

Treatment of simulated oil and gas production wastewater using *Typha latifolia* in a pilot-scale constructed wetland

Oludamilola Alalade, Jeremy Ferguson, John Pichtel

Ball State University, Natural Resources and Environmental Management, Muncie, Indiana, U.S.A

Corresponding author: John Pichtel, Ball State University, Natural Resources and Environmental Management, Muncie, Indiana 47306-0495, U.S.A.; Phone: 765-285-2182; E-mail: jpichtel@bsu.edu

Key words: constructed wetlands, hydraulic fracturing, phytoremediation, produced water, *Typha latifolia*

Received in February 2017. Published in September 2017.

ABSTRACT

During hydraulic fracturing ('fracking'), large volumes of high-pressure, chemically-treated water are pumped into subsurface strata to free trapped petroleum and natural gas. Chemically-enriched water, along with brine and groundwater, collectively termed oil and gas production water (PW), are eventually recovered from the well. PW poses environmental and health risks; however, it can be reused if potentially hazardous constituents are removed. A two-stage pilot-scale constructed

wetland containing cattail (*Typha latifolia*) was tested for treatment of synthetic PW. After 49 days, PW pH increased from 4.2 to 7.0, and electrical conductivity decreased from 22,100 to 3,300 μ S \cdot cm⁻¹. *Typha* shoots had bioconcentration factors for Pb ranging from 2.8 (Stage 1 of constructed wetland) to 8.0 (Stage 2). Transfer factors for Pb were 0.67 (Stage 1) and 1.37 (Stage 2). These results indicate that *Typha* may be effective for Pb removal from PWs. The present study may be of practical value to oil and gas production companies that plan to recycle or properly dispose of large quantities of oil and gas production wastewater.

INTRODUCTION

Wastewater produced by hydraulic fracturing

Hydraulic fracturing ('fracking') is defined as the process of creating and propagating a fracture within a rock layer by means of applying hydraulic pressure in order to release petroleum, natural gas, coal seam gas, or other potential fuels for extraction (Earthworks 2015). The injection of a highly pressurized fluid creates new channels in the strata which increase extraction rates and recovery of fossil fuels (Veil et al. 2004). The injected fluid is typically a slurry of water, proppants, and various chemical additives.

Following initial injection into the well, a portion of the injected water returns to the surface immediately and is termed 'flowback.' The remaining fluids either permeate

the formation or return to the surface over the life of the active well and are termed 'produced water' (Earthworks 2015). Both types of wastewater may contain hydraulic fracturing fluids, naturally occurring brines, heavy metals, and other compounds from the formation (Fontenot et al. 2013; Kassotis et al. 2015; Warner et al. 2012). The United States generates an estimated 21 billion barrels of produced water annually (Aqwatec 2015). In this report, oil and gas flowback water, produced water, and hydraulic fracturing fluids collectively will be termed oil and gas production wastewater (PW).

A number of papers have described the effects of hydraulic fracturing on surface water quality, groundwater quality, and soil properties (Fon tenot et al. 2013; Pichtel 2016; Warner et al. 2012). PW may pose a threat to public

health and the environment as some constituents are known to be acutely toxic, some are carcinogenic, and others are believed to be endocrine disruptors (Bergman et al. 2013; Kassotis et al. 2015). The composition of PW varies markedly and its chemical and physical properties depend on the geographic location of the field, the geologic formations in contact with the water over time, and the treatment chemicals and extraction techniques that are used (Benko and Drewes 2008; Murray Gulde et al. 2003; Veil et al. 2004). However, three common fractions of PWs are salts, metals/metalloids and hydrocarbons (O'Rourke and Connolly 2003; Veil et al. 2004).

PW management falls under two broad categories: underground injection and surface management. Selection of a management option for PW is based on numerous considerations, including the composition and volume of the PW, the technical feasibility of a treatment option, and the options allowed by regulations (NPC 2011). Current PW management strategies include minimization of the volumes generated, utilization for enhanced recovery and pressure maintenance, disposal into underground formations, surface discharge, and beneficial use at the surface (Khatib and Verbeek 2003; Veil et al. 2004).

In the United States, more than 98% of produced water from onshore wells is injected annually; approximately 59% is injected into producing formations to maintain pressure, and 40% into non-producing formations for disposal. The remaining produced water is managed in evaporation ponds, shipped offsite for commercial disposal, or applied for beneficial purposes, for example, irrigation, land application, and livestock and wildlife watering (Clark and Veil 2009; Pichtel 2016).

The need for alternative sources of water resources and increasingly stringent water quality discharge standards have stimulated the drive for increased water reuse (USEPA 2004). Integrating water reuse into water management strategies can lessen the demand on existing water resources and partially alleviate the need for development of new water sources (Veil et al. 2004).

Constructed wetlands for treatment of PWs

A range of technologies, both chemical and physical, are available for treatment of contaminants from PW. These technologies vary in terms of complexity of operation, portability, and cost.

Constructed wetlands (CWs) are engineered systems designed to improve the quality of point and nonpoint sources of water pollution including storm water runoff, domestic wastewater, agricultural wastewater, and coal mine drainage. Constructed wetlands are also used to treat petroleum refinery wastes, compost and landfill leachates, and pretreated industrial wastewaters, such as those from paper mills and textile mills (USDA-NRCS 2015). Constructed wetlands are classified into two categories according to mode of water flow and dominant aquatic plant species (Kadlec et al. 2010):

1. Free water surface CWs consist of basins with a layer of soil or sediment to support the growth of rooted macrophytes. The wastewater is directed horizontally through a dense mat of plants. Water flow is above the ground surface.

2. Subsurface flow CWs consist of basins filled with a granular medium such as gravel, sand, or soil. Water flow is below the ground surface. A drainage tube at the base of the outlet area allows for effluent removal.

Typha latifolia

Some aquatic plants have been documented as having the ability to transfer nutrients (Chung et al. 2008; Gottschall et al. 2007; Moshiri 1993; Mungur et al. 1997) and heavy metals (Deng et al. 2004; Fritioff and Greger 2006; Maine et al. 2006; Miretzky et al. 2004; Skinner et al. 2007) from aquatic environments. Researchers have addressed the phytoremediation of aquatic environments and contaminated sediment by aquatic macrophytes (Osmolovskaya and Kurilenko 2001; Panich-Pat et al. 2004). *Typha latifolia* L. (cattail) is a wetland plant that grows extensively in temperate regions (Ye et al. 1997). *T. latifolia* is widely used in CW systems due to its high yield, non-invasive characteristics and resilience (Brisson and Chazarenc 2009). *T. latifolia* additionally has a high capacity for tolerating and taking up heavy metals without serious physiological damage (McNaughton et al. 1974; Pip and Stepianiuk 1992).

The objective of the reported research was to determine the effectiveness of pilot-scale constructed wetlands (CWs) for treating PWs for possible reuse. The specific objectives were as follows: (1) to evaluate the ability of *T. latifolia* to ameliorate pH and electrical conductivity, and to sorb heavy metals from PW; and (2) to assess the ability of *T. latifolia* to take up and accumulate Na, Cu, and Pb for phytoextraction purposes.

EXPERIMENTAL METHODS

Synthetic PW

Synthetic PW was prepared using reagent grade chemicals (Sigma) mixed with deionized water. The chemical composition was based on data from Maguire-Boyle and Barron (2014), FracFocus (2015), and Marcellus (2010). Salts included AlCl_3 , AlF_3 , $\text{Al}(\text{NO}_3)_3$, CuSO_4 , MgCO_3 , $\text{Mg}(\text{NO}_3)_2$, K-acetate, KCl, Na-acetate, Na_2CO_3 , and NaCl. Hydrocarbons included diesel fuel, ethanol, ethylene glycol, glycerol, hexane, 2-propanol, and toluene. For pH adjustment, NaOH, acetic acid, H_3BO_3 , HCl, and H_3PO_4 were used.

The pH of the PW was determined with a glass electrode pH meter (Accumet® model AP115), and its electrical conductivity with an EC meter (Hanna Instruments model HI 993310). Total Ca, Mg, Cu, Na, and Pb concentrations were determined via flame atomic absorption spectrophotometry (FAAS) (Perkin Elmer AAnalyst 200), and total K via flame atomic emission spectrophotometry (APHA 2017).

Constructed wetland study

Bench-scale constructed wetlands (Free-Water-Surface mode) were established in a greenhouse. The system included 20-liter plastic trays measuring 90cm in length, 40cm in width and 15cm in height. Each tray was filled with 10kg of Glynwood soil (fine, illitic mesic Aquic Hapludalf). Soil was obtained from the surface 20cm of agricultural fields in central Indiana, air-dried, and sieved to pass a 2-mm mesh sieve.

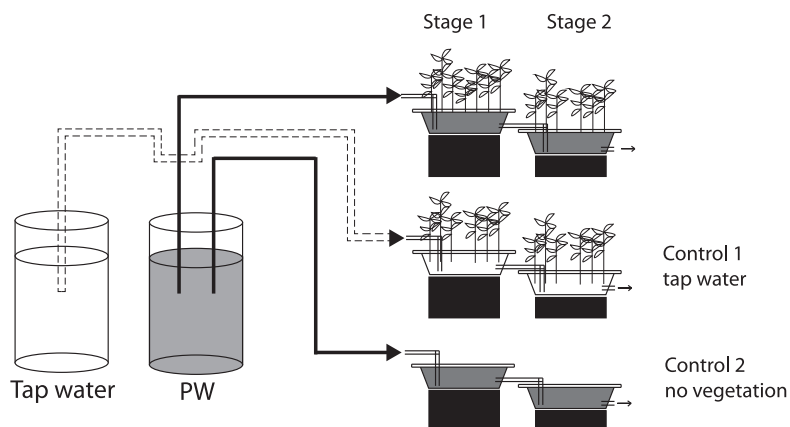


Figure 1. Schematic of the pilot-scale constructed wetland system.

There were three variants, the treatment and two controls, and three replicates of each variant. Each variant consisted of two trays ('Stage 1' and 'Stage 2') in series (Figure 1). In the treatment group and Control 1, the trays were planted with 15 rhizomes of cattail (*T. latifolia*) in each tray; no rhizomes were planted in Control 2.

The rhizomes were collected from a natural wetland located in central Indiana. The plants were treated with tap water for 63 days (1000mL per week) and allowed to acclimate to greenhouse conditions. Then the treatment group and Control 2 received 1000mL of PW weekly for 49 days, while Control 1 received tap water only. The PW was added by gravity from carboys, and all trays were maintained in a saturated condition.

Characterization of soil properties

Soil pH was determined using a glass electrode pH meter (Accumet® AP115) with a 1:10 mixture of soil:deionized H₂O. Electrical conductivity (EC) was measured using an EC meter (Hanna Instruments HI 993310). Total organic carbon was determined via the Walkley-Black method (Walkley and Black 1934), and total N by the Kjeldahl method (Black 1965). Soil P was measured by the Bray-II method (Bray and Kurtz 1945), and extractable K via flame atomic emission spectrophotometry (Perkin Elmer AAnalyst 200) after NH₄OAC extraction (Helmke and Sparks 1996). Extractable metal (Na, Cu, Pb) concentrations were

measured after DTPA extraction; samples were extracted with 0.05M diethylene triamine pentaacetic acid (DTPA) for 2h on an oscillating shaker (120osc·min⁻¹) (Burau 1982). The mixtures were filtered through Whatman no. 2 filter paper and analyzed using FAAS. Soil particle size distribution was determined by the hydrometer method (Allen et al. 1974).

Characterization of constructed wetland (CW) effluent and *Typha latifolia*

After 49 days of treatment, liquids exiting Stage 2 of each variant were collected for analysis. Effluents were filtered using Whatman no. 42 filter paper to remove sediment before determination of pH, EC, and concentrations of Ca, Mg, Cu, Na, and Pb, as described for the raw PW.

Entire plants were removed from the trays and separated into shoots and roots using an Exacto® knife. Plant tissue was oven-dried at 80°C for 4 days and its dry weight was recorded. Dried plant tissue was cut into small pieces with stainless steel scissors. One-half gram (d.w.) of plant tissue was transferred to an acid digestion vessel. Concentrated (70%) HNO₃ was added and the mixture digested using a MARS microwave digestion apparatus (CEM Corporation). Total metal (Na, Cu, Pb) concentrations of the digests were determined using FAAS.

Metal uptake by *Typha*

Several factors were calculated to determine metal uptake and translocation by *Typha*. The bioconcentration factor (BCF) is defined as the ratio of the metal concentration in a plant part to the extractable metal concentration in the rhizosphere soil (Rezvani and Zaefarian 2011):

$$BCF_{\text{shoot}} = C_{\text{shoot}}/C_{\text{soil}}$$

$$BCF_{\text{root}} = C_{\text{root}}/C_{\text{soil}}$$

where C_{shoot} and C_{root} are the metal concentrations in the shoot and root, respectively, and C_{soil} is the metal concentration in the soil.

The translocation factor (TF) was calculated by dividing the metal concentration in the shoot by the metal concentration in the root:

$$TF_{\text{shoot}} = C_{\text{shoot}}/C_{\text{root}}$$

where C_{shoot} and C_{root} are the metal concentrations in shoot and root, respectively.

RESULTS AND DISCUSSION

Properties of PW

The synthetic PW had a pH of 4.2 and an EC of $22,100\mu\text{S}\cdot\text{cm}^{-1}$ (Table 1). Concentrations of Na, Cu and Pb were 4.7, 4.4,

and $4.1\text{mg}\cdot\text{L}^{-1}$, respectively. Igunnu and Chen (2014) measured a pH of 4.3 in oil field produced water. In contrast, ALL (2009) noted a pH of 8.1. Igunnu and Chen (2014) measured an EC of $4,200\mu\text{S}\cdot\text{cm}^{-1}$ in produced water and Na concentrations ranging from 132 to $97,000\text{mg}\cdot\text{L}^{-1}$. The same authors found Cu concentrations ranging from <0.02 to $1.5\text{mg}\cdot\text{L}^{-1}$, and Pb concentrations from 0.002 to $8.8\text{mg}\cdot\text{L}^{-1}$. ALL (2009) measured Na levels of $486\text{mg}\cdot\text{L}^{-1}$. Such variations in pH and in other analyte concentrations in PWs are common, due to the wide range of formulations for preparing hydraulic fracturing fluids as well as the varying geochemistry of subsurface water.

Soil properties

The Glynwood soil had a pH of 6.7 (Table 2). Total C and N contents were 3.9 and 0.36%, respectively. Levels of extractable Na, Cu and Pb were consistent with those of non-contaminated soil. The soil texture was silt loam.

Table 1. Chemical characteristics of synthetic oil and gas production water (PW).

Characteristic	Value
pH	4.2
EC ($\mu\text{S}\cdot\text{cm}^{-1}$)	22,100
Metals ($\text{mg}\cdot\text{L}^{-1}$)	
Mg	4.4
Ca	7.1
K	4.8
Na	4.7
Cu	4.4
Pb	4.1

Table 2. Chemical and physical characteristics of soil used in the constructed wetland.

Characteristic	Value
pH	6.7
EC ($\mu\text{S}\cdot\text{cm}^{-1}$)	1,100
TOC* %	3.9
Total N %	0.36
Bray-II P ($\text{mg}\cdot\text{kg}^{-1}$)	13.0
K ($\text{mg}\cdot\text{kg}^{-1}$)	86.9
Extractable metals ($\text{mg}\cdot\text{kg}^{-1}$)	
Na	0.31
Cu	0.22
Pb	0.50
Texture (%)	
Sand	28.0
Silt	51.0
Clay	21.0

*TOC, total organic carbon

Properties of PW after CW treatment

After CW treatment, the effluent pH was 7.0 (Table 3); the effluent pH of Control 2 (no *Typha*) was 6.7. Glynwood soil is formed upon dolomitic limestone deposits (USDA-NRCS 2017) and imparts substantial acid buffering capacity. Salinity decreased markedly after CW treatment (Table 3). The values of EC were $2,900\mu\text{S}\cdot\text{cm}^{-1}$ after Stage 1 and $3,300\mu\text{S}\cdot\text{cm}^{-1}$ after Stage 2, constituting an 87 and 85% decrease, respectively, from that of the raw PW (Table 1). The EC of effluent from Control 2 was $18,600\mu\text{S}\cdot\text{cm}^{-1}$, which demonstrates that *Typha* was primarily responsible for reducing salinity. Cattail has been found capable of tolerating and treating saline wastewater (Coon et al. 2000). In a study of CW treatment of high-salinity wastewater, Jesus et al. (2014) measured salinity reductions of 52%.

Sodium concentrations after all CW treatments ranged between $2.7\text{--}4.3\text{mg}\cdot\text{L}^{-1}$, which is only a modest decline from that of the fresh PW ($4.7\text{mg}\cdot\text{L}^{-1}$, Table 1). Copper concentrations in the effluent from Stages 1 and 2 ranged from $0.03\text{--}0.04\text{mg}\cdot\text{L}^{-1}$ (Table 3), which was a 99% reduction from the Cu concentration in raw PW ($4.4\text{mg}\cdot\text{L}^{-1}$, Table 1). Similarly, Lesage (2006) and Gersberg et al. (1984) reported >90% copper removal in PW CWs. Using a constructed wetland, Bandaruk and Waara (2014) measured a 77% reduction in Cu concentration. Knox et al. (2010), Vymazal (2005) and Kröpfelová et al. (2009) reported similar results.

Total Pb concentration after treatment was 0.69 (Stage 1) and $0.76\text{mg}\cdot\text{L}^{-1}$ (Stage 2). These values constitute an 83 and 82% decrease from the Pb concentration in the raw PW ($4.1\text{mg}\cdot\text{L}^{-1}$). The observed Pb concentrations were slightly lower than those in Control 2 ($0.88\text{mg}\cdot\text{L}^{-1}$). Khan et al. (2009) noted a 50% Pb removal rate with *Typha* in a CW. Arroyo et al. (2010) found a 48% reduction in Pb concentration. Lesage (2006) used a CW to treat domestic wastewater and reported 48.3% and 81% removal of Cu and Pb, respectively. Walker and Hurl (2002) monitored wetlands treating stormwater for metals over a four-month period. They found Cu and Pb levels were reduced by 48 and 71%, respectively.

Soil properties after CW treatment

Soil pH was 6.97 and 7.06 in Stages 1 and 2, respectively (Table 4). This compares with a pH of 4.18 in Control 2 (no *Typha*). CW Stages 1 and 2 had markedly lower EC values ($3,000$ and $3,400\mu\text{S}\cdot\text{cm}^{-1}$, respectively) than Control 2 ($22,100\mu\text{S}\cdot\text{cm}^{-1}$) (Table 4). These results demonstrate the effectiveness of *Typha* in removing salts from the soil solution. Pantip and Suwanchai (2004) found that *Typha* had the ability to grow well in saline wastewater.

Soil Na concentrations were 2.9 and $43.0\text{mg}\cdot\text{kg}^{-1}$ (Stage 1 and Stage 2, respectively) (Table 4), and $4.3\text{mg}\cdot\text{kg}^{-1}$ in Control 2. These values for Na are considered relatively low and will not cause detrimental effects to *T. latifolia*. Coon et al. (2000) found that *T. latifolia* produced substantial biomass at Na concentrations of $12,000\text{mg}\cdot\text{kg}^{-1}$ in sediment.

Soil Cu concentrations measured 5.1 and $1.0\text{mg}\cdot\text{kg}^{-1}$ in Stages 1 and 2, respectively (Table 4), and $3.2\text{mg}\cdot\text{kg}^{-1}$ in Control 2. The Glynwood soil in this experiment contained $0.2\text{mg}\cdot\text{kg}^{-1}$ Cu (Table 2). This soil contained 3.9% TOC (Table 2), which gives it a moderate sorption capacity for metals. Copper forms strong bonds with organic matter (Zhou and Wong 2001); humic acids and other organic molecules interact readily with Cu (Klucakova 2012; Otero et al. 2015).

Soil Pb concentrations measured 8.8 and $2.9\text{mg}\cdot\text{kg}^{-1}$ (Stages 1 and 2, respectively), and $4.2\text{mg}\cdot\text{kg}^{-1}$ in Control 2 (no *Typha*). The non-contaminated Glynwood soil contained $0.5\text{mg}\cdot\text{kg}^{-1}$ Pb (Table 2). The results for Stages 1 and 2 are due in part to Pb uptake by *Typha*. It is also likely that Pb precipitated from solution and/or was sorbed in the *Typha* rhizosphere in Stages 1 and 2. Wetland sediments are generally considered a sink for metals (Arroyo et al. 2010; Burton and Scott 1992) and may contain high concentrations of metals in a reduced state (Weis and Weis 2004). The major processes responsible for metal removal in wetlands include adsorption to sediments and soils, precipitation as insoluble salts, and uptake by plants and microorganisms (Kadlec et al. 2010). Plant activities influence and modify the distribution of trace metals between the solid and aqueous phases (Kim et al. 2008).

Table 3. Chemical characteristics of effluents from the constructed wetland after 49 days ($n=3$, mean \pm standard deviation).

Treatment	pH	EC ($\mu\text{S}\cdot\text{cm}^{-1}$)	Mg ($\text{mg}\cdot\text{L}^{-1}$)	K ($\text{mg}\cdot\text{L}^{-1}$)	Na ($\text{mg}\cdot\text{L}^{-1}$)	Cu ($\text{mg}\cdot\text{L}^{-1}$)	Pb ($\text{mg}\cdot\text{L}^{-1}$)
Stage 1	7.02 ± 0.14	$2,900\pm 427$	3.07 ± 0.36	1.00 ± 0.37	2.66 ± 0.60	0.03 ± 0.01	0.69 ± 0.26
Stage 2	7.05 ± 0.19	$3,300\pm 279$	2.95 ± 0.14	1.31 ± 1.01	3.10 ± 1.10	0.04 ± 0.02	0.76 ± 0.23
Control 1	8.20 ± 0.06	840 ± 123	2.28 ± 0.15	4.87 ± 0.01	4.27 ± 0.02	0.20 ± 0.21	BDL*
Control 2	6.69 ± 0.10	$18,600\pm 1,009$	4.57 ± 0.17	2.13 ± 1.08	3.26 ± 0.77	0.02 ± 0.01	0.88 ± 0.01

Control 1, treated with tap water, with cattails

Control 2, treated with PW, no cattails

BDL*, below detectable limits

Table 4. Chemical characteristics of soil in constructed wetlands after 49 days ($n=3$, mean \pm standard deviation).

Treatment	pH	EC (mg·L ⁻¹)	K (mg·L ⁻¹)	Na (mg·L ⁻¹)	Cu (mg·L ⁻¹)	Pb (mg·L ⁻¹)
Stage 1	6.97 \pm 0.12	2,998 \pm 475	0.64 \pm 0.01	2.91 \pm 1.19	5.12 \pm 1.25	8.83 \pm 0.90
Stage 2	7.06 \pm 0.02	3,481 \pm 728	0.38 \pm 0.05	43.0 \pm 4.5	1.03 \pm 0.28	2.88 \pm 0.94
Control 2	4.18 \pm 0.10	22,150 \pm 1,897	4.87 \pm 0.01	4.27 \pm 0.02	3.20 \pm 0.21	4.24 \pm 0.26

Control 2, treated with PW, no cattails

Table 5. Total dry mass production (g) of *Typha latifolia* in the constructed wetlands ($n=3$, mean \pm standard deviation).

Treatment	Shoots	Roots
Stage 1	18.30 \pm 0.79	2.50 \pm 0.48
Stage 2	18.90 \pm 0.63	7.20 \pm 0.95
Control 1	10.70 \pm 1.4	6.60 \pm 0.72

Control 1, tap water, with cattails

Biomass production of *Typha latifolia*

Shoot production by *Typha* was substantially greater in the CW stages treating PW than in Control 1 (Table 5). It is possible that, although toxic elements (such as Pb) and excess salinity were present in the PW, the high concentrations of Ca, Mg, and K not only compensated for the presence of these substances but even increased plant growth. Vegetative growth of *Typha* is increased by addition of nutrients, and *Typha* can quickly form monotypic stands in fertile wetland systems (Svengsouk and Mitsch 2000; Woo et al. 2002).

Root biomass production in Stage 1 of the CW (2.5g) was markedly lower than that in Stage 2 and Control 1 (7.2 and 6.6g, respectively) (Table 5). It is possible that *Typha* root was negatively affected by excess EC, and by high Na and Pb concentrations, as this was the first stage in which plants contacted the PW. Many plants will form Pb-phosphate and

other Pb complexes in roots to prevent Pb uptake; however, root growth may be impaired (Blaylock and Huang 2000; Munzuroglu and Geckil 2002).

Metal uptake and accumulation by *Typha*

Sodium content of *Typha* shoots was 15.2 and 94.3mg·kg⁻¹ in Stages 1 and 2 of CW treatment, respectively (Table 6). This compares with 35.8mg·kg⁻¹ in Control 1. Most freshwater wetland macrophytes have low Na requirements, with concentrations in above-ground biomass below 2,000mg·kg⁻¹ (Boyd 1978).

Typha shoots contained 3.7 and 2.9mg·kg⁻¹ Cu in Stages 1 and 2, respectively (Table 6). This compares with 0.9mg·kg⁻¹ Cu in Control 1. Copper uptake by *Typha* roots was somewhat greater than that by shoots: the roots contained 5.8 and 3.6mg·kg⁻¹ in Stages 1 and 2, respectively. *Typha* roots in the Control contained 1.1mg·kg⁻¹.

Table 6. Metal content (mg·kg⁻¹) in *Typha latifolia* shoots and roots in constructed wetlands after 49 days ($n=3$, mean \pm standard deviation).

	K	Na	Cu	Pb
Shoots				
Stage 1	25.64 \pm 0.76	15.16 \pm 3.70	3.68 \pm 0.90	24.74 \pm 6.21
Stage 2	142.36 \pm 35.80	94.32 \pm 35.30	2.92 \pm 0.40	22.92 \pm 7.07
Control 1	105.54 \pm 4.76	35.78 \pm 1.40	0.90 \pm 0.20	1.45 \pm 0.20
Roots				
Stage 1	48.24 \pm 0.04	114.48 \pm 55.4	5.84 \pm 1.10	36.82 \pm 2.27
Stage 2	91.16 \pm 0.26	51.62 \pm 16.80	3.64 \pm 0.80	16.70 \pm 0.10
Control 1	40.86 \pm 0.26	16.74 \pm 2.10	1.1 \pm 0.50	2.12 \pm 0.10

Control 1, tap water, with cattails

Table 7. Bioconcentration Factors (BCF) and Transfer Factors (TF) for Na, Cu and Pb in *Typha latifolia*.

	Na	Cu	Pb
Bioconcentration Factors			
Shoots			
Stage 1	5.40	0.71	2.80
Stage 2	2.20	2.80	8.00
Roots			
Stage 1	40.90	1.10	4.19
Stage 2	1.20	3.50	5.82
Transfer Factors			
Stage 1	0.13	0.63	0.67
Stage 2	1.83	0.80	1.37
Control 1	2.14	0.77	0.81

Control 1, tap water, with cattails

In Stage 1, shoots of *Typha* accumulated almost as much Pb as did roots (24.7 versus 36.8mg·kg⁻¹, respectively) (Table 6). These concentrations of Pb were higher than concentrations considered phytotoxic (<5mg·kg⁻¹) by Markert (1992). Kabata-Pendias (2010) reported that the Pb content of plants varies between 0.05 and 3.0mg·kg⁻¹. Ye et al. (1997) found Pb in *Typha latifolia* leaves to range from 4.7 to 40.0mg·kg⁻¹; however, the amount in roots varied widely (25-3628mg·kg⁻¹). Carranza-Alvarez et al. (2008) reported Pb concentrations to range from 10 to 25mg·kg⁻¹, with maximum Pb accumulation in roots. Dunbabin and Bowmer (2002) reported that metal uptake by *Typha* was highest in roots, and that leaves had the lowest metal concentrations.

Typha tolerates increased levels of metals in tissue without serious physiological damage (Sasmaz et al. 2008). Many plants possess specific mechanisms to increase metal bioavailability and accumulate metals in roots (Romheld and Marschner 1986), for example, by blocking the binding of ions to ion carriers. This association often results in decreased plant growth (Pahlsson 1989); however, *T. latifolia* grew well and tolerated moderate Pb concentrations.

Bioconcentration Factor (BCF)

The bioconcentration factor reflects the progressive accumulation of metal from soil into a specific plant part (Branquinho et al. 2007). *Typha* shoots had BCF values for Cu ranging from 0.7 (Stage 1) to 2.8 (Stage 2), and for Pb ranging from 2.8 (Stage 1) to 8.0 (Stage 2) (Table 7). BCF values for shoots >1.0 indicates an ability of the plant to absorb and transport metals from sediment and subsequently store them in above-ground biomass (Baker et al. 1994; Brown et al. 1994; Wei et al. 2002). *Typha* roots had BCF >1 for Pb (4.19 in Stage 1 and 5.82 in Stage 2) (Table 7), indicating its ability to uptake Pb from sediments to roots.

Kaewtubtim et al. (2016) found BCF values of vetiver (*Vetiveria zizanioides*) leaves to range from 0.4-9.0 for Cu and 0.2-22.7 for Pb.

Transfer Factor (TF)

The transfer factor (TF) is used to estimate a plant's potential to transfer a metal between roots and aboveground parts (leaves and stems) for phytoremediation purposes. In the present study, *Typha* had a TF <1 for Pb in Stage 1 of the CW (Table 7). TF values <1 indicate low metal translocation to shoots. These results are consistent with those from terrestrial plants grown in other metal-contaminated soils (Meeinkuirt et al. 2012; Phaenark et al. 2009). In a study by Sasmaz et al. (2008), transfer factors for metals in *T. latifolia* ranged between 0.39 and 1.18. Kaewtubtim et al. (2016) found TFs in various species to range from 0.2 to 4.4 for Cu and 0.1 to 7.9 for Pb. Mojiri et al. (2013) found a TF of 1.0 using *Typha domingensis*, which was an effective accumulator plant for phytoremediation of several heavy metals.

The extent of metal accumulation depends upon both plant mechanisms and sediment chemistry (Chaudhuri et al. 2014). Aerial roots of many plant species diffuse oxygen into the substrate so that oxidation occurs in the rhizosphere, resulting in metal accumulation in fine roots (Chaudhuri et al. 2014; Machado et al. 2005; Marchand et al. 2011). The large surface area and high density of the *Typha* root system may encourage metal uptake, along with adsorption of metals (Lacerda et al. 1992, 1993; Marchand et al. 2011; Otero et al. 2006).

Typha had a TF of 1.4 for Pb in Stage 2 of the CW (Table 7). Plants with a TF >1 efficiently translocate metals from roots to above-ground parts (Murray et al. 2009). This effect is most likely due to efficient metal transporter systems (Zhao et al. 2003), and probably to sequestration of metals in leaf vacuoles and apoplast (Lasat et al. 2000). Baker (1981) and Zu et al.

(2005) reported TFs that were greater than 1.0 in metal accumulator species, and TFs that were typically <1.0 in metal excluder species. In the current study, *Typha latifolia* may be categorized as a Pb accumulator as it had TF and BCF values >1 (except for Stage 1, where the TF was 0.67).

SUMMARY

Saline and metal-enriched wastewater is a concern to oil and gas producing companies, many of whom rely on purchased water and recycled wastewater to support drilling operations. Recycling PW is a continuous, long-term process which requires a reliable and effective system. In a pilot-scale constructed wetland, the pH of PW increased markedly, from 4.2 to 7.0, and electrical conductivity decreased substantially. *Typha* plants grown in both Stages 1 and 2 produced substantial biomass, perhaps from receiving a large dose of Ca, Mg and K. Bioconcentration and transfer factors indicate that *Typha* is effective for metal removal from PWs. The present study may be of practical value to the oil and gas production industries, which generate large quantities of contaminated drilling wastewater.

ACKNOWLEDGEMENTS

Support from the Ball State University Sponsored Projects Administration is gratefully acknowledged.

REFERENCES

- ALL Consulting. 2009. Ground Water Protection Council, Modern Shale Gas Development in the United States: A Primer. U.S. Department of Energy, Office of Fossil Energy, Washington, DC.
- Allen, S.E., M.H. Grimshaw, J.A. Parkinson, C. Quarmby. 1974. Chemical Analysis of Ecological Materials (ed. S.E. Allen). 386p. Blackwell Scientific Publications, Oxford London, Edinburgh, Melbourne.
- APHA (American Public Health Association). 2017. Metals by flame atomic absorption spectrometry, Method 3111. Standard Methods for the Examination of Water and Wastewater. Washington, DC.
- Aqwatec. 2015. Produced water beneficial use case studies, Produced Water Treatment and Beneficial Use Information Center. <http://aqwatec.mines.edu/produced-water/assessbu/case/>, accessed January 27, 2017.
- Arroyo, P., G. Ansola, E. de Luis. 2010. Effectiveness of a full-scale constructed wetland for the removal of metals from domestic wastewater. *Water Air Soil Pollution* 210: 473-481.
- Baker, A.J.M. 1981. Accumulators and excluders—strategies in the response of plants to heavy metals. *Journal of Plant Nutrition* 3: 643-654.
- Baker, A.J.M., R.D. Reeves, A.S.M. Hajar. 1994. Heavy metal accumulation and tolerance in British populations of the metallophyte *Thlaspi caerulescens* J.&C Presl (Brassicaceae). *New Phytologist* 127: 61-68.
- Bandaruk, T., S. Waara. 2014. Metal, metalloid and sulphur sequestration in a constructed wetland for treatment of landfill leachate during 2003-2012. Conference Proceedings for Linneus-Eco Tech. Nov. 24-26, 2014, Kalmar, Sweden.
- Benko, K.L., J.E. Drewes. 2008. Produced water in the western United States: Geographical distribution, occurrence, and composition. *Environmental Engineering Science* 25: 239-246.
- Bergman, A., J.J. Heindel, S. Jobling, K.A. Kidd, R.T. Zoeller. 2013. State of the science of endocrine disrupting chemicals. World Health Organization. <http://www.who.int/ceh/publications/endocrine/en/>, accessed January 8, 2017.
- Black, C.A. 1965. Nitrogen-Total. *Methods of Soil Analysis. Chemical And Microbiological Properties*. American Society of Agronomy, Madison, WI.
- Blaylock, M.J., J.W. Huang. 2000. Phytoextraction of metals. In: *Phytoremediation of Toxic Metals: Using Plants to Clean Up the Environment* (ed. I. Raskin, B.D. Ensley), pp. 53-71. New York, John Wiley & Sons.
- Boyd, C.E. 1978. Chemical composition of wetland plants. In: *Freshwater Wetlands. Ecological Processes and Management Potential* (ed. R.E. Good, D.F. Whigham, R.L. Simpson), pp. 155-167. Academic Press, NY.
- Branquinho, C., H.C. Serrano, M.J. Pinto, M.A. Martins-Loucao. 2007. Revisiting the plant hyperaccumulation criteria to rare plants and earth abundant elements. *Environmental Pollution* 14: 437-443.
- Bray, R.H., L.T. Kurtz. 1945. Determination of total, organic, and available forms of phosphorus in soils. *Soil Science* 59: 39-45.
- Brisson, J., F. Chazarenc. 2009. Maximizing pollutant removal in constructed wetlands: Should we pay more attention to macrophyte species selection? *Science of the Total Environment* 407: 3923-3930.
- Brown, S.L., R.L. Chaney, J.S. Angle, A.J.M. Baker. 1994. Phytoremediation potential of *Thlaspi caerulescens* and bladder campion for zinc and cadmium-contaminated soil. *Journal of Environmental Quality* 23: 1151-1157.
- Bureau, R.G. 1982. Lead. In: *Methods of Soil Analysis. Part 2*. (ed. A.L. Page, R.H. Miller, D.R. Keeney), pp. 347-365. American Society of Agronomy, Madison, WI.
- Burton, G.A., K.J. Scott. 1992. Assessing contaminated aquatic sediments. *Environmental Science and Technology* 26: 2068-2075.
- Carranza-Alvarez, C., A.J. Alonso-Castro, M.C. Alfaro-De La Torre, R.F. Garcia-De La Cruz. 2008. Accumulation and distribution of heavy metals in *Scirpus americanus* and *Typha latifolia* from an artificial lagoon in San Luis Potosi, Mexico. *Water Air Soil Pollution* 188: 297-309.
- Chaudhuri, P., B. Nath, G. Birch. 2014. Accumulation of trace metals in grey mangrove *Avicennia marina* fine nutritive roots: The role of rhizosphere processes. *Marine Pollution Bulletin* 79: 284-292.
- Chung, A.K.C., Y. Wu, N.F.Y. Tam, N.F. Wong. 2008. Nitrogen and phosphate mass balance in a sub-surface flow constructed wetland for treating municipal wastewater. *Ecological Engineering* 32: 81-89.
- Clark, C.E., J.A. Veil. 2009. Produced water volumes and management practices in the United States. *Environmental Science Division, Argonne National Laboratory*. 64 p. ANL/EVS/R-09/1.
- Coon, W.F., J.M. Bernard, F.K. Seischab. 2000. Effects of a cattail wetland on water quality of Irondequoit Creek near Rochester, New York. *Water-Resources Investigations Report 2000-4032*. <https://pubs.usgs.gov/wri/2000/4032/wri20004032.pdf>, accessed April 19, 2017.
- Deng, H., Z.H. Ye, M.H. Wong. 2004. Accumulation of lead, zinc, copper and cadmium by 12 wetland plant species thriving in metal-contaminated sites in China. *Environmental Pollution* 132: 29-40.
- Dunbabin, J.S., K.H. Bowmer. 1992. Potential use of constructed wetlands for treatment of industrial wastewaters containing metals. *The Science of the Total Environment* 111: 151-168.

- Earthworks. 2015. Hydraulic Fracturing 101. Hydraulic fracturing—What it is. https://www.earthworksaction.org/issues/detail/hydraulic_fracturing_101#.WG6gxH0aJ-Y, accessed January 27, 2017.
- Fontenot, B.E., L.R. Hunt, Z.L. Hildenbrand, D.D. Carlton, Jr., H. Oka, J.L. Hopkins, A. Osorio, B. Bjorndal, Q.H. Hu, K.A. Schug. 2013. An evaluation of water quality in private drinking water wells near natural gas extraction sites in the Barnett Shale formation. *Environmental Science & Technology* 47: 10032–10040.
- FracFocus. 2015. Hydraulic fracturing the process. <https://fracfocus.org/hydraulic-fracturing-how-it-works/hydraulicfracturing-process>, accessed January 12, 2017.
- Fritioff, A., M. Greger. 2006. Uptake and distribution of Zn, Cu, Cd and Pb in an aquatic plant *Potamogeton natans*. *Chemosphere* 63: 220–227.
- Gersberg, R.M., S.R. Lyon, B.V. Elkins, C.R. Goldman. 1984. The removal of heavy metals by artificial wetlands. In: *Proceedings of the Conference on the Future of Water Use*, pp. 639–648.
- Gottschall, N., C. Boutin, A. Crolla, C. Kinsley, P. Champagne. 2007. The role of plants in the removal of nutrients at a constructed wetland treating agricultural (dairy) wastewater, Ontario, Canada. *Ecological Engineering* 29: 154–163.
- Helmke, P.A., D.L. Sparks. 1996. Lithium, sodium, potassium, rubidium, and cesium. In: *Methods of Soil Analysis. Part 3. Chemical Methods* (ed. J. Bartels, J.M. Bigham), pp. 555–574. Soil Science of America, Madison, WI.
- Igunnu, E.T., G.Z. Chen. 2014. Produced water treatment technologies. *International Journal of Low-Carbon Technologies* 9: 157–177.
- Jesus, J.M., C.C. Calheiros, P.M. Castro, M.T. Borges. 2014. Feasibility of *Typha latifolia* for high salinity effluent treatment in constructed wetlands for integration in resource management systems. *International Journal of Phytoremediation* 16: 334–346.
- Kabata-Pendias, A. 2010. *Trace Elements in Soils and Plants*. 548 p. CRC Press, Boca Raton, FL.
- Kadlec, R., S. Roy, R. Munson, S. Charlton, W. Brownlie. 2010. Water quality performance of treatment wetlands in the Imperial Valley, California. *Ecological Engineering* 36: 1093–1107.
- Kaewtubtim, P.W. Meeinkuir, S. Seepom, J. Pichtel. 2016. Heavy metal phytoremediation potential of mangrove plant species of Pattani Bay, Thailand. *Applied Ecology* 14: 367–382.
- Kassotis, C.D., D.E. Tillitt, C.-H. Lin, J.A. McElroy, S.C. Nagel. 2015. Endocrine-disrupting chemicals and oil and natural gas operations: potential environmental contamination and recommendations to assess complex environmental mixtures. *Environmental Health Perspectives* <https://ehp.niehs.nih.gov/wp-content/uploads/advpub/2015/8/ehp.1409535.acco.pdf>, accessed January 27, 2017.
- Khan, S., I. Ahmad, M.T. Shah, S. Rehman, A. Khaliq. 2009. Use of constructed wetland for the removal of heavy metals from industrial wastewater. *Journal of Environmental Management* 90: 3451–3457.
- Khatib, Z., P. Verbeek. 2003. Water to value—produced water management for sustainable field development of mature and green fields. *Journal of Petroleum Technology*: 26–28.
- Kim, K.R., G. Owens, R. Naidu, K.H. Kim. 2008. Influence of vetiver grass (*Vetiveria zizanioides*) on rhizosphere chemistry in long-term contaminated soils. *Korean Journal of Soil Science and Fertilizer* 41: 55–64.
- Klucakova, M. 2012. Comparative study of binding behaviour of Cu(II) with humic acid and simple organic compounds by ultrasound spectrometry. *The Open Colloid Science Journal* 5: 5–12.
- Knox, A.S., E.A. Nelson, N.V. Halverson, J.B. Gladden. 2010. Long-term performance of a constructed wetland for metal removal. *Soil and Sediment Contamination* 19: 667–685.
- Kröpfelová, L., J. Vymazal, J. Švehla, J. Štichová. 2009. Removal of trace elements in three horizontal sub-surface flow constructed wetlands in the Czech Republic. *Environmental Pollution* 157: 1186–1194.
- Lacerda, L.D., M.A. Fernandez, C.F. Calazans, K.F. Tanizaki. 1992. Bioavailability of heavy metals in sediments of two coastal lagoons in Rio de Janeiro, Brazil. *Hydrobiologia* 228: 65–70.
- Lacerda, L.D., C.E.V. Carvalho, K.F. Tanizaki, A.R.C. Ovalle, C.E. Rezende. 1993. The biogeochemistry and trace metals distribution of mangrove rhizospheres. *Biotropica* 25: 252–257.
- Lesage, E. 2006. Behaviour of heavy metals in constructed treatment wetlands. PhD thesis. 247 p. Department of Applied Analytical and Physical Chemistry, Ghent University, Belgium.
- Lasat, M.M., N.S. Pence, D.F. Garvin, S.D. Ebbs, L.V. Kochian. 2000. Molecular physiology of zinc transport in the Zn hyperaccumulator *Thlaspi caerulescens*. *Journal of Experimental Botany* 51: 71–79.
- Machado, W., B.B. Gueiros, S.D. Lisboa-Filho, L.D. Lacerda. 2005. Trace metals in mangrove seedlings: role of iron plaque formation. *Wetlands Ecology and Management* 13: 199–206.
- Maguire-Boyle, S.J., A.R. Barron. 2014. Organic compounds in produced waters from shale gas wells. *Environmental Science Processes & Impacts* 16: 2237–2248.
- Maine, M.A., N. Sune, H. Hadad, G. Sanchez, C. Bonetto. 2006. Nutrient and metal removal in a constructed wetland for wastewater treatment from a metallurgic industry. *Ecological Engineering* 26: 341–347.
- Marcellus. 2010. List of 78 Chemicals Used in Hydraulic Fracturing Fluid in Pennsylvania. <http://marcellusdrilling.com/2010/06/list-of-78-chemicals-used-in-hydraulic-fracturing-fluid-in-pennsylvania>, accessed August 23, 2016.
- Marchand, C., M. Allenbach, E. Lallier-Vergès. 2011. Relationships between heavy metals distribution and organic matter cycling in mangrove sediments (Conception Bay, New Caledonia). *Geoderma* 160: 444–456.
- Markert, B. 1992. Presence and significance of naturally occurring chemical elements of the periodic system in the plant organism and consequences for future investigations on inorganic environmental chemistry in ecosystems. *Vegetatio* 103: 1–30.
- McNaughton, S.J., T.C. Folsom, T. Lee, F. Park, C. Price, D. Roeder, J. Schmitz, C. Stockwell. 1974. Heavy metal tolerance in *Typha latifolia* without the evolution of tolerant races. *Ecology* 55: 1163–1165.
- Meeinkuir, W., M. Kruatrachue, J. Pichtel, T. Phusantisampan, P. Saengwilai. 2016. Influence of organic amendments on phytostabilization of Cd-contaminated soil by *Eucalyptus camaldulensis*. *ScienceAsia* 42: 83–91.
- Meeinkuir, W., P. Pokethitiyook, M. Kruatrachue, P. Tanhan, R. Chaiyarat. 2012. Phytostabilization of lead by various tree species using pot and field trial experiments. *International Journal of Phytoremediation* 14: 925–938.
- Miretzky, P., A. Saralegui, A.F. Cirelli. 2004. Aquatic macrophytes potential for the simultaneous removal of heavy metals (Buenos Aires, Argentina). *Chemosphere* 57: 997–1005.
- Mojiri, A., H.A. Aziz, M.A. Zahed, S.Q. Aziz, M.R.B. Selamat. 2013. Phytoremediation of heavy metals from urban waste leachate by southern cattail (*Typha domingensis*). *International Journal of Scientific Research in Environmental Sciences* 1: 63–70.
- Moshiri, G.A. 1993. *Constructed Wetlands for Water Quality Improvement*. 633 p. CRC Press, Boca Raton, FL.
- Mungur, A.S., R.B.E. Shutes, D.M. Revitt, M.A. House. 1997. An assessment of metal removal by a laboratory scale wetland. *Water Science and Technology* 35: 125–133.
- Munzuroglu, O., H. Geckil. 2002. Effects of metals on seed germination, root elongation, and coleoptile and hypocotyl growth in *Triticum aestivum* and *Cucumis sativus*. *Archives of Environmental Contamination and Toxicology* 43: 203–213.
- Murray Gulde, C., J.E. Heatley, T. Karanfil, J.H. Rodgers Jr., J.E. Myers. 2003. Performance of a hybrid reverse osmosis-constructed wetland treatment system for brackish oil field produced water. *Water Research* 37: 705–713.
- Murray, H., K. Thompson, S.M. Macfie. 2009. Site- and species-specific patterns of metal bioavailability in edible plants. *Botany* 87: 702–711.

- NPC (National Petroleum Council). 2011. Management of Produced Water from Oil and Gas Wells, Paper 2–17. NPC North American Resource Development Study. https://www.npc.org/Prudent-Development-Topic-Papers/2-17_Management-of-Produced-Water-Paper.pdf. accessed January 27, 2017.
- O'Rourke, D., S. Connolly. 2003. Just oil? The distribution of environmental and social impacts of oil production and consumption. *Annual Review of Environmental Resources* 28: 587–617.
- Osmolovskaya, N.G., V.V. Kurilenko. 2001. Biogeochemical aspects of heavy metals phytoindication in urban aquatic systems. In: *Biogeochemical Processes and Cycling of Elements in the Environment* (ed. J. Weber), pp. 217–218. Polish Society of Humic Substances, Wrocław.
- Otero, A., S. Fiol, J. Antelo, F. Arce. 2015. Studying and modeling the effect of organic matter on the sorption of inorganic ions on goethite. *Goldschmidt 2015. Abstracts*, <http://goldschmidt.info/2015/uploads/abstracts/finalPDFs/2365.pdf> accessed December 14, 2016.
- Otero, X.L., T.O. Ferreira, P. Vida-Torrado, F. Macias. 2006. Spatial variation in pore water geochemistry in a mangrove system (Pai Matos island, Cananea-Brazil). *Applied Geochemistry* 21: 2171–2186.
- Pahlsson, A.M.B. 1989. Toxicity of heavy metals (Zn, Cu, Cd, Pb) to vascular plants. *Water Air Soil Pollution* 47: 287–319.
- Panich-Pat, T., P. Pokethitiyook, M. Kruatrachue, E.S. Upatham, P. Srinives, G.R. Lanza. 2004. Removal of lead from contaminated soils by *Typha angustifolia*. *Water, Air and Soil Pollution* 155: 159–171.
- Pantip, K., N. Suwanchai. 2004. Constructed treatment wetland: a study of eight plant species under saline conditions. <http://dspace.library.tu.ac.th/handle/3517/1435>, accessed January 27, 2017.
- Phaenark, C., P. Pokethitiyook, M. Kruatrachue, C. Ngersansaruay. 2009. Cd and Zn accumulation in plants from the Padaeng zinc mine area. *International Journal of Phytoremediation* 11: 479–495.
- Pichtel, J. 2016. Oil and gas production wastewater: Soil contamination and pollution prevention. *Applied and Environmental Soil Science*. p. 1–24. downloads.hindawi.com/journals/aess/aip/2707989.pdf, accessed December 14, 2016.
- Pip, E., J. Stepaniuk. 1992. Cadmium, copper and lead in sediments. *Archiv für Hydrobiologie* 124: 337–355.
- Rezvani, M., F. Zaefarian. 2011. Bioaccumulation and translocation factors of cadmium and lead in *Aeluropus litoralis*. *Australian Journal Agricultural Engineering* 2: 114–119.
- Romheld, V., H. Marschner. 1986. Mobilization of iron in the rhizosphere of different plant species. *Advances in Plant Nutrition* 2: 155–204.
- Sasmaz, A., E. Obek, H. Hasar. 2008. The accumulation of heavy metals in *Typha latifolia* L. grown in a stream carrying secondary effluent. *Ecological Engineering* 33: 278–284.
- Skinner, K., N. Wright, E. Porter-Goff. 2007. Mercury uptake and accumulation by four species of aquatic plants. *Environmental Pollution* 145: 234–237.
- Svengsouck, L.J., W.J. Mitsch. 2000. Dynamics of mixtures of *Typha latifolia* and *Schoenoplectus tabernaemontani* in nutrient-enrichment wetland experiments. *The American Midland Naturalist* 145: 309–324.
- USDA-NRCS (US Department of Agriculture-Natural Resources Conservation Service). 2015. A Handbook of Constructed Wetlands <https://www.epa.gov/sites/production/files/2015-10/documents/constructed-wetlands-handbook.pdf>. pp 6, accessed December 14, 2016.
- USDA-NRCS. 2017. Soil Survey for Delaware County, Indiana. <https://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx>, accessed December 01, 2017.
- USEPA (United States Environmental Protection Agency). 2004. Chapter 2: Guidelines for water reuse. EPA/625/R-04/108, Washington, D.C.
- Veil, A., M.G. Ruder, D. Elcock, R.J. Redweik, Jr. 2004. A white paper describing produced water from production of crude oil, natural gas, and coal bed methane. 87 p. United States Department of Energy, National Energy Technology Laboratory, Contract W-31-109-Eng-38.
- Vymazal, J. 2005. Horizontal sub-surface flow and hybrid constructed wetlands systems for wastewater treatment. *Ecological Engineering* 25: 478–490.
- Walker, D.J., S. Hurl. 2002. The reduction of heavy metals in a stormwater wetland. *Ecological Engineering* 18: 407–414.
- Walkley, A., I.A. Black. 1934. An examination of Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Science* 37: 29–37.
- Warner, N.R., R.B. Jackson, T.H. Darrah, S.G. Osborn, A. Down, K. Zhao, A. White, A. Vengosh. 2012. Geochemical evidence for possible natural migration of Marcellus formation brine to shallow aquifers in Pennsylvania. *Proceedings of the National Academy of Sciences of the United States of America* 109: 11961–11966.
- Wei, C.Y., T.B. Chen, Z.C. Huang. 2002. Cretan bake (*Pteris cretica* L.): an arsenic-accumulating plant. *Acta Ecologica Sinica* 22: 777–782.
- Weis, J.S., P. Weis. 2004. Metal uptake, transport and release by wetland plants: Implications for phytoremediation and restoration review. *Environment International* 30: 685–700.
- Woo, I., J.B. Zedler. 2002. Can nutrients alone shift a sedge meadow towards dominance by the invasive *Typha X Glauca*? *Wetlands* 22: 509–521.
- Ye, Z.H., A.J.M. Baker, M.H. Wong, A.J. Willis. 1997. Zinc, lead and cadmium tolerance, uptake and accumulation by *Typha latifolia*. *New Phytologist* 136: 469–480.
- Zhao, F.J., E. Lombi, S.P. Mc Grath. 2003. Assessing the potential for zinc and cadmium phytoremediation with the hyperaccumulator *Thlaspi caerulescens*. *Plant and Soil* 249: 37–43.
- Zhou, L.X., J.W.C. Wong. 2001. Effect of dissolved organic matter from sludge and sludge compost on soil copper sorption. *Journal of Environmental Quality* 30: 878–883.
- Zu, Y.Q., J. Li, Y. Chen, H.Y. Chen, L. Qin, C. Schwartz. 2005. Hyperaccumulation of Pb, Zn and Cd in herbaceous grown on lead-zinc mining area in Yunnan, China. *Environment International* 31: 755–762.