THE EFFECT OF THE REDOX-POTENTIAL ON THE RETENTION OF PHOSPHORUS IN A SMALL CONSTRUCTED WETLAND

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ABSTRACT
Building wetlands in small arable streams is a popular supplement to best management practice on arable fields. Particle bound phosphorus settle in the small constructed wetlands (CWs), receiving agricultural diffuse pollution. The sorption behavior of phosphorus is, however, redox-sensitive, and bound phosphorus may be remobilized in periods with low redox potential. This paper investigates changes in the redox potential in the free water of wetland Berg (Norway) during a three-year period, and how these redox changes affects the total phosphorus (TP) and total reactive phosphorus (TRP) retention. Despite eutrophic conditions in the wetland, the redox potential was never negative, and usually higher than 400 mV, indicating aerobic conditions. The relative retention was 44 % and 43 % for TP and TRP, respectively. The specific retention was 100 g TP and 43 g TRP m^{-2} yr^{-1}. Loss of phosphorus was only observed during less than 19 % of the total period of time. The net loss was less than 5 % of the specific retention. The high positive redox potential probably conserves the redox-sensitive phosphorus in the wetland sediment as long as water flows through the CW.

Keywords : Agricultural pollution; Nordic climate; runoff; temperature; total reactive phosphorus; redox

INTRODUCTION
Constructed wetlands (CWs) can reduce diffuse pollution from arable land. However, due to the topography, Norwegian CWs are rather small, often only 0.1 % of the watershed surface area. Still CWs have proved to be useful supplements to best management practice (BMP) *on* arable fields. On average, the retention of total phosphorus (TP) in four CWs varied from 21 to 44 % of the input, even though the mean hydraulic loads were rather high, 0.7-1.8 m d^{-1} (Braskerud, 2002). Because of the positive results, Norwegian agricultural authorities sponsor 70 % of the CW building costs. Construction of wetlands seems to be quite popular; e.g. 100 CWs were built in 2002. The popularity is probably due to their multi-functionality in the arable landscape. In addition to cleaner water, CWs are esthetical elements including aquatic plants and animals, increasing the biological diversity locally. As an extra benefit CWs have a potential for removing pesticides from arable streams (Braskerud and Haarstad, 2003).

However, there has been some concern regarding the fate of phosphorus within the wetlands. The retention of particle bound phosphorus dominates in small CWs. Is there a possibility that bound phosphorus is remobilized at certain physio-chemical conditions in the wetland? Could anoxic periods e.g. cause the release of particle bound phosphorus by reducing reduce Fe(III) to Fe(II) (Uusitalo and Turtola, 2003) ? If this is the case, when will it happen and how much can be lost from the CWs? This paper investigates how changes in the redox-potential in the surface water in a Norwegian CW, influences the retention of total phosphorus (TP) and total reactive phosphorus (TRP, also used to estimate *potential* algae available phosphorus).

MATERIALS AND METHODS
Site description
The wetland Berg receives runoff from a 1.5 km^2 watershed, which is located about 50 km east of Oslo, Norway. The climate is typical continental, with frost 4 - 5 months per year. The annual precipitation is approximately 700 mm. The arable soil consists of silty clay loam (26-32 % clay). The loss of ignition in the topsoil varies from 5 - 10 %. Only 17 % of the watershed is arable, the rest is forest. Spring cereals dominate the agricultural production in the watershed. However, 20 % of the farmland is used as pasture for dairy herds. Slope gradients are rather gentle for Norwegian conditions (0-12 %). In previous years annual average loss of soil particles (TSS), phosphorus (TP) and nitrogen (TN) were 3260, 2.8 and 41 kg ha^{-1} arable land accordingly (Braskerud, 2001). The pH in the stream water varies from 6.3 to 7.5 (median 6.7) and the conductivity (25 ^{O}C) 3-26 mS m^{-1} (median 7).

The free water surface (FWS) constructed wetland Berg was built in 1990 by expanding the stream banks (Fig. 1). The CW is 100 m long and has a surface area of 900 m^2.

Depths during *low water flow* were originally 1 m in the sedimentation basin and 0.5 m in the wetland filter. However, the wetland has become shallower as a result of sedimentation of soil particles. Thus, in 2001 depths were approximately 0.5 m and 0.25 m, respectively.

The entire wetland was covered with vegetation, mainly *Glyceria fluitans* L. (floating manna grass), *Equisetum fluviatile* L (water horsetail), *Typha latifolia* L (cattail), *Scirpus lacustris* L (bulrush), *Acorus calamus* L (sweet flag), *Phragmites australis* (Cav.) Trin. ex Steud. (common reed) and *Callitriche hamulata* Kütz (intermediate waterstarwort). The vegetation cover always exceeded 80 %.

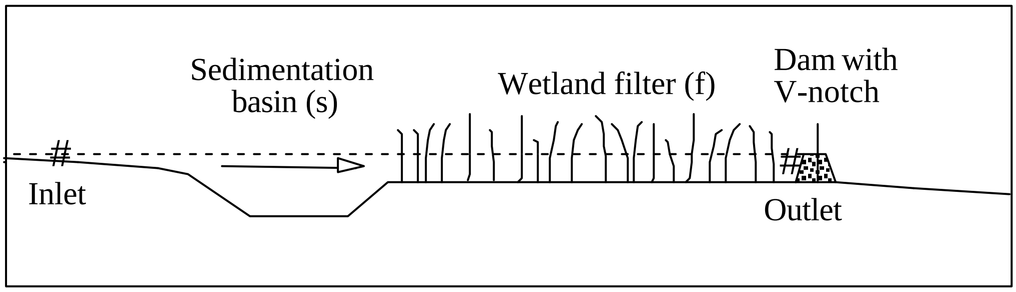

Figure 1. Berg constructed wetland, with composite samplers (#) in the inlet and outlet. Redox electrode was located close to the outlet sampler. The CW covers 0.06 % of the watershed area.

Water flow, redox and composite sampling measurements

A 120^{o} V-notch weir was installed at the dam outlet. A logger using a pressure gauge recorded the discharge, and controlled a *water flow proportional sampling system* in the inlet and outlet. On average, 12 sub-samples were collected daily and pumped to a plastic sample container. A 1-liter subsample was taken from the sample container, usually in 9 to 12-day intervals. Heating cables prevented pumps and tubes from freezing and enabled sampling throughout the entire year. The *redox electrode* (Hanna model HI3932 B, type AmpHel) with a 20 mm^2 platinum surface, was connected to a logger. The logger monitored every minute and collected the average half-hour value, as for runoff and temperature. The platinum electrode was situated at the outlet approx. 15 cm above the wetland sediment. The electrode was cleaned and calibrated towards a 250 mV solution, every month in the warm part of the year (April-October). The redox potential was monitored from May 1998 to November 2001. Times with no flow or errors in the inlet or outlet composite sampling are deleted from this period (13 episodes or 28 % of the total time). As a result, 68 samples were collected. In addition, the "annual" runoff and retention may be slightly higher than if the full year was used, since episodes with larger input are over represented.

Chemical analysis

Total suspended solids (TSS) and total phosphorus (TP) were analyzed according to standard Norwegian methods. TSS was determined on Whatman GF/A-filtered samples. Organic particles (org-SS) are defined as loss of ignition of TSS. TP was determined after digestion with potassium peroxo disulphate solution. Total reactive phosphorus (TRP) is analyzed on unfiltered samples according to (Murphy and Riley, 1962). In samples high in TSS, the samples are filtered (0.45 µm Millipore filter) after addition of reagents (minus acorbic acid). TRP is equivalent to RP(unf) according to (Haygarth and Sharpley, 2000).

Statistical methods

Simple and multiple linear regressions were applied. Retention is calculated as the percentage difference in mass between input and output. To avoid large negative outliers in cases where outlet > inlet , negative retention was calculated as -(100 - inlet·100·outlet^{-1}) %. Hence, the maximum loss from the CW was -100 %. *Stepwise mixed selection* was conducted among the 30 explanatory variables: The TP, TRP, TSS and org-SS (concentration in the inlet, specific load and differences between P-fractions and TSS in the inlet and outlet), hydraulic load (HLR), runoff (minimum, maximum, average and median), pH, conductivity, age of CW, water and air temperature, season, redox, and more. *Variance inflation factors* (VIFs) were used to test multi-co-linearity among the explanatory variables in the regression analysis. Only analyses that accomplish the following quality criteria were used: (i) the variables were statistically significant (P<0.05 or *), (ii) residuals normally distributed, and (iii) VIF less than 5. For more details on Berg, the sampling program, analyses and watershed characteristics, see Braskerud (2001, 2002).

RESULTS AND DISCUSSION

Flux of water and phosphorus, and redox conditions

Wetlands receiving runoff from small watersheds have a large variability in hydraulic load, e.g., fig. 2. The figure shows observations of 68 composite sampled episodes: The average runoff was 24 L s^{-1}, which equals a hydraulic load of 2.3 m^3 water per m^2 CW-surface per day, or 2.3 m d^{-1}. This equals an average theoretical retention time of only 4.3 hours, due to the shallow depth.

The redox potential in the outlet water was always positive, and often rather high (median 550 mV). From September 1999 to August 2000 the redox potential fell to a stable level of approx. 260 mV, due to an error in the redox-electrode (Figure. 2). The redox-potential in sediment without vegetation was measured occasionally with a similar electrode. It was always negative (-200 to -500 mV). Oxygen is the electron acceptor for redox potentials higher than 300 mV. Nitrate and manganese reduction occurs in the interval from 100 to 300 mV (NO_3 to N_2, and Mn(IV) to Mn(II)). When the redox potential is reduced to -100 to 100 mV, Fe(III) converts to Fe(II).

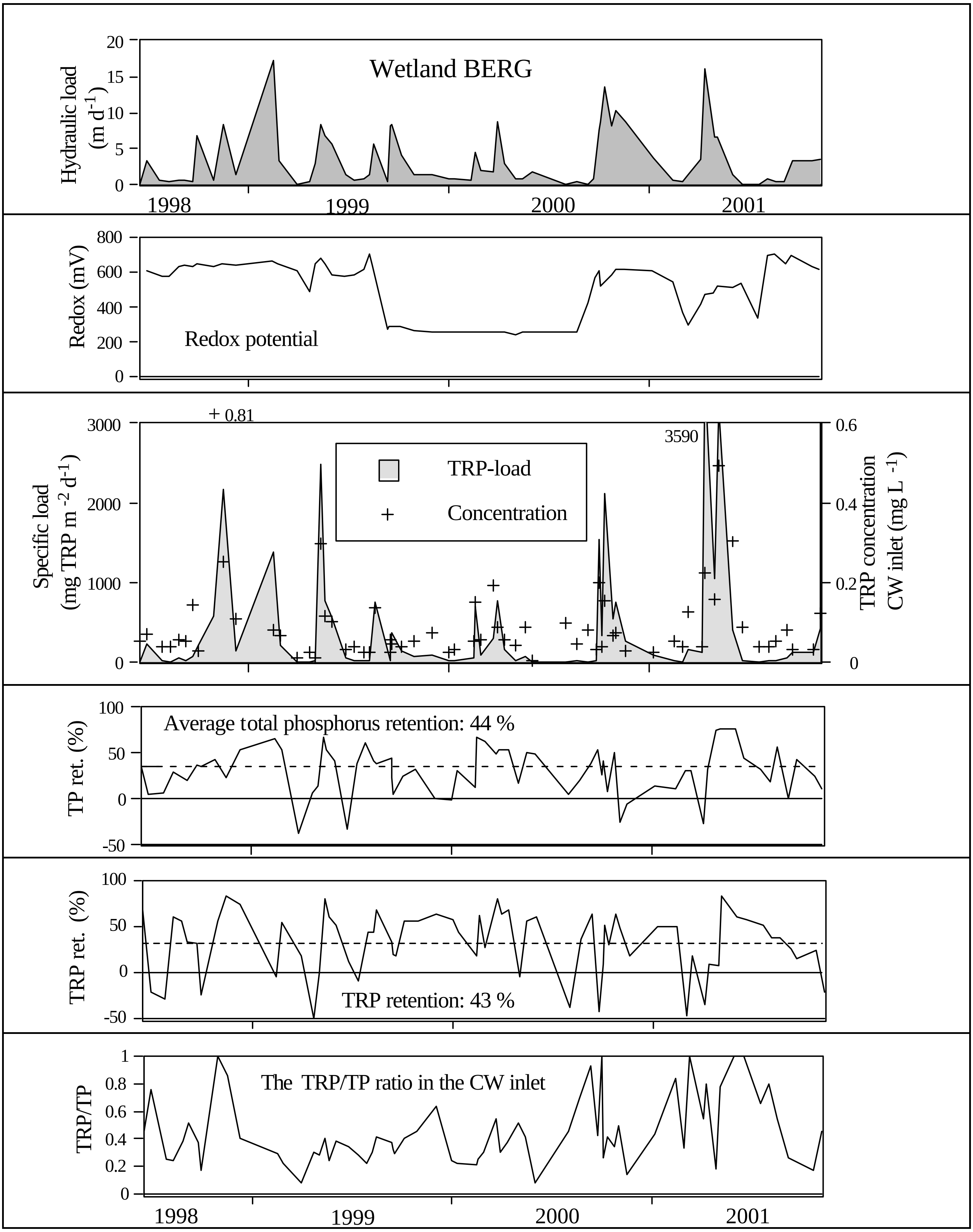

Figure 2. Variables investigated throughout the study period (n = 68).

There was usually a positive correlation between the input of total phosphorus (TP) or total reactive phosphorus (TRP) and runoff (r^2 = 0,64* and 0.54*, respectively). As a result the P-load was very variable (Fig. 2). On average, the load was 617 mg TP and 264 mg TRP m^2 d^{-1}. The bottom graph in Fig. 2 shows how the relationship between TP and TRP changes. Fig. 2 also shows the changes in TRP-concentration in the CW inlet. On average, it was 0.11 mg L^{-1}, while the TP concentration was 2.5 times higher (0.27 mg L^{-1}). The soil particle content in stream water was also very variable and shifted from 30 mg L^{-1} to 1300 mg L^{-1} (median 127 mg L^{-1}). The retention of TP and TRP changes throughout the investigated period (Fig. 2). The average specific retention was 274 mg TP and 116 mg TRP m^{2} d^{-1}.

Factors influencing P-retention

Two statistical models present the explanatory variables that are most important for the phosphorus retention. Before statistical analysis the data collected during the period with malfunctioning redox electrode were removed (remaining n = 49). The multiple linear statistical analyses, however, did not select the redox potential as a statistical significant variable in the models estimating the retention of TP and TRP. Therefore the full dataset was included in our analyses. Note that regression coefficients are standardized, or dimensionless to indicate the relative importance of the individual variable. For example, ±1.0 indicates a strong positive or negative influence on the phosphorus retention, while 0 indicates no influence. The result are presented in [1] and [2]:

TP (% ret.) = 0.55diffTP/TSS +0.37TSS(%ret) +0.24TPsetling velocity +0.23$C_{TPinlet}$ -0.22runoff(max.) +0.22water temp. (n=68, r^2=0.76) [1]

TRP (% ret.) = 0.66diffTRP/TSS +0.36org-SS(%ret) +0.33$C_{TRPinlet}$ +0.30diffTRP/TP -0.23runoff(max.) +0.12summer (n=68, r^2=0.83) [2]

where *diffTP/TSS*, *diffTRP/TSS* and *diffTRP/TP* are a reduction in the relationship between e.g. phosphorus and suspended solids between the inlet and outlet (TP/TSS_{inlet} - TP/TSS_{outlet}). The effect of decreasing the phosphorus on soil particles was very important in [1] and [2]. In a similar way a decrease in the *TRP part of TP* was important for the TRP retention in [2]. A decrease in the ratio TRP/TSS and TRP/TP can be interpreted as a decrease in possible bio-available phosphorus, because particles with low P-content have a higher potential in adsorbing P than particles high in phosphorus.

Several of the variables describing the retention of TP and TRP are the same or are closely related:

- It is well known that phosphorus is closely associated with soil particles (TSS). Hence, the retention of suspended solids *(TSS(%ret))* was important for TP. TRP, however, seems to be closer related to the retention of organic particles *(org-SS(%ret))*. Krogstad and Løvstad (1991) found a close relationship between organic matter and growth of algae. Perhaps some of the TRP is bound to the organic fraction in TSS, e.g., in aggregates of cohesive particles?
- Retention increases when the P-concentration in the inlet increases ($C_{TPinlet}$ and $C_{TRPinlet}$), indicating the mechanism of first-order kinetics (see Kadlec and Knight, 1996).
- Increased *runoff* (max.) had a negative effect on TP and TRP retention because of shorter detention time in the CW. It was the effect of the runoff peak that gave the best response in the models (e.g., *max.*).
- Increased *water temperature* increases the retention of TP, and is probably closely related to the positive effect of *summer* for TRP retention. This could be an effect of biological processes like P-uptake in algae and vegetation.

Effect of erosion in the watershed.

The TP retention is closely related to the *settling velocity* of phosphorus on TSS. The settling velocity is estimated by using the first-order area model (Kadlec and Knight, 1996), and is described in detail in Braskerud (2002). When *runoff* increases, larger soil particles and aggregates are eroded and transported to the wetland. As a result, the negative effect of lower detention time is balanced by an increased settling velocity, as found by Braskerud (2002).

Although the average relative retention of TP and TRP was similar (44 % and 43 %, respectively) and several of the variables in [1] and [2] seem related, the correlation between TP and TRP retention was rather week (r^2 = 0.14*). The results indicate that the significance of the individual retention processes varies in a complex way.

Loss of phosphorus

Loss of phosphorus from the CW was only observed during less than 19 % of the total period of time. The net loss was less than 5 % of the specific retention. Six of 68 episodes had a net loss of TP. The maximum TP loss was -508 mg m^{2} d^{-1} (median -80 mg m^{2} d^{-1}). TRP was lost from the CW in 12 episodes (Fig. 2). Due to the error in the redox electrode 10 observations are presented in Fig. 3. The largest specific loss occurred during periods with short detention times (Fig. 3-A). As the detention time increased, the amount of phosphorus lost decreased. The relative loss decreased as the redox potential increased (Fig. 3-B). This was probably an effect of increased oxygen content in Berg CW. Penn *et al*. (2000) has shown that an oxidized microlayer exists in the upper lake sediment under well-mixed conditions in the spring and fall. This layer partly inhibits the release of sediment bound phosphorus. Our redox electrode was too large to detect the mm-thin layer.

Changes in redox potential and runoff from one of the composite samples included in Fig. 3 are shown in Fig. 4 (12/3-1/4). The net loss was -28 % and -34 % for TP and TRP, respectively. The specific loss was -91 mg TP and -68 mg TRP m^{2} d^{-1}. Even though the redox potential was relatively high, the oxidized microlayer may be reduced in periods with low runoff, allowing a phosphorus release. Loss of phosphorus was observed in two FWS-wetland systems as the O_2 content and redox potential in water decreased, even though the redox potential was over 320 mV (Ahn and Mitsch, 2002).

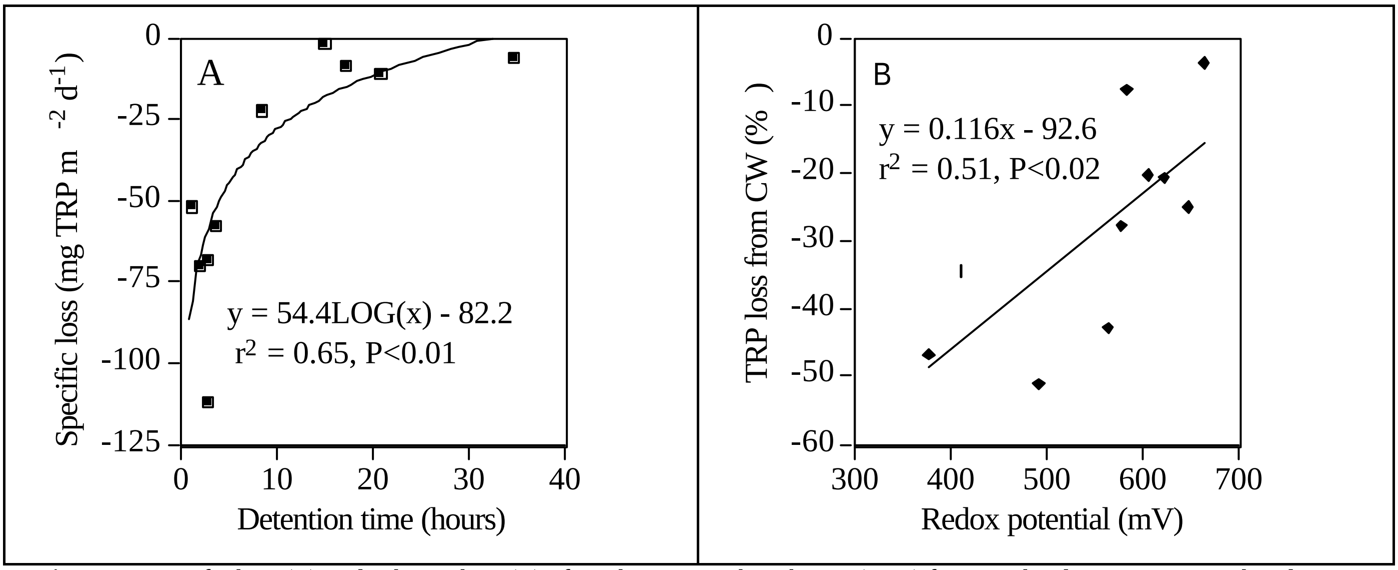

Figure 3. *Specific loss (A) and relative loss (B) of total reactive phosphorus (TRP) from wetland Berg was correlated to changes in the detention time and redox potential in the CW, respectively.*

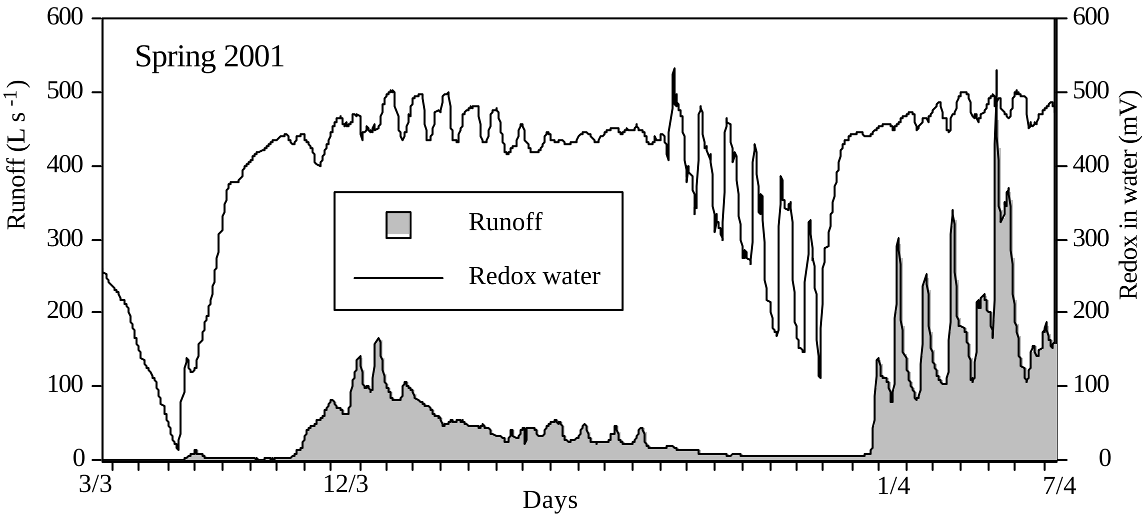

Figure 4. *Half-hourly observations of runoff and redox potential in Berg CW. The period covers 3 composite sample episodes (start and stop at indicated dates).*

The influence of runoff and temperature on the redox potential

Figure. 4 illustrates how runoff influences the redox potential. After a period of low flow, redox dropped to a minimum of 12 mV. However, a small increase in runoff (March 6), made the redox increase to more than 400 mV within few days. The same happened from March 23 onwards: As runoff decreases, redox levels decreases. However, we observed an interesting *indirect* effect of air temperature (not shown) when runoff was below approx. 15 L s^{-1}: As temperature increased at daytime (3 to 8 ^{o}C), snow was melting, and we observed increased runoff. At night water froze (-12 to -18 ^{o}C), and runoff decreased. As a result, the redox potential was correlated to the air temperature (r = 0.49*). During the periods March 8 to 16 and from March 30 onwards, air temperature never fell below 0 ^{o}C at night. As a result, runoff increased and the redox potential always exceeded 400 mV. The water temperature held a steady -0.5 ^{o}C throughout the period.

Runoff had the same effect on the redox potential during summer (r = 0.52*). With nearly no runoff, however, the temperature effect was most significant. In this part of the year the water temperature is closely correlated to the air temperature. An increase in the redox potential was expected as temperature increased due to increased O_2 production by vegetation and algea. However, we observed the opposite (r = - 0.60*), as Ahn and Mitsch (2002) did. This could be a result of increased decomposing of organic matter as water temperature increased. There was no statistically significant difference in specific or relative loss between seasons in Berg.

CONCLUSION

This study shows that the redox potential in the free surface water in the CW is positive. High hydraulic loads supplied the wetland with sufficient water to keep it aerobic. As a result, retention of phosphorus was significant, and periods with phosphorus loss from the CW, were rare. The high positive redox potential was probably the main reason why *redox* was not a significant variable for explaining the retention of TP and TRP. The redox potential did, however, influence the loss of phosphorus. Generally the absolute and relative retention will increase if the ratio of wetland surface area to watershed area increases. The need for long detention times could, however, reduce the redox potential. As a result, wetlands would occasionally observe P-leakage from the sediment. Retention of soil particles rich in phosphorus may be relative permanent in small CWs. However, the situation could be different for wetlands receiving water from watersheds with more life stock and arable land, compared to Berg CW.

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