Faculty of Science

University of South Bohemia

# Inorganic Indicators of Redox Conditions in a Horizontal Subsurface Flow Constructed Wetland

Rigorous Thesis

České Budějovice 2010

Kateřina Diáková

Supervised by RNDr. Jan Šíma, Ph.D.

Diáková K., Holcová V., Šíma J. & Dušek J. (2006). The distribution of iron oxidation states in a constructed wetland as an indicator of its redox properties. *Chemistry & Biodiversity*, 3, 1288-1300.

Šíma J., Diáková K. & Holcová V. (2007). Redox processes of sulfur and manganese in a constructed wetland. *Chemistry & Biodiversity*, 4, 2900-2912.

Šíma J., Diáková K., Pavelcová L. & Havelka M. (2009). Redox Properties of a Constructed Wetland: Theoretical and Practical Aspects. *Chemistry & Biodiversity*, 6, 341-355.

**Annotation**

These three consequent studies include monitoring of redox conditions in a horizontal subsurface flow constructed wetland for wastewater treatment over several years. Suitable analytical methods for determination of iron and sulfur oxidation forms were verified and a proportion of oxidized and reduced form of both, respectively, served as redox indicators in water samples taken at the inflow, the outflow and selected sampling points in a vegetation bed over a year. Other parameters were measured or analyzed in order to supplement knowledge of system operation.

**Stanovisko spoluautorů**

Potvrzuji, že Kateřina Diáková přispěla významnou měrou ke vzniku předložených prací.

Jan Šíma

**Prohlášení**

Prohlašuji, že svoji rigorózní práci jsem vypracovala samostatně pouze s použitím pramenů a literatury uvedených v seznamu citované literatury.

Prohlašuji, že v souladu s § 47b zákona č. 111/1998 Sb. v platném znění souhlasím se zveřejněním své rigorózní práce, a to v úpravě vzniklé vypuštěním vyznačených částí archivovaných Přírodovědeckou fakultou elektronickou cestou ve veřejně přístupné části databáze STAG provozované Jihočeskou univerzitou v Českých Budějovicích na jejích internetových stránkách.

V Českých Budějovicích dne 11. května 2010

Kateřina Diáková

# The Distribution of Iron Oxidation States in a Constructed Wetland as an Indicator of Its Redox Properties

by **Kateřina Diáková** [a)], **Veronika Holcová** [a)], **Jan Šíma**[*b)], and **Jiří Dušek** [a)]

a) Department of Ecology and Hydrobiology, University of South Bohemia, Faculty of Biological Sciences, Branišovská 31, CZ-370 05 České Budějovice, Czech Republic.

b) Department of Mathematics, Physics and Chemistry, University of South Bohemia, Faculty of Biological Sciences, Branišovská 31, CZ-370 05 České Budějovice, Czech Republic

(phone: +420387772 223; fax: +420385310366; e-mail: sima@bf.jcu.cz)

Wastewater-treatment processes taking place inside constructed wetlands are closely connected with chemical properties of these systems. The aeration of a wetland *via* the roots of the vegetation (and a subsequent formation of redox-potential gradients) strongly influences the wastewater treatment efficiency, and thus it represents one of the most important characteristics of the wetland. The concentration ratios of individual iron oxidation states ($Fe^{II}$ and $Fe^{III}$) were determined as the indicator of the redox properties of the constructed wetland reed bed during this study. Interstitial water from the wetland was sampled eleven times throughout the year 2005. The spectrophotometric method using 1,10-phenanthroline was properly optimized (limits of detection and quantification, sensitivity, linear dynamic range, repeatability, and accuracy values were assessed) and applied for iron determination. Most of iron, ca. 98%, is reduced to the $Fe^{II}$ form in raw wastewater and water from the inflow zone of the constructed wetland, however, at the outflow and in the vegetation bed both iron oxidation states are usually detected. The presence of $Fe^{III}$ in the reed bed (*ca*. 10–30% for some samples) demonstrates the aeration of the wetland by the vegetation (*Phragmites australis*) resulting in a re-oxidation of $Fe^{II}$.

# Redox Processes of Sulfur and Manganese in a Constructed Wetland

by **Jan Šíma** [*a]), **Kateřina Diáková** [b]), and **Veronika Holcová** [b])

[a]) Department of Mathematics, Physics and Chemistry, University of South Bohemia, Faculty of Biological Sciences, Branišovská 31, CZ-37005 České Budějovice
(phone: +420387772223; fax: +420385310366; e-mail: sima@bf.jcu.cz)
[b]) Department of Ecology and Hydrobiology, University of South Bohemia, Faculty of Biological Sciences, Branišovská 31, CZ-370 05 České Budějovice

Constructed wetlands are very popular in terms of wastewater treatment today. Formation of redox potential gradients inside such a system strongly influences the wastewater-treatment efficiency. Individual oxidation forms of sulfur, and dissolved and precipitated manganese forms were determined in the vegetation bed of the constructed wetland. The aim of the speciation analysis was to contribute to the characterization of its redox properties. Sulfur was mostly oxidized at the inflow. The concentration of sulfates at the inflow varied from 25 to 55 mg/l, while concentration of sulfides was always lower than 6.0 mg/l and mostly even lower than 1.0 mg/l. However, sulfates were reduced during the pretreatment and the wastewater flow through the vegetation bed. The concentration of total manganese varied from 0.2 to 0.8 mg/l. Approximately 60% of Mn was precipitated at the inflow. The content of precipitated Mn forms declined to *ca*. 40 –50% at the inflow zone, this content was almost constant across the vegetation bed to the outflow when water was sampled from 60-cm depth. However, the content of precipitated Mn forms increased to *ca*. 74% for samples from 20-cm depth. With respect to the aeration of the system, manganese can be precipitated as $MnO_2$ in these samples.

# Redox Properties of a Constructed Wetland:

# Theoretical and Practical Aspects

by **Jan Šíma** [*a]), **Kateřina Diáková** [b]), **Lenka Pavelcová** [c]), and **Michal Havelka** [d])

[a]) Institute of Chemistry and Biochemistry, University of South Bohemia, Faculty of Science, Branišovská 31, CZ-37005 České Budějovice
(phone: +420387772223; fax: +420385310366; e-mail: sima@prf.jcu.cz)
[b]) Department of Ecosystem Biology, University of South Bohemia, Faculty of Science, Branišovská 31, CZ-37005 České Budějovice
[c]) Department of Biological Sciences, University of South Bohemia, Faculty of Agriculture, Studentská 13, CZ-37005 České Budějovice
[d]) Department of General Biology, University of South Bohemia, Faculty of Science, Branišovská 31, CZ-37005 České Budějovice

Constructed wetlands represent a progressive approach to the wastewater treatment. A fundamental prerequisite of the efficient water quality improvement is the presence of redox potential gradients (connected with the aeration of the system) inside the vegetation bed. Redox properties of a constructed wetland were tested in three longitudinal transects crossing the vegetation bed from the inflow zone to the outflow using diverse indicators (*e.g.*, $Fe^{III}/Fe^{II}$, $SO_4^{2-}/S^{2-}$). Approximately 10–25% of iron was reoxidized in samples taken 10 m from the inflow zone in 2006. Redox processes of iron in artificial (constructed wetland) and natural (peat bog) ecosystems were compared. The peat bog was characterized with higher percentages of $Fe^{II}$ (usually *ca.* 90–100%). Thus, the aeration of the peat land was lower in comparison with the constructed wetland. The constructed wetland efficiently reduced sulfates (average concentrations of 44.7 and 11.2 mg/l at the inflow and the outflow, resp., in 2007). Organics, expressed as $COD_{Cr}$ and $BOD_5$, and $NH_4^+$ were removed with efficiencies of 86.4, 92.2, and 60.4%, respectively. However, total phosphorus (redox processes play a negligible role in this case) was removed only with 39.6% efficiency. Redox properties of the wetland did not significantly depend on the heterogeneity of the treated wastewater flow.