Tracers and isotopes in constructed wetland studies

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Actual and potential uses of tracer and isotope techniques in studies of constructed wetlands performance are presented. Conservative tracers reveal hydraulic characteristics while stable and radioactive isotopes of carbon, nitrogen and phosphorus can be used to trace cycling of these elements in wetlands. Isotope techniques that are successfully employed in addressing various questions related to aquatic environment are so far rarely used in studies of constructed wetlands.

Introduction

Wetlands are land areas inundated or saturated with water where the growth of emergent plants is supported. Natural wetlands have been used for discharging wastewaters for centuries while constructed wetlands are built in order to treat wastewaters of various origin with some degree of control over purification processes. A complex interplay of biological and physicochemical processes that occur in wetlands results in improvement of water quality. Construction, operation and maintenance of constructed wetlands are relatively simple and inexpensive comparing to the traditional waste treatment plants. Additional benefits are wetland habitat restoration and biodiversity enhancement. Constructed wetlands are rapidly growing world-wide with several thousands of systems operating in Germany, UK, Denmark, France, Nordic countries, Poland, Czech Republic and other European countries.

Constructed wetland technology is described in detail in extensive literature on this subject (e.g. KADLEC et al., 2000; KADLEC & KNIGHT, 1996). There are two main types of constructed wetlands: free water surface (FWS) and subsurface flow (SSF) systems. FWS wetlands are channels or ponds with submerged, emergent or free floating macrophytic plants. SSF wetlands are characterised by subsurface flow of wastewaters through porous medium (gravel or sand). Treatment wetlands improve water quality through removal of suspended solids, organics (BOD), nitrogen, phosphorus, pathogens (bacteria, parasites, viruses) and metals. Transformation and removal of pollutants from wastewaters occur via numerous interrelated physical, chemical and biological processes including biodegradation of organics by bacteria, ammonification – nitrification – denitrification of organic nitrogen by bacteria, uptake of nitrogen and phosphorus by plants, diffusion of N_2 and N_2O and adsorption of phosphorus. Bacteria, that constitute a crucial factor for pollutant transformations, are supported by macrophytic plants which provide surfaces for bacterial growth and are a source of reduced carbon necessary for denitrification. Particulates in properly designed treatment wetlands are usually removed very effectively by sedimentation and filtration while removal of soluble forms of pollutants can be inefficient. It must be noted that soluble pollutants are transformed and removed mainly through processes that occur at surfaces of plants, debris or sorbing media. Therefore the efficiency of pollutants removal is related to the degree of contact between wastewaters and the reactive surfaces.

Design and operation of an effective constructed wetland rely on models that describe in a quantitative manner how removal of a given pollutant is related to wastewater loading (both volume and quality), wetland design (dimensions, types of sorbing media, plant species) and to environmental factors (weather conditions). Any quantitative consideration of constructed wetland performance has to address two key aspects: wastewater hydraulics and purification processes. Residence time distribution function (RTD) is within this context a basic characteristic of wetland hydraulic properties as it describes length of time that wastewater fractions spend in the wetland and during which they can interact with the reactive surfaces. This information can be mathematically coupled with expressions describing mass transformations of pollutants to form a deterministic model of pollutant removal.

Tracer and isotope techniques can potentially provide valuable insights into both aspects of wetland performance. Conservative tracers are used to obtain wastewater residence time distributions and other hydraulic properties. Substances labelled with stable or radioactive isotopes can be used as non-conservative tracers to study transformations and retention of the respective chemical elements in constructed wetlands. Environmental isotopes can be in effect treated as tracers even if they are not intentionally introduced into the studied system. Variations of stable isotope ratios of environmental isotopes that are a common tool used to trace biogeochemical cycling of elements in various aquatic environments are, surprisingly, not so widely employed in studies of constructed wetlands.

This work is aimed at presenting some theoretical and practical aspects of the use of tracers for determination of RTD and process tracing in constructed wetlands, as well as to discuss potential use of environmental isotopes to trace water flow patterns and biogeochemical transformations of selected pollutants (organic material, nitrogen, phosphorus) within constructed wetlands.

Hydrology of constructed wetlands

Tracers most frequently used in constructed wetlands are fluorescent dyes (e. g. TORRES, 1997a,b; SHILTON, 1996; DOREGO, 1996) and inorganic ions with low natural and anthropogenic background concentrations like Br^- and Li^+ (e. g. KADLEC, 1994; KING, 1997; TANNER, 1998). Ionic tracers are injected as solutions of easily soluble salts (KBr, LiCl) and their concentrations are determined by ion chromatography, atomic absorption spectrophotometry, ion selective electrodes or other instrumental methods. Despite many examples of successful use of these tracers, there is some evidence of their non-conservative behaviour in wetlands. For instance Rhodamine B is sorbed by organic substances and was not completely recovered in wetland tracer tests (KADLEC, 1994) and bromide can be taken up by plants (KUNG, 1990; WHITMER et al., 2000). The amount of tracer that has to be used in order to obtain adequate information on the RTD depends on the active volume of the system and on the detection limit of the tracer. In case of salts the required mass of tracer can be in the order of kilograms or tens of kilograms. Injection of such concentrated solutions can influence flow and mixing patterns, especially in FWS systems, due to density currents and stratification (SCHMID, 2002). Tritium is free of these drawbacks as it is not retained by any chemical or biological processes and does not influence physical properties of water. Tritium, however, can be removed from the wetland via evapotranspiration. This loss of tritium can be accounted for when water budget is known for the studied system.

The most significant components of the water budget of constructed wetland are wastewater load, precipitation and evapotranspiration (KADLEc et al., 2000). Stochastic variations of precipitation as well as diurnal and seasonal fluctuations of wastewater load and evapotranspiration result in variations in flow rate. Constructed wetlands can thus operate in conditions that are far from the hydraulic steady state. The influence of this flow variability on tracer behaviour is found to be negligible (KADLEC, 1994) or is not considered at all in most cases.

Hydraulic characteristics of wetlands are inferred from the breakthrough curve on the basis of an assumed hydraulic model. Only the actual mean residence time of a tracer can be calculated independently of the chosen model as the ratio of the first to the zeroth moment of the breakthrough curve (system response to the instantaneous injection of tracer). Models used to interpret constructed wetland RTDs are often based on concepts developed in chemical engineering to characterize chemical reactors (KADLEC, 1994; DOREGO & LEDUC, 1996; TORRES et al., 1999). Constructed wetlands are considered in this approach as chemical reactors with different flow regimes: plug-flow, plug-flow with axial dispersion, complete-mix reactors or their combinations. Stagnant zones can be included in models to explain long tails of tracer response curves. Hydraulic parameters are estimated by the method of moments applied to the breakthrough curve or by fitting the theoretical RTD derived for the given model to the experimental data. Dispersive characteristics expressed as dispersion number or Peclet number reflect mixing properties of the constructed wetland. A comparison of the actual mean tracer residence time and the water residence time yields the ratio of the active water volume to the total water volume in the system. The active volume of the wetland and thus mean wastewater residence time can be smaller than the nominal values due to presence of stagnant zones and, in case of SSF systems, due to clogging of bed material with organic matter (Sanford 1995; TANNER et al., 1998; TANNER & SUKIAS, 1998).

Interpretation of RTDs obtained in tracer tests might reveal existence of stagnant zones and give some quantitative estimation of their extent. However, RTD analysis cannot locate stagnant zones within the wetland. Properly designed survey of stable isotope composition of water within the given wetland system should yield important information concerning spatial heterogeneity of isotopic composition of water in this system, which can be further linked to structure of water flow. The water flowing through constructed free surface wetlands will undergo partial evaporation. This process is associated with heavy isotope enrichment of the liquid phase. The magnitude of this enrichment is governed by physical parameters (temperature of water, relative humidity over the evaporating surface, wind velocity) and by the hydrology of the system, specifically the ratio of the total water inflow to evaporation, as well as by technological design of the given wetland system (single retention pool or interconnected pools). In situations when the isotopic composition of water being processed in constructed wetlands differs significantly from the isotopic composition of local groundwater, the survey of stable isotope composition of water within the given system may be used to localize the zone(s) of active inflow of groundwater into the system.

Process tracing

Organic carbon and nutrients are transformed, recycled and stored in wetlands. Isotopically labelled substances and environmental isotopes can help to reveal pathways of these processes and to quantify fluxes and reaction rates associated with them. Isotope tracers are used both *in situ* and in laboratory experiments. In cases when the use of isotopically labelled tracers in the whole wetland is impractical, micro- or mesocosm experiments can be performed. These well-established methodologies are, however, practically not employed in studies of the performance of constructed wetlands. Isotope techniques could potentially provide information important for development of conceptual and quantitative models of pollutant removal. It must be noted that results obtained with isotope techniques for natural wetlands may not always be directly applicable to constructed wetlands. These two categories of wetlands differ in hydraulic, physical and ecological aspects. Constructed wetlands have artificial soil structure, extremely high loadings of nutrients, support only one or few macrophyte species and in cold periods wastewaters are warmer than waters feeding natural wetlands.

Carbon

Stable (^{12}C, ^{13}C) and radioactive (^{14}C) isotopes of carbon are extensively used in studies of carbon cycling in aquatic environments including natural wetlands. From the viewpoint of constructed wetlands performance, the most important are processes that result in removal of organic material via aerobic and anaerobic degradation by heterotrophic bacteria. Final products of organic matter degradation are CO_2 and CH_4. Both gases can be released from the wetland into the atmosphere or leached with the effluent, but significant fractions of CO_2 and CH_4, the latter after oxidation to CO_2, are photosynthetically assimilated by autotrophic organisms including the macrophytic plants. Decomposition of dead macrophytes and algae results in replenishment of dissolved organic matter pool. The overall performance of constructed wetlands with respect to organic material reflects dynamic interaction of transformation, removal and storage processes.

Examples of successful use of carbon isotopes in studies of carbon cycling in aquatic environments are numerous and some of these experiences could be used in the field of constructed wetland research. Stable and radioactive isotopes of carbon are used to identify and quantify sources and transformations of dissolved organic and inorganic carbon as well as to refine carbon budgets in lakes, rivers and groundwaters (e. g.: NASCIMENTO et al., 1997; WACHNIEW & ROZANSKI, 1997; TELMER & VEIZER, 1999; RAYMOND & BAUER, 2001). Isotope techniques are frequently employed in studies related to methanogenesis and CO_2 production in wetlands, for example to reveal methane production (NEUE 1997), identify methanogenesis mechanisms (HORNIBROOK, 1997), trace methanogenesis substrates (MIYAJIMA, 1997) and reveal mechanisms of CO_2 and CH_4 transport in wetland macrophytes (CHANTON & WHITING, 1996).

Nitrogen

Organic nitrogen contained in wastewaters is removed by sequential processes of ammonification, nitrification and denitrification whose final products are N_2 and N_2O. Ammonia, nitrates and gaseous forms of nitrogen are also assimilated and fixed by wetland plants but their degradation releases organic nitrogen back to the wetland. The ultimate sinks of nitrogen are therefore release of N_2 and N_2O into the atmosphere and volatilisation of ammonia. Nitrogen has two stable isotopes (^{14}N, ^{15}N). Applications of nitrogen isotope tracers in hydrology and ecology are reviewed by KENDALL (1998), KENDALL & ARAVENA (1998) and ROBINSON (2001). Environmental isotopes of nitrogen are used, sometimes in combination with isotopes of oxygen, to distinguish nitrate sources. Denitrification in constructed wetlands can be estimated using variations in natural abundances of nitrogen isotopes (LUND et al., 2000). Nitrogen compounds labeled with ^{15}N are used in micro- mesocosm and even field-scale experiments (KENDALL & ARAVENA, 1998).

Phosphorus

Phosphorus has one stable (^{31}P) and two artificial, short-lived radioisotopes (^{32}P – 14.2 d, ^{33}P – 25.3 d). Phosphorus is removed from wastewaters by adsorption, chemical precipitation and uptake by living organisms which provide short- and long-term storage of this nutrient. Isotopically labelled phosphorus could be used in constructed wetlands to quantify short-term retention of phosphorus and to trace phosphorus distribution between system components. Radisotopes of phosphorus are used to trace phosphorus interactions with soils and plants in agricultural and forestal systems (e. g. CHEPKWONY et al., 2001; LEHMANN & MURAOKA, 2001; WAHID, 2001).

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