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Reed die-back related to increased sulfide concentration in a coastal mire in eastern Hokkaido, Japan

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Abstract

A drastic decline of *Phragmites australis* was observed along the middle reaches of Ichibangawa River in Kiritappu Mire, eastern Hokkaido, Japan, during the last 50 years. In an area of ∼30 ha, reed-sedge vegetation and alder forest have been replaced by bare soil and patches of salt marsh vegetation. A gradual increase in frequency of flooding by brackish water probably was the ultimate cause of the vegetation change. We measured redox potentials and oxygen and sulfide concentrations in soil profiles using needle electrodes. Measurements were carried out in areas where reed has disappeared and in sites where reed stands were still healthy. The concentration of selected ions in the surface water was also measured at various sites. Surface water in low-lying areas was clearly influenced by seawater. Very high sulfide concentrations were measured in bare peat sites (more than 600 μmol l^{-1}), which exceeded *P. australis* tolerance 2–3 times. In a healthy reed zone adjacent to an area with poor fen vegetation, sulfide concentration in the rooting zone of *Phragmites* was also high (300–400 μmol l^{-1}), particularly during the night. The fact that *Phragmites* in this zone was still healthy indicates that sulfide did not reach toxic levels in the direct vicinity of the roots. Sulfide that is produced in this area is probably fixed by iron, which is supplied through a continuous discharge of iron-rich groundwater. An increase in frequency of flooding by brackish water could be related to ongoing subsidence of this part of the Pacific coast which is located at the Kuril subduction zone. Sea level rise could also contribute to a stronger inflow of seawater into the mire system.

Introduction

Reed die-back of lake side *Phragmites australis* stands has been reported from many European countries (Boar et al. 1989; Ostendorp 1989; Ostendorp et al. 1995; Van der Putten 1997). In Central and Eastern Europe in particular, *P. australis* stands have markedly decreased along lakes and rivers (Sukopp and Markstein 1989).

Several authors relate this to a combination of increased availability in nutrients (eutrophication) and changes in the water level regime (Rea 1996; Armstrong et al. 1996a, b). Eutrophication of surface water leads to increased levels of sulfate and nitrogen and to the development of algal blooms. Combined with the more stable water regime of lakes in agricultural areas (lower water levels in winter, higher levels in summer) this has often led

to anoxic conditions in the root zone of *P. australis* stands. *Phragmites* is able to protect itself to some extent by the diffusion of oxygen from its roots, which oxidizes the immediate area around the roots. Under anoxic conditions, phytotoxins such as sulfide (Havill et al. 1985; Fürtig et al. 1996; Lamers et al. 1998) and organic acids (Armstrong et al. 1996a; Armstrong and Armstrong 2001) can reach critical levels. Sulfide toxicity harms mostly the root system of the *Phragmites* plants (Fogli et al. 2002). Phytotoxins can lead to increased bud and root death in *P. australis* (Armstrong et al. 1996b), which makes *Phragmites* stands more vulnerable to catastrophic events, such as extreme wave action during storms (Ostendorp et al. 1995).

Phragmites australis can survive in regularly flooded mires, and even in brackish salt marshes, where the species does not seem to be negatively affected by anaerobic conditions or high levels of dead organic matter (Olff et al. 1993; Güsewell and Klötzli 1998; Bart and Hartman 2000). In most groundwater fed mires, large quantities of iron (Fe) are present that can bind sulfide as FeS, which is harmless to plants. If the iron supply is insufficient, however, this protective mechanism does not function, and sulfide accumulations can reach toxic levels (Smolders and Roelofs 1995).

We report here of a drastic decline in *P. australis* along the Ichibangawa River, a small river in the southern part of Kiritappu Mire, eastern Hokkaido, Japan. During the last 50 years, vegetation changes have occurred in an area of ~30 ha, most of which lies north of the river adjacent to a large (~3000 ha) groundwater-fed mire with some acid oligotrophic sites. The mire is similar to poor fens in the Scandinavian classification system (Hotes et al. 2001). In the Kiritappu fen area, a large part of the reed-sedge vegetation has been replaced by bare soil, part of which is permanently inundated by brackish surface water. Patches of alder (*Alnus japonica*) trees have also died. This die-back could be caused by increased anaerobic conditions in the root-zone, which could be related to land subsidence which has been reported for this part of Japan (Uda et al. 1992). Land subsidence would lead to increased inflow of seawater that is rich in sulfate. Under anaerobic conditions and in the presence of organic material, sulfate is reduced to sulfide by micro-organisms. This process is most pronounced during the night when oxygen production by algae is minimal. In order to test the hypothesis that sulfide concentrations may have reached toxic levels, we measured redox potentials and oxygen and sulfide concentrations in soil profiles using needle electrodes. The measurements were carried out in areas where reed vegetation has died and also in sites where it is still healthy.

Methods

Nomenclature

The nomenclature for phanerogams follows the list of the Japanese Environment Agency (Kankyocho 1987).

Study area

The study area is located at 145°3′00″E, 43°2′50″N in the southern part of Kiritappu Mire, near Hamanaka Town, eastern Hokkaido, Japan (Figure 1). According to the 1 : 25,000 topographical map, elevation is ~2.5 m above sea level, but preliminary ground height measurements by Inoue (unpublished data) suggest that it is probably lower, between 0 and 0.5 m. The low-lying area extends ~1400 m from east to west and ~500 m from north to south along the middle reaches of Ichibangawa River. The eastern part of the low-lying area is largely free of vegetation. Bare peat surfaces with dead roots and rhizomes of *Phragmites* and *Carex* species are widespread, and large areas are permanently flooded by brackish water. In these shallow water bodies, *Zostera nana* sometimes occurs. *Carex subspathacea* is still present in the western part of the affected fen, but bare peat surfaces or small water courses separate the patches. Dead stumps of trees and shrubs are scattered throughout the tidal marsh. Salt marsh species (e.g., *Carex subspathacea*, *Aster tripodium*, *Puccinellia kurilensis*, *Triglochin maritima*, and *Glaux maritima*) are growing around the dead tree stumps.

Analysis of aerial photographs

A series of black and white aerial photographs from the Kiritappu Mire Center that were taken in 1947, 1975, 1978, and 1990 were used to gain a first overview of how the area that was affected by
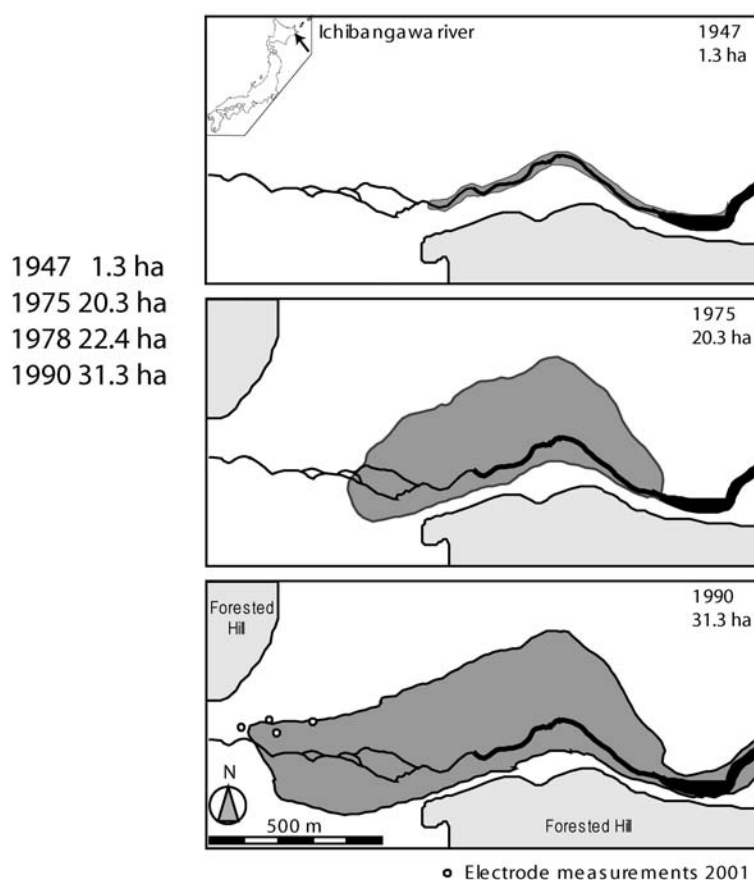
Figure 1. Increase in bare mud flats in the reed marsh south of Kiritappu mire in Eastern Hokkaido, Japan, between 1947 and 1990. The locations of the needle-electrode measurements are also indicated.

vegetation change expanded during almost 50 years. Water appeared on the photographs as dark gray to black (unless it reflected direct sunlight in which case it could appear white). Bare peat surfaces show up as dark gray, though generally in a lighter color than open water. Alder forest was medium gray, whereas mostly herbaceous mire vegetation appeared in different shades of light gray. Based on these observations, the border between living and dead vegetation was drawn. Changes in surfaces were calculated using the Geographical Information System ARCVIEW.

Water level monitoring and composition of surface water

An automatic water level recorder was installed in the Ichibangawa River on July 6, 2001. Water levels

were recorded every hour between July 6 and August 28, 2001 and the data were stored in a data logger.

In July, electrical conductivity of the surface water was measured in open water on bare mud flats using a pH/EC meter 24-D from Horiba Ltd.

On July 6, surface water samples were taken from four sites; the poor fen, the Ichibangawa River, the surviving reed stands bordering the fen, and from a ditch draining the bare mud flats. Samples were stored in PVC bottles and analyzed in the Laboratory of Plant Ecology in Groningen. Anions were measured using an autoanalyzer (Skalar Analytical), while cations were analyzed by atomic absorption spectrometry (AAS).

Micro-electrode measurements

In situ measurements of oxygen saturation, redox potential, and sulfide concentrations were carried
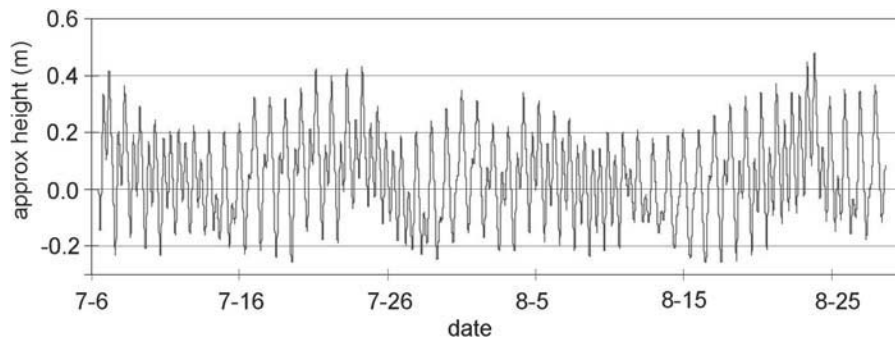
Figure 2. Water level fluctuation of the Ichibangawa River measured between July 6 and August 28, 2001.

out between July 5 and July 7, 2001. Stainless steel needle electrodes (Visscher et al. 1991; Van Gemerden 1993; Adema and Grootjans 2003) were attached to a micro-manipulator and used to measure profiles with a maximal resolution of 0.01 mm and a maximal depth of 25 cm. Vertical profile measurements were conducted on July 6 between 10:30 and 13:00 at four sites: two bare sites, a *C. subspathacea* dominated site, and a *P. australis* dominated site (Figure 1). Oxygen saturation, redox potential, and sulfide concentration were measured in duplicate with electrodes attached to the micro-manipulator. Between 0 and 10 mm, electrode tips were lowered in 0.5 mm steps; between 10 and 25 mm, in 1 mm steps; between 25 and 50, in 5 mm steps; and between 50 and 250 mm, in 10 mm steps. Temporal changes during a day/night/day period were measured in a bare patch (between 16:20 on July 5 and 10:00 on July 6) and in a site with healthy *Phragmites* plants at the margin of the affected area (between 13:20 on July 6 and 10:00 on July 7). All data were stored in a data logger.

Results

Aerial photographs

The expansion of the area affected by vegetation die-back between 1947 and 1990 is shown in Figure 1. In 1947, bare surfaces occupied ∼1.3 ha and were restricted to a belt 30–50 m wide along the river. In 1975, the bare area had increased to 20.3 ha and the border of the bare zone had shifted ∼200 m to the north and 50 m to the south. The area lost almost all of the living vegetation and appears to be permanently covered by water now, although long-term measurements of water levels are not available. Between 1975 and 1990, this trend continued, and the western border moved 150–200 m westwards. A slight expansion was also found along north, east, and south margins. A rough estimation of the present surface of bare soil indicates that the expansion between 1990 and 2001 seems to have slowed down, but die-back has not stopped.

Water level monitoring

Water levels of Ichibangawa River measured between July 6 and August 28, 2001 showed the influence of tidal cycles (Figure 2). The 12-h-cycle, as well as the 14-day-cycle shifts (caused by the lunar phase), are reflected in the data. It is noteworthy that peaks during the 12 h-cycle rhythmically went through phases in which the first and the second maximum differed strongly. The difference gradually became smaller until both daily peaks were about the same, and then the peak that was more pronounced before, gradually diminished until the cycle began again.

The amplitude of tidal fluctuations in Ichibangawa River reached up to 60 cm. According to ground height measurements, the whole area along the south–north transect was flooded up to a point 150 m north of the river at least every two weeks.

Composition of surface water

The analysis of the surface water showed that the water of the poor fen was low in dissolved minerals

Table 1. Composition of surface water from various sites in the Kiritappu Mire area.

	Bog	Reed	River	Ditch
EGV mS m^{-1}	3.8	894.0	821.0	3270.0
pH	4.9	4.5	6.2	7.1
HCO$_3^-$ µmol l^{-1}	0.0	8.0	514.0	1768.0
Fe µmol l^{-1}	19.2	536.3	14.3	14.8
K$^+$ µmol l^{-1}	1.5	1565.2	1445.4	6624.4
SO$_4^{2-}$ µmol l^{-1}	56.8	2659.1	2587.7	15416.1
Ca^{2+} µmol l^{-1}	33.9	1454.3	1530.4	6293.5
Mg^{2+} µmol l^{-1}	29.2	6508.6	6514.5	29211.8
Na$^+$ mmol l^{-1}	0.2	71.4	57.9	388.4
Cl$^-$ mmol l^{-1}	0.2	72.4	63.5	327.1

and also had a low pH (4.7; Table 1). The ditch that drained part of the mud flats showed very high values of sulfate and chloride, which were much higher than concentrations in the river. Both the river water and the mud flat were clearly influenced by sea water, since they had relatively high values of sulfate, magnesium, sodium, and chloride. Highest iron concentrations were found in the surface water of the reed zone along the fen.

Measurements of surface water electrical conductivity yielded similar results. Electrical conductivity was about 3200 mS m^{-1}, which is comparable with values measured in the drainage ditch.

Needle electrode measurements

Profile measurements showed differences in redox potential and sulfide concentration between the bare patches, the *Carex* stand, and the *Phragmites* stand (Figure 3). Oxygen saturation measurements are not shown, since they were always practically zero in all profiles, except for the top 5 mm. Sulfide measurements were available from only one electrode, since the other yielded only zero values. Sulfide concentrations were high in the bare soil sites and the *Carex* site below 150 mm. At one bare soil site, values increased from 102 µmol l^{-1} at 160-mm depth to 339 µmol l^{-1} at 190 mm depth. The other bare soil site yielded much lower values and reached values not higher than 100 µmol l^{-1}. At the *Carex* site, sulfide concentration increased below 100 mm and reached 226 µmol l^{-1} at a depth of 250 mm below the surface. At the *Phragmites* site, the sulfide concentration increased only slightly from 1 to 4 µmol l^{-1} over the whole profile. Redox potentials generally were negative and

dropped with increasing depth. The lowest values were measured at the *Carex* site where both electrodes gave similar results. At the *Phragmites* site, redox values in deeper layers were much higher than in the *Carex* site. The two bare sites gave intermediate results.

The time series measurements in a bare patch yielded reliable results only during 6:00 and 10:00 in the morning (Figure 4). During the rest of the night, the electrodes did not respond properly due to heavy rain. Sulfide concentrations were zero at 5 mm depth, but at 50 mm, values were very high and ranged between 700 and 800 µmol l^{-1}. Redox potential was also low (between -120 and -150 mV). In the *Phragmites* stand time series, only one sulfide electrode functioned properly during the night. The measurements showed that sulfide concentrations increased during the night and remained high (between 200 and 350 mV) until measurements were stopped the next day at 10:30 in the morning.

Discussion

The area in which drastic vegetation shifts have occurred since 1947 is particularly low-lying. Although elevation measurements are only approximations due to a lack of accurate benchmarks in the vicinity, it is probable that the surface is less than 0.5 m above sea level. This area can be distinguished from the adjacent higher mire area already on the 1947 aerial photograph due to its lighter color, and because patches of dark alder stands line the border between the lower and higher portions of the mire. These vegetation changes suggest that a relative increase in water level has taken place. The fact that the area affected by vegetation change has continued expanding to the present day suggests that the water level is still rising, although at a reduced rate. This leads to the question of what causes the rise. Both land subsidence and eustatic sea level rise can play a role at Kiritappu Mire. The Pacific coast of eastern Hokkaido is located at the Kuril subduction where the Pacific plate glides under the Eurasian plate. This causes horizontal as well as vertical displacement of the earth's crust. Okazaki (1986) postulates subsidence for Kiritappu Mire, and the Geographical Survey Institute published a map
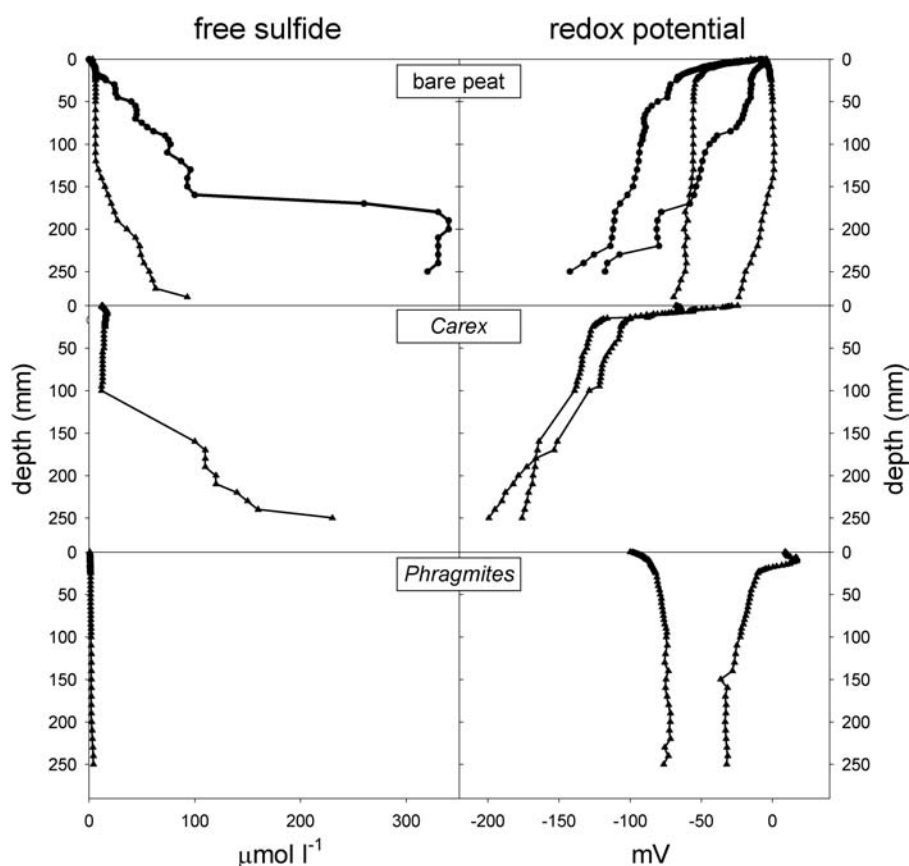
Figure 3. Free sulfide concentrations (μmol l^{-1}) and redox potentials (mV) measured in soil profiles with needle-electrodes in two sites with bare soil, one site with vegetation dominated with *C. subspathacea*, and one site dominated by *P. australis*. At each site, two different needle electrodes were used simultaneously.

indicating subsidence of about 70 cm for eastern Hokkaido over the past 100 years.

Eustatic sea level changes have greatly influenced coastal ecosystems in Hokkaido during the Holocene (Ohira et al. 1994; Sawai and Kashimura 1996). With the current tendency towards higher mean temperatures worldwide, melting of the polar ice caps is increasing, and this is expected to lead to higher sea levels. The rate of change in the northeastern part of Japan is estimated to be about 4–5 mm year^{-1} (Uda et al. 1992), which over a period of 50 years could amount to 20–25 cm. Combined with a subsidence rate of 7 mm year^{-1}, we may expect an increase in surface water level of over 50 cm from 1947 onwards.

Water level fluctuations of the Ichibangawa River are clearly influenced by tidal fluctuations. The 0.74 m amplitude is similar to that measured at

Kotoiso Bridge at the mouth of the river (Hotes et al. 2001). Electrical conductivity of surface water in the mud flats were only slightly lower than those of Pacific seawater (Saito et al. 1997), indicating that the water in the river is mostly supplied from the sea and to lesser extent from the catchment area. These findings were supported by analyses of surface water samples showing very high chloride, sodium, and sulfate values in water leaving the mud flats.

Changes in oxygen saturation, redox potential, and sulfide concentration with depth showed differences between the bare patches, the *Carex* stand, and the *Phragmites* stand. The pattern for oxygen saturation shows a thin hyper-saturated surface layer, below which oxygen is quickly depleted. Hyper-saturation is probably caused by photosynthetic activity of micro-organisms in the
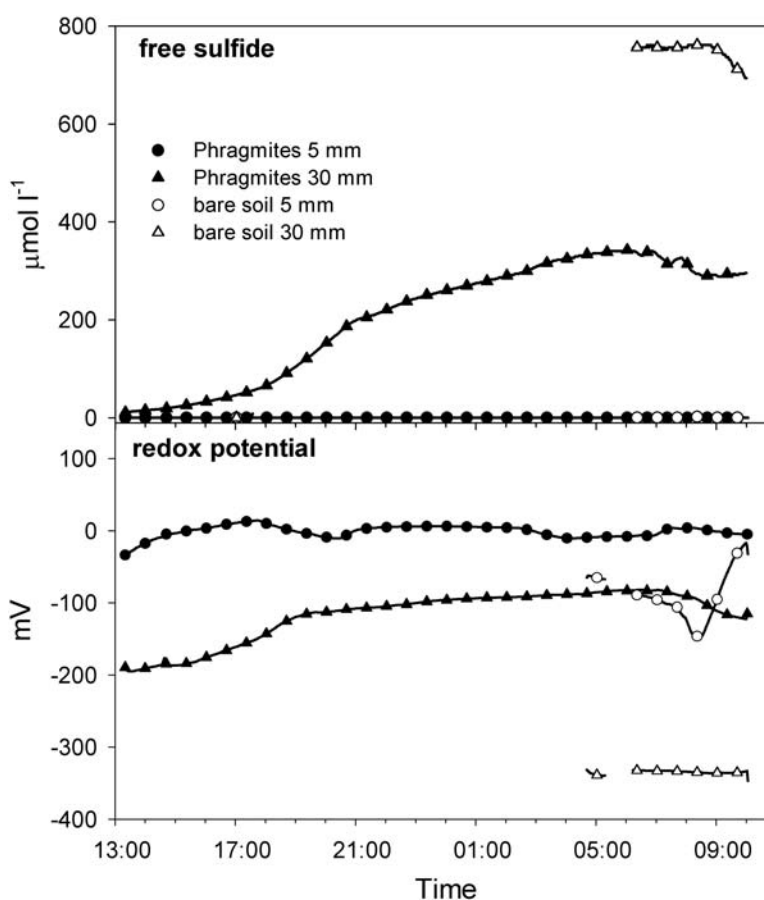
Figure 4. Free sulfide concentrations (μmol l^{-1}) and redox potentials (mV) measured in a *P. australis* site and a site with bare soil during the night and early morning at a depth of 5 cm below the surface.

top layer (Van Gemerden 1993). The lack of such an enriched layer in the *Carex* stand might indicate that such microbes were not present at the locations where the electrodes were inserted. High oxygen saturation at a soil depth of 150 mm at the *Phragmites* site perhaps was caused by oxygen diffusion from a plant root.

Redox potential results do not fully support the hypothesis that bare patches should show the lowest, *Carex* stands an intermediate, and *Phragmites* stands the highest values. A large variation in redox potential was found in the bare soil and the *Phragmites* site, whereas the *Carex* stand showed the lowest values and the fastest decrease with increasing depth. Increasing redox potentials measured with the electrodes at "bare soil 1" and "*Phragmites*" are difficult to interpret. Possibly, oxygen transport to deeper layers has taken place

in the *Phragmites* stands, and it may have also occurred in bare soil sites through dead rhizomes and stems in the peat (Brix 1989).

Sulfide electrodes sometimes failed during the time series measurements, probably due to rainfall that disturbed data transfer to the data logger. Only one profile for each location could be obtained, but these exhibit the expected pattern. High concentrations were found in the bare patches, medium values in the *Carex* stand, and very low values in the *Phragmites* stand. These differences corresponded with differences in redox potential: low in one bare soil site and the *Carex* sites, and high in the other bare site and in the *Phragmites* site. Sulfide production can take place in a redox potential range between 0 and -150 mV (Sikora and Keeney 1983) so that sulfide could be present at all depths. However, sulfide production
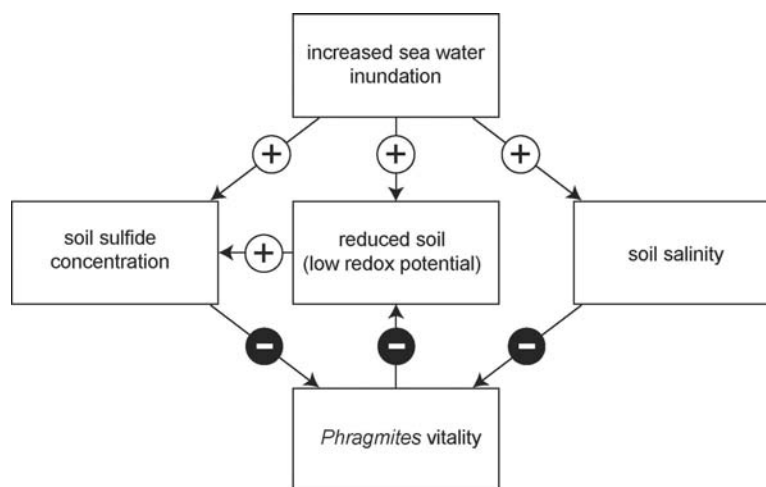
Figure 5. Tentative scheme of *Phragmites* die-back in the Kiritappu mud flats in Eastern Hokkaido. Increased seawater inundation leads to increased chloride and soil sulfide concentrations, both of which can harm the health of *Phragmites* plants. Oxygen transport through the roots diminishes, resulting in lower soil redox potentials. Sulfate reduction is also stimulated which leads to increased sulfide production. This is a positive feedback loop that may result in the observed *Phragmites* die-back.

depends on more factors than just the redox potential (Van Gemerden 1993), which may explain why sulfide concentrations do not closely follow changes in redox potential.

Time series measurements during the night at 50 mm below the surface yielded very interesting results, although the electrodes failed in the bare soil site during most of the night. Electrode measurements support the hypothesis that sulfide toxicity is the reason for the observed vegetation change at the middle reaches of Ichibangawa River. For some aquatic macrophytes such as *Stratiotes aloides* and *Potamogeton compressus*, sulfide concentrations as low as 10 μmol l^{-1} can be toxic (Smolders and Roelofs 1995), and the values measured at the bare peat sites and the *Carex* site are up to 34 times higher than this. Measured sulfide concentrations (more than 600 μmol l^{-1}) in the bare soil exceeded *P. australis* tolerance 2–3 times (Chambers et al. 1998). In the reed zone, values of 300–400 μmol l^{-1} were reached, which is in the range where *Phragmites* roots can be damaged, but this occurred only during short periods in the night. The fact that *Phragmites* in this zone was still very healthy indicates that most of the sulfide produced there was fixed, probably by iron. This supply of iron no doubt originates from the poor fen. *Phragmites* is situated in the seepage zone of the fen, which is

indicated by the bacterial film on the water surface, showing the presence of iron-rich water.

The results of our investigations suggest that supply of sulfate-rich water to a site with anaerobic substrate conditions and small sulfide binding capacities due to a lack of iron has led to accumulation of sulfide concentrations that are toxic to macrophytes.

Flooding with brackish water may lead to values of up to 300 μmol l^{-1} in the surface water. According to Chambers et al. (1998) this will decrease *Phragmites* growth by 70–80% under laboratory conditions. So, it appears that *Phragmites* is not only negatively affected by high sulfide concentrations, but possibly also by high chloride concentrations (Figure 5). Transport of oxygen through the roots diminishes, which results in lower soil redox potentials in the soil. Consequently, sulfate reduction is stimulated even more leading to increased sulfide production. This is a positive feedback loop that may result in the observed reed die-back.

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