# Constructed Wetlands for Treatment of Organic and Engineered Nanomaterial Contaminants of Emerging Concerns [Project #4334]

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Sources including upstream wastewater discharges are currently and will be increasingly in the future discharging contaminants of emerging concern (CECs), such as organic chemicals and engineered nanomaterials (ENMs), into surface waters that serve as drinking water supplies. Following the concept that multiple barriers can serve as pathogen protection in finished water (which includes watershed controls), it is believed that engineered wetlands may play a role in reducing CECs in drinking water intakes. The current criteria design approaches for constructed wetlands include hydraulic loading rates, wetland depth, carbon loading rates from wetland plants, and amount of planted versus open wetland area. While constructed wetland design has been optimized for denitrification and/or establishment of ecological habitat, few design guidelines exist for removing CECs in these engineered systems. Thus, this study is aimed at identifying factors influencing removal of organic and nanomaterial CECs in constructed wetlands, with the goal of establishing design criteria suitable for CEC removal in wetlands located between CEC sources and raw potable water supplies.

## OBECTIVES

The goal of this project was to determine hydraulic and carbon loading rates for constructed wetlands required for achieving different levels of organic and nanomaterial contaminants of emerging concern (CECs) removal in constructed wetlands. Specific research objectives included the following:

1. Determine dominant removal mechanisms (abiotic, biotic) for different classes of emerging pollutants.
2. Develop design relationships based on laboratory experiments and computational models.
3. Assess validity of design relationships based on targeted sampling at full-scale constructed wetlands.
4. Assess changes in other key water quality parameters (organics and nitrates) across constructed wetlands that may impact water supplies.

5. Develop recommendations for utilities on the potential benefits from constructed wetlands for treating surface waters.

## BACKGROUND

Constructed wetlands are usually considered a low-cost alternative to treat or polish wastewater treatment plant (WWTP) effluents. Traditionally designed to remove bulk-level pollutants and nutrients, these wetlands also hold the promise to remove different types of CECs, such as pharmaceuticals, personal care products, endocrine disruptors, some disinfection by-products (nitrosamines), engineered nanomaterials, and other compounds. There is evidence that wetlands can remove CECs through a multitude of abiotic processes (e.g., sorption, photolysis, and hydrolysis) and biodegradation, yet their relative importance for a broad spectrum of CECs with different chemical properties is not known. In contrast, mechanisms for removing bulk pollutants, e.g., biological oxygen demand (BOD), chemical oxygen demand (COD), nitrogen, and phosphorus in constructed wetlands are well documented. Designing wetlands for removing these bulk pollutants requires controlling hydraulic flow through wetlands (i.e., hydraulic loading rates, minimize short-circuiting) and controlling the amount of plant growth in wetlands (i.e., carbon loading rates).

## APPROACH

In this study, several CECs were selected for their potential to be removed in wetlands using different processes. Seven organic chemicals (17$\beta$-estradiol, testosterone, atrazine, carbamazepine, caffeine, primidone and parachlorobenzoic acid) and two engineered nanomaterials (functionalized nano-silver, aqueous fullerenes) were studied. Selective monitoring of CECs in two full-scale wetlands was conducted. Laboratory continuous-flow microcosms were constructed and operated under different hydraulic loading rates. To simulate plant cessation, wetland plant material was harvested from full-scale wetlands, dried, cut into 1-inch pieces, and then added weekly to the microcosms to achieve different carbon loading rates. Nutrient amended tap water was used to simulate wastewater effluent, and feed continuously to the microcosms. Over a period of nearly 18 months, the microcosms were operated continuously to achieve different steady-state operating conditions, based on nitrogen transformation and dissolved organic carbon (DOC) in the effluent. Removal of CECs across the microcosms was monitored under a range of conditions, and the results used to calculate areal CEC removal rates ($ng/cm^2$-day).

Laboratory batch experiments were conducted to separately study the processes that were potentially involved in CEC removal (sorption/desorption to plant material, sunlight photolysis, hydrolysis, aerobic and anaerobic biodegradation, and aggregation of nanomaterial CECs). These were conducted using buffered distilled water and wetland effluent water. Data from these experiments were used to estimate partition coefficients, rate constants, and other parameters associated with CEC removal by each process. A steady state mathematical model was developed that could simulate different hydraulic conditions, carbon loading rates, and mechanisms for CEC removal. Simulations were performed to determine areal CEC removal rates under a range of typical wetland design criteria.

Laboratory scale microcosms were used to study natural attenuation of pollutants in wetlands or other natural systems. One of the potential applications of microcosms in this project is that it allows investigating the effect of loading rates on pollutant removal through the operation of microcosms at varying loading rates. This type of investigation would not be practical if pilot or full-scale wetlands were used. Batch experimental protocols to investigate different removal mechanisms for CECs (including hydrolysis, photolysis, and sorption) are also discussed. Batch-scale experiments are a convenient way to understand the mechanisms responsible for removal of contaminants in wetlands. Strategies for full-scale monitoring are discussed with a brief description of the sampling sites. The rationales behind selection of the CECs and development of the analytical methods with instrumental details are also summarized.

**RESULTS/CONCLUSIONS**

The major conclusions of this project are summarized below.

- CECs with higher sorption tendency represented by higher values of partitioning coefficients with plant materials showed less desorption tendency. Desorption was least for Estradiol (E2) followed by testosterone, carbamazepine, and atrazine.
- CECs including atrazine, testosterone, and E2 were phototransformed in wetland water. However, the rate of photolysis slowed with increasing levels of plant-leached DOC. Among the CECs investigated, atrazine experienced highest photolysis, followed by testosterone and E2. The remaining list of CECs, e.g., carbamazepine, primidone, and caffeine experienced negligible photolysis.
- Microbial activity supported by the decaying plant biomass removed organic CECs. Between the two steroidal organic CECs investigated, testosterone removal was faster than E2 in aerobic conditions.
- In anoxic conditions, increasing the decaying plant biomass quantity led to complete denitrification in the wetland microcosms.
- Presence of $NO_3^-$ was found important for E2 removal in denitrifying conditions. Removal was significantly higher when 2 mM $NO_3^-$ was present as opposed to its absence in anoxic conditions. Conducting mass balance showed that greater removal of E2 in $NO_3^-$ amended conditions was due to biotransformation not bio-sorption.
- Influence of water matrix on ENM stability was evident. Higher conductivity due to dissolved salts aggregated ENMs, where higher DOC leached from plant stabilized ENMs.
- ENMs were found to be removed by sorption onto the wetland plant materials. Between aq-n$C_{60}$ and *fn*-Ag NMs, aq-*n*$C_{60}$ had better sorption affinity for wetland plants.
- Ag NMs in the microcosm effluent were found to associate with colloidal materials produced by the decaying plants.
- The effect of HRT on removal varied among different types of organic CECs. HRT had significant impact on atrazine and primidone removal ($p<0.05$); however, the effect was not pronounced on the removal of estradiol, testosterone, caffeine, carbamazepine, and NDMA ($p>0.05$).
- Steroidal organic compound experienced highest removal among all the CECs investigated. Removal for these CECs varied between 70~99% in the microcosms. Atrazine, caffeine, and primidone experienced partial removal in the microcosms (0 ~ 50% for atrazine, 30~60% for caffeine and 10~65% for primidone). Carbamazepine removal efficiencies were low during all investigations (0~13%). Partial removal of NDMA was also observed in the microcosms varying between 20~68%.

- Denitrification in the wetland microcosms was a function of HRT. Complete denitrification in wetlands receiving a high level of $NO_3^-$ (28 mg/L $NO_3^-$-N) was achieved with an HRT of 4.5d.
- In a wetland microcosm where the influent $NO_3^-$ was completely denitrified at an HRT of 4.5d, areal removal rates for E2, atrazine, caffeine, primidone, carbamazepine, and NDMA were 12, 5, 6.4, 5, 0.45, and 1.7 ng/cm$^2$-d, respectively.
- In parallel with organic CECs, a comparative removal of ENMs was observed in the microcosms. During the pulse-input studies, maximum removal for both *fn*-Ag and aq-*n*$C_{60}$ was found to be at 60%, which is comparable with the observed removal of E2 (70%).
- Monitoring studies showed that organic CECs can enter wetlands when WWTP effluents are discharged.
- Atrazine concentrations detected in the City of Kingman wetlands were very low. This is attributable to the ability of atrazine to undergo efficient phototransformation (observed in batch-scale photolysis studies). Carbamazepine, a refractory organic CEC that showed insignificant removal in the microcosm studies experienced partial removal in full-scale wetlands.
- Most of the target organic CECs were present at very low levels in the City of Kingman wetlands, especially steroids. Although steroids were the most efficiently removed CECs in lab-scale studies, their very low concentrations did not allow investigating their removal in full-scale wetlands.
- Between the two principal design loading rates of constructed wetlands, hydraulic loading rate was more important than the carbon loading rate for organic CEC removal.
- Areal removal rates of the CECs increased significantly ($p<0.05$) with hydraulic loading rate except for carbamazepine.
- Carbon loading rate can increase removal of the organic CECs that are significantly removed by sorption. When the wetland needs to be operated at a higher hydraulic loading rate (>5 cm/d) due to land area limitations, increasing the carbon loading rate can improve removal of these organic CECs.
- Design configurations influence the contribution of removal mechanisms and ultimately CEC removal in a wetland. Wetlands with a greater area of an open water zone will enhance CEC removal by photolysis; however, wetlands with a larger vegetated area will support sorption as the main removal mechanism. Thus, decreasing the open pond area or increasing the vegetated area of a wetland will favor Class 3 and 4 organic CECs while it will lower the removal for the other two classes, especially Class 1, which are mainly removed by photolysis.
- Without increasing the net HRT, a wetland with both open-water and vegetated zones (in a single basins or sequentially in separate cells) will perform better than wetlands that are only open-water or completely vegetated.

## APPLICATIONS/RECOMMENDATIONS

This research provides design criteria for selected wetlands for the removal of CECs upstream of drinking water intakes. Wetlands can be constructed to polish wastewater effluent, polish part of a streamflow, or improve water quality in the entire streamflow passing through. CECs will be partially attenuated through wetlands, and the relative proportion of open pond area versus planted vegetation area can be balanced to permit sunlight photolysis of CECs as well as CEC removal, with minimal desorption. Wetlands can be designed to efficiently remove nitrate and other bulk pollutants, while simultaneously removing CECs. However, higher carbon loading rates (large planted areas) can release dissolved organic carbon (DOC) into water. This DOC can react with disinfectants in water treatment to form regulated disinfection by-products. The model developed in this study provides an integrative tool to assess nitrate removal, CEC removal, and DOC release. As such, this study provides greater insight into the concept that wetlands "polish" CECs from wastewater effluent.

**PARTICIPANTS**

Field sampling of full-scale constructed wetlands receiving wastewater was conducted in Kingman, AZ, and Tucson, AZ. Involvement of staff at those facilities in coordinating and assisting in sampling collection is greatly appreciated.

**RESEARCH PARTNERS:**

- Water Environment Research Foundation
- U.S. Environmental Protection Agency