.

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