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Plants and soil amendments for remediation of soil affected by synthetic oil and gas production wastewater

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ABSTRACT

Oil and gas production water (PW) is brought to the surface when hydrocarbon reservoirs deep within geologic strata are extracted. Large volumes of PW present environmental challenges when released to the land surface due to high levels of salinity and potentially toxic elements. The effects of PW on soil chemical properties and plant response were investigated in both growth chamber and field studies. In the growth chamber, wheat (*Triticum aestivum*) and red clover (*Trifolium repens*) were grown in soil which was flooded with synthetic PW. The PW was enriched with several metals (Na, Cu, Cr, Pb) and had an acidic pH (2.5) and EC of 33,650 dSm^{-1}. Soil amendments included food waste compost, composted biosolids, gypsum ($CaSO_4$) and NPK 10-10-10 fertilizer. Metal concentrations in soil and plants were determined using flame atomic absorption spectrophotometry. The food waste compost provided for maximal uptake by clover of Cu, Cr and Pb compared to all other amendments. In several soil treatments both wheat and clover behaved as metal hyperaccumulators having high bioconcentration factors (BCF, ratio of metal concentrations of plant tissue to soil). Clover was the most efficient in accumulating Cu and Cr in shoots (BCF = 22.2 and 30.6, respectively). Greatest metal uptake in both plant species occurred in either the biosolids or compost treatment. In a field study, plots were flooded with synthetic PW and grown to corn (*Zea mays*) and a turf mixture (Kentucky bluegrass, *Poa pratensis* and perennial ryegrass, *Lolium perenne*). Both corn and turf accumulated substantial soil Cu and Pb. Corn experienced significant die-off; however, turf survived the PW application. Turf mixtures, clover and/or wheat may be suitable for phytoremediation of PW-affected soil. Addition of organic amendments to soil may enhance metal uptake by plants.

INTRODUCTION

Oil and gas production water (PW), also known as oil field brine, flowback water, or formation water, is generated as a by-product of oil and gas production (Roach et al., 1993; Ramirez, 2002; Veil et al., 2004). A large operating oil field can produce several hundred thousand barrels of water daily (Collins, 1975). Approximately 21 billion barrels of produced water were generated in 2012 by on-shore and off-shore facilities (Produced Water Society, 2016), 87% of which originated from oil production activities (Clark and Veil, 2009). As much as 15% to 100% of PW may be returned to the surface and require disposal (Wang et al., 2014; Rahm, 2011). Produced water has historically been disposed by deep injection into underground injection control (UIC) class II wells (US EPA, 2017). Other management methods include placement in evaporation ponds, application to fields, spreading on roads, and/or treatment and reuse for future oil and gas operations (Wiseman, 2008; Deutch et al., 2001; Gilmore et al., 2014; Lee et al., 2011). The determination of whether PW can be used for agricultural purposes (i.e., irrigation, land application, stock watering) depends both on the quality of the produced water and on the characteristics of the recipient site (Colorado, 2009). In Southern California, 21 million gallons of oil field water are recycled daily for irrigation of 45,000 acres of fruit trees and other crops (Cart, 2014). Thousands of acres in the Powder River Basin (WY) have been transformed to productive agricultural land using produced water (Aqwatec, 2015; deJoia, 2002; Adams, 2011; Bern et al., 2013). At some drilling sites, however, over-application of drilling fluid waste has resulted in contaminated soil that could not adequately support vegetation to meet state regulatory requirements for well site closure (Wolf et al., 2015).

Contamination of soil by PW can also occur through spills during drilling and fracturing processes, during transport by truck or through wastewater pipelines, failure of well casings, equipment failures and corrosion of pipes and tanks (Pichtel, 2016). Between 2009 and 2013 over 1900 spills were documented in Colorado (NRDC, 2015). In 2013, spills at 550 active wells were reported in Colorado. An analysis of permitted Pennsylvania wells shows a spill rate of 2% (103 of 5,580 active wells) (NRDC, 2015). More than 640 spills from oil and gas wells occurred in 2015 (Soraghan and King, 2016).

The composition of PW varies widely and is a function of geologic setting and location of the producing formation, depositional environment of the formation, depth and age of the well, and type of hydrocarbon being produced (Rice and Nuccio, 2000; Veil et al., 2004; Benko and Drewes, 2008). Common naturally-occurring constituents of concern in PW include organic compounds, total suspended solids (Veil et al., 2004; Benko and Drewes, 2008; Wang et al., 2014), radionuclides, salts, and metals (Kemmer, 1988; Knight et al., 1999; Veil et al., 2004). Copper (Cu), chromium (Cr), lead (Pb) and other metals have been identified in PW from oil and gas operations (US EPA, 1982). In addition, PW can contain chemical additives that were used during oil production (Veil et al., 2004). For example, Cu may be added to breaker fluids, which decrease fluid viscosity, and Cr occurs in cross-linked gels to provide better transport of additives. Several components of PW, when present in high concentrations, can pose threats to terrestrial plants when discharged, for example, when used for irrigation or accidentally via pipeline rupture.

Soils near well spills are affected by excess salinity and high concentrations of sodium (Na) (Sontag and Gebeloff, 2014; Alberta, 2001) and other metals. Salinity and metallic contaminants are linked with a number of adverse effects to plants including decreased chlorophyll content and stomatal conductance, decreased enzyme activity, chlorosis, reduced shoot and root length, inhibition of germination, and reduced flowering and seed production. (Sharma and Sharma, 1993; Panda and Patra, 2000; Hussain et al., 2013). The degree of toxicity depends on the properties of the contaminant and its concentration (Duruibe et al. 2007).

To sustainably remediate metallic contamination of soil, effective and low-cost technologies are required. Phytoremediation has become an attractive option for treatment of metal-affected soils, as it is a low-cost, solar-driven green technology which imparts few adverse environmental effects (Marchiol et al. 2013). Phytoremediation is commonly divided into six categories. Phytoextraction involves the uptake of metals by plant roots followed by translocation to shoots (Dary et al. 2010). In phytostabilization, extensive plant root systems sorb soil contaminants, thus preventing leaching or lateral migration. In rhizosphere biodegradation, microorganisms residing in the plant root zone enhance biological degradation of contaminants. Phytovolatilization involves plants taking up water containing organic contaminants and releasing them into the air via the stomata. In phytodegradation, plants metabolize and destroy contaminants within their tissue (Pichtel, 2007). Hydraulic control involves the use of trees to control groundwater movement.

A range of organic materials has been evaluated as supplements for enhancing phytoremediation (Gholami et al. 2012; Wang et al. 2013). Examples include animal manures, humified lignite (Saengwilai et al., 2017), composted food waste, composted biosolids and others. Inorganic compounds such as gypsum ($CaSO_4$) may stabilize Na-enriched soil, improve aggregation, and in some cases immobilize heavy metals (Illera et al., 2004). The utilization of organic amendments has been found to improve the metal accumulating potential of plants, depending on plant species and amendment properties (Zubillaga et al. 2012; Wiszniewska et al. 2016). In metal-contaminated soils, amendments have increased plant tolerance and altered rates of metal accumulation (Walker et al. 2004; Chaiyarat et al. 2011). The presence of macronutrients and micronutrients in organic materials stimulates plant biomass production. Additionally, organic amendments improve soil aeration, water infiltration, and water and nutrient holding capacity, which increase crop yield (Paulin, 2005).

Many papers have addressed the effects of oil and gas production wastewaters on the quality of groundwater and surface water; however, significantly less information is available on the effects of PWs to soil productivity. Furthermore, reclamation of PW-affected soils has received minimal attention in the scientific literature. The present study investigates the influence of soil amendments (composted biosolids, composted food waste, calcium sulfate, NPK fertilizer) and of two plants, wheat (*Triticum aestivum*) and red clover (*Trifolium repens*), on soil chemical properties after contamination from PW in growth chamber experiments. Additionally, the potential for bioaccumulation of soil metals is assessed. In a field study, metal uptake by corn (*Zea mays* L.) and mixed turf species from PW was investigated.

MATERIALS AND METHODS

Properties of synthetic PW

Synthetic PW was prepared using reagent grade chemicals (Sigma) mixed with deionized (DI) water. Salts included $AlCl_3$, AlF_3, $Al(NO_3)_3$, $CuSO_4$, $MgCO_3$, $Mg(NO_3)_2$, K-acetate, KCl, Na-acetate, Na_2CO_3, and NaCl. Hydrocarbons included diesel fuel, ethanol, ethylene glycol, glycerol, hexane, 2-propanol, and toluene. Solution pH was adjusted dropwise using NaOH or H_3PO_4 (Alalade et al. (2017);

Maguire-Boyle and Barron (2014); Marcellus (2016); FracFocus (2015).

The pH of the PW was determined using a glass electrode pH meter (Accumet® model AP115, Thermo Fisher Scientific, Waltham MA USA) and electrical conductivity with an EC meter (Hanna instruments model HI 993310, Woonsocket, RI, USA). Total Na, Cu, Cr and Pb concentrations were determined via flame atomic absorption spectrophotometry (FAAS) (Perkin Elmer AAnalyst 200, Shelton, CT, USA), and K via flame atomic emission spectrophotometry.

Characterization of soil

Soil pH was analyzed using a glass electrode pH meter (Accumet® AP115) on a 1:10 mixture of soil:DI H_2O and electrical conductivity 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 determined by the Bray-II method (Bray and Kurtz, 1945) and extractable K via flame atomic emission spectrophotometry (Perkin Elmer AAnalyst 2000) after NH_4OAc extraction (Sparks, 1996). Extractable metal (K, Na, Cu, Cr, Pb) concentrations were analyzed after DTPA extraction; samples were extracted with 0.05 M diethylene triamine pentaacetic acid (DTPA) for 2 h on an oscillating shaker (120 osc./min). The suspensions 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).

Growth Chamber Study

Treatments

In the growth chamber, plastic pots containing 1 kg soil were packed with Glynwood silt loam (fine, illitic mesic Aquic Hapludalf). Soil was obtained from the surface 20 cm from agricultural fields in central Indiana, air-dried for 7 days, and sieved to pass a 2-mm mesh sieve.

Soil was saturated with PW and allowed to incubate at ambient temperatures for 7 days. The soil was subsequently amended with either composted municipal wastewater biosolids (1:20 w/w ratio), composted food waste (hereafter termed ‘compost’) (1:20 ratio), calcium sulfate (50 g kg^{-1}), or 10-10-10 NPK fertilizer (15 g kg^{-1}). The biosolids were obtained from the Southwesterly Compost Facility, Columbus, OH. Composted food waste was prepared using a mixture of fruit and vegetable scrap which was composted for 60 d. Turning was provided twice per week. Amendments were mixed with soil using a stainless steel rod. The experimental design was a randomized complete block with four replications.

The soil was cultivated with wheat (*Triticum aestivum*) and red clover (*Trifolium repens*). Wheat was sown at 10 seeds per pot. Clover was sown into pots at a rate of approx. 14 kg ha^{-1}. Pots were kept in a growth chamber with a 16/8 h light/dark cycle, a day/night temperature of 22/17°C, and a relative humidity of 70% (Joner and Leyval, 2001). Plants were watered with tap water to 75% of field capacity for a total of 90 days.

After 90 days incubation, soil material was collected from each pot and analyzed for pH and electrical conductivity. Samples were extracted with 0.5 M DTPA and analyzed for concentrations of Na, Cu, Cr and Pb as described above. Plant tissue was harvested by cutting at the soil surface using a stainless steel Exacto™ knife.

Plant tissue analysis

Plant tissue was oven-dried at 80°C for 24 h and dry weight was recorded. Dried 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% Baker analyzed®) HNO_3 was added and the mixture digested using a MARS microwave digestion apparatus. Total metal (Na, Cu, Cr, Pb) concentrations of the digests were determined using FAAS.

Several parameters were calculated to determine metal uptake and translocation by both plant species. The bioconcentration factor (BCF) is defined as the ratio of metal concentration in the shoot to the extractable metal concentration in rhizosphere soil (Rezvani and Zaefarian, 2011):

$$\mathrm{BCF}_{\mathrm{shoot}} = C_{\mathrm{shoot}}/C_{\mathrm{soil}}$$

where C_{shoot} is metal concentration in shoot, and C_{soil} is the metal concentration in soil.

Metal uptake indicates metal concentration in plant shoots (Meeinkuirt et al. 2016):

$$\mathrm{M\ uptake} = \mathrm{M}_{\mathrm{shoot}} \times \mathrm{plant\ dry\ biomass}$$

where M is the concentration in shoots.

Field study

Plots measuring 2 x 3 m were prepared on Glynwood soil in Indiana, USA. Plots received N, P and K at 140, 200 and 120 kg ha^{-1}, respectively. Plant treatments consisted of corn (*Zea mays* L.); mixed turf species (Kentucky bluegrass, *Poa pratensis*; and perennial ryegrass, *Lolium perenne*); and no vegetation. Plants were watered by rainfall only. Plants were allowed to grow for a total of 8 weeks prior to application of PW.

The synthetic PW was applied to the plots at the rate of 12 L m^{-2} as a topdress. Control plots were grown to the same plant species on non-contaminated soil.

Plots were sampled four weeks after PW application. Soil material was collected from each plot from an upper (0-20 cm) and a lower horizon (20-40 cm) using a stainless steel sampling tool. In the laboratory, soil material for each treatment was homogenized, air-dried, and sieved to pass a 2-mm mesh sieve.

Entire plants were removed from the soil and separated into shoots and roots using an Exacto™ knife. In the laboratory, roots were washed with tap water to remove attached soil particles and then rinsed with DI water.

Soil analysis

Soil chemical properties (pH, extractable K, Na, Cu, Cr and Pb concentrations) were analyzed as described for the growth chamber study.

Plant tissue analysis

Plant tissue was oven-dried at 80°C for 24 h and dry weight was recorded. Dried plant tissue was microwave-digested and tested for Na, Cu, Cr and Pb concentrations as described for the growth chamber study.

Quality Control

To assess analytical precision, soil standard reference material (NIST SRM® 2710a Montana soil) was used to determine accuracy and precision of the sample data. Percent recovery for the soil samples was in the range of 95.4–107.5%. Flame atomic absorption spectrophotometer detection limits were as follows: 0.3, 1.5, 3, 15 and 3 ugL^{-1} for Na, Cu, Cr, Pb and K, respectively.

Statistical analysis

One-way analysis of variance (ANOVA) was performed for comparing data among plant and soil treatments using SigmaStat™; least significant difference (LSD) was used for post-hoc comparisons ($p \leq 0.05$).

RESULTS AND DISCUSSION

Properties of PW

The synthetic PW had a pH of 2.5 and an EC of 33,650 µS/cm (Table 1). The pH of concentrated brines usually is less than 7.0. Igunnu and Chen (2012) measured a pH of 4.3 and an EC of 4,200 µS/cm in oil field produced water. Produced water discharges from oil platforms in the North Sea are reported to have pH levels of 6-7.7, while those from gas platforms are more acidic (approx. 3.5-5.5) (Jacobs et al., 1992). In some brines with little buffering capacity, pH was as low as 2.9 (Produced Water Society, 2016). In contrast, however, US DOE (2006) noted a pH of 8.1 in PW.

Table 1. Selected chemical and physical properties of synthetic produced water. (*n* = 3)

Parameter	Value
pH	2.5±0.01
EC, dS m^{-1}	33,650±4900
Specific gravity	1.81±0.44
Metals, mg l^{-1}	
K	1343.5±19.8
Na	2011.5±65.9
Cu	921.7±3.7
Cr	444.0±25.0
Pb	127.3±6.8

Concentrations of Na, Cu, Cr and Pb were 2011, 921, 444 and 127 mg l^{-1} respectively (Table 1). US DOE (2006) measured 486 mg l^{-1} Na in PW, and Igunnu and Chen (2012) measured Na concentrations ranging from 132-97,000 mg l^{-1}. The US Geological Survey Produced Waters Database (USGS, 2016) recorded Cu and Pb concentrations up to 75 mg l^{-1} and 8187 mg l^{-1}, respectively. In contrast, Igunnu and Chen (2012) found Cu concentrations to range from < 0.02 to 1.5 mg l^{-1} and Pb from 0.002 to 8.8 mg l^{-1}. Such variations in pH and concentrations of other PW consitutents are expected, given the wide range of formulations for preparing hydraulic fracturing fluids as well as the varying geochemistry of subsurface water (Aqwatec, 2015).

Growth chamber study

Soil and Amendment Properties

The pH of the Glynwood soil was 6.4 (Table 2), total C and N contents were 3.9 and 0.36%, respectively. Levels of extractable Cu, Cr and Pb (5.0, 4.9 and 3.7 mg kg^{-1}, respectively) were consistent with those for non-contaminated soil. Soil texture was silt loam. The pH of the biosolids and compost were 6.8 and 7.9, respectively, and TOC levels were 42.2 and 35.9%, respectively. Metal concentrations in both materials were low, with the exception of Cu in the biosolids (236 mg kg^{-1}). Sodium concentrations measured 310 and 255 mg kg^{-1} in the biosolids and compost, respectively.

Soil properties after treatment

In the Glynwood soil grown with wheat, pH ranged from 5.6 in the $CaSO_4$ treatment to 6.2 in the control (Table 3). In the clover-treated soils, pH values ranged from 5.5 (NPK treatment) to 5.9 (biosolids). The PW in this study was extremely acidic (pH 2.2); however, Glynwood soil is formed upon dolomitic limestone deposits (USDA-NRCS, 2017) which imparts substantial acid buffering capacity. No soil pH values were significantly different ($p > 0.05$) as a function of plant or soil treatment.

Soil EC values were lowest in the non-amended soil (7.3 and 9.6 dS/m, respectively), and highest in the NPK (29.0 dS/m and 35.9 dS/cm, respectively). The NPK fertilizer was provided as a soluble salt, which accounts for the high EC values.

Soil Na concentrations averaged 1611 and 1621 mg kg in the wheat and clover treatments, respectively (Table 3). No soil Na values were significantly different ($p < 0.05$) for any soil treatment.

Table 2. Selected chemical and physical properties of the Glynwood soil, and biosolids and food compost amendments.

Parameter	Glynwood	Biosolids	Compost
pH	6.4	6.8	7.9
EC, µS/cm^{-1}	1,100	4,500	3,350
TOC*, %	3.9	42.2	35.9
Total N, %	0.36	1.1	1.8
Bray-1 P, mg kg^{-1}	13.0	4.2	2.7
Extractable (mg kg^{-1})			
K	86.9	3480	1,500
Na	110.1	310	255
Cu	5.0	236	69.4
Cr	4.9	21	10.2
Pb	3.7	210	56.16
Texture, %			
Sand	28.0	-	-
Silt	51.0	-	-
Clay	21.0	-	-

***TOC**= Total Organic Carbon

Table 3. Selected chemical properties of soil after 90 d, growth chamber study. (*n* = 4)

Crop	**Soil Treatment**	**pH**	**EC**	**Na**	**Extractable**		
					Cu	**Cr**	**Pb**
			dS m^{-1}			mg kg^{-1}	
Wheat							
	Compost	5.78 ± 0.09^{a1}	13.1	1636.4 ± 43.6^{a}	$95.9+36.2^{a}$	75.20 ± 19.9^{a}	95.9 ± 36.2^{a}
	Biosolids	5.63 ± 0.08^{a}	12.5	1622.9 ± 65.7^{a}	$84.8+60.8^{a}$	53.4 ± 22.6^{a}	84.8 ± 60.8^{a}
	$CaSO_4$	5.58 ± 0.07^{a}	22.4	1566.4 ± 33.2^{a}	$39.3+23.1^{a}$	55.4 ± 19.3^{a}	39.3 ± 23.1^{a}
	NPK	5.71 ± 0.10^{a}	29.0	1613.3 ± 50.1^{a}	$59.1+55.0^{a}$	72.0 ± 23.0^{a}	59.1 ± 55.0^{a}
	None	6.21 ± 0.09^{a}	7.3	1615.8 ± 23.2^{a}	$25.8+4.4^{b}$	65.9 ± 9.0^{a}	25.8 ± 4.4^{b}
Clover							
	Compost	5.77 ± 0.08^{a}	7.9	1593.2 ± 44.2^{a}	$22.6+8.1^{a}$	61.2 ± 11.4^{a}	22.6 ± 8.1^{a}
	Biosolids	5.93 ± 0.11^{a}	11.1	1632.0 ± 64.4^{a}	$21.1+14.3^{a}$	62.2 ± 11.8^{a}	21.1 ± 14.3^{a}
	$CaSO_4$	5.69 ± 0.09^{a}	21.4	1646.2 ± 56.6^{a}	$42.1+31.9^{a}$	63.0 ± 28.0^{a}	42.1 ± 31.9^{b}
	NPK	5.54 ± 0.08^{a}	35.9	1615.6 ± 17.7^{a}	$58.0+26.0^{a}$	55.6 ± 19.2^{a}	58.0 ± 26.0^{b}
	None	5.88 ± 0.10^{a}	9.6	1618.8 ± 56.0^{a}	$20.1+6.2^{b}$	50.3 ± 28.2^{a}	20.1 ± 6.2^{a}

[1] Means followed by the same number are not significantly different at $\alpha = 0.05$.

Among all plant and soil treatments, extractable Cu concentration was greatest in the compost and biosolids treatments cultivated with wheat (95.9 and 84.8 mg kg^{-1}, respectively) (Table 3). The biosolids and compost amendments contained 236 and 69 mg kg^{-1} Cu, respectively (Table 2). In contrast, however, low extractable Cu occurred in the compost and biosolids treatments cultivated to clover (22.6 and 21.1 mg kg^{-1}, respectively). The differences in extractable Cu are attributed to differences in root properties of wheat, a grain crop, versus clover, a legume. Changes in bioavailability of soil metals often results from root-induced changes to soil properties (Tao et al., 2004), including metal binding by root exudates, detoxification of metals by phytochelatins, root-induced microbial activities, and root depletion as a consequence of plant uptake (Ernst, 1996; Koo et al., 2010).

Certain microbial processes enhance metal solubility, thereby increasing bioavailability, whereas other processes result in immobilization, with subsequent decrease in bioavailability. Solubilization of metals can occur by autotrophic and heterotrophic mobilization mostly by the release of inorganic and organic acids, siderophores and other complexing agents, thereby accelerating redox, methylation, demethylation and biodegradation (Krebs et al., 1997). On the other hand, microbially-induced metal immobilization can occur by biosorption, precipitation, reduction, accumulation, intracellular deposition, localization and sequestration (Gadd et al., 2010). Soil Cu concentrations in the amended treatments were significantly ($p < 0.05$) greater than those of non-amended treatments.

Soil Cr concentrations averaged 64 mg kg^{-1} for the wheat treatment and 58 mg kg^{-1} for the clover treatment (Table 3). Typical Cr values in natural soils range from 7 to 221 mg kg^{-1} (McBride, 1994). Soil Pb concentrations averaged 61 mg kg^{-1} for the wheat treatment and 32.8 mg kg^{-1} for the clover treatment (Table 3). High soil Pb concentrations may be inhibitory to the growth of plants; an upper limit for Pb concentration of non-contaminated soil is suggested at 70 mg kg^{-1} (Pichtel, 2007).

Metal uptake by plants

Tissue Na content ranged from 10,850 (NPK) to 15,946 mg kg^{-1} in the wheat treatment, and from 10,683 to 15,411 mg kg^{-1} in the clover (Table 4). Sodium is required by plants in only minute quantities and can impart toxic effects when at high levels (typically > 200 mg/kg) (Legg, 2017). Vymazal et al. (2007) found, however, that reed canarygrass (*Phalaris arundinacea*) accumulated 20,376 mg kg^{-1} Na.

Clover germination was unsuccessful in the NPK treatment. This may be due to the high EC in this treatment (35.9 dS/m; Table 3). Soil salinity imposes ion toxicity, nutrient (N, Ca, K, P, Fe, Zn) deficiencies, nutritional imbalances, osmotic stress and oxidative stress on plants (Shrivastava and Kumar, 2015; Ashraf, 2004). Excess salinity may cause adverse effects on plant growth and development at physiological and biochemical levels (Ashraf, 2004), and at the molecular level (Bano and Fatima, 2009). Salinity hinders seed germination; seedling growth; enzyme activity; DNA, RNA and protein synthesis; and mitosis (Munns, 2002; Munns and James, 2003).

Copper content of wheat ranged from 24.0 (NPK) to 189.6 mg kg^{-1} ($CaSO_4$) ($p > 0.05$) (Table 4), and the Cu content of clover ranged from 24.8 (control) to 358.4 mg kg^{-1} (compost). Copper uptake by clover was markedly higher compared with wheat – mean Cu content of the clover treatment was 187.6 mg kg^{-1}, compared with a mean value of 81.1 mg kg^{-1} in wheat (Table 4). These data correspond with the lower soil Cu concentrations in the clover treatment (mean 32.8 mg kg^{-1}) versus that for wheat (mean 51.0 mg kg^{-1}) (Table 3). Metal concentrations in plants vary markedly by species (Huang and Cunningham, 1996). Soil pH influences metal uptake, i.e., acid conditions will favor metal solubilization. Soil pH in the clover and wheat treatments were both slightly acidic (5.7 and 5.8, respectively).

Table 4. Metal contents of plants grown on Glynwood soil after 90 d, growth chamber study. (*n* = 4)

Crop	Soil Treatment	Na	Cu	Cr	Pb
		------------------ mg kg^{-1} ------------------			
Wheat					
	Compost	14924.0±1485.6^a	45.6+29.5^a	1289.6±118.0^a	679.2+962.4^a
	Biosolids	15946.4±2365.1^a	92.8+37.0^a	928.0±351.0^a	836.8+667.3^a
	$CaSO_4$	14384.8±3516.8^a	189.6+131.4^a	1308.8±374.5^a	197.6+283.2^a
	NPK	10850.4±633.6^b	24.0+3.6^a	816.8±344.6^a	760.0+1043.9^a
	None	12493.6±3555.4^b	53.6+52.8^a	1106.4±106.8^a	144.0+209.5^a
Clover					
	Compost	15411.2±2766.7^a	358.4+332.5^a	1297.6±331.6^a	1372.8+1038.5^a
	Biosolids	10674.4±3869.7^b	100.8+77.5^a	1147.2±278.7^a	260.0+537.8^a
	$CaSO_4$	14356.8±2540.5^a	266.4+180.3^a	1252.0±239.8^a	1079.2+877.2^a
	NPK	*	*	*	*
	None	10683.2±5996.1^b	24.8+26.3^a	1044.8±254.9^a	451.2+385.0^a

*No plants survived in this treatment. Means followed by the same number are not significantly different at α = 0.05.

Nan et al. (2002) found that wheat was capable of growing on soil containing up to 364 mg kg^{-1} Cu. Rorison (1980) suggested the involvement of a Cu complexing mechanism during Cu detoxification in certain grasses. In copper-contaminated soil in P.R. China, leaf Cu concentration in *Rumex acetosa*, a perennial grass, ranged from 340 to 1102 mg/kg; *Commelina* communis contained from 19 to 587 mg/kg, and *Elsholtzia haichowensis* contained from 18 to 391 mg/kg Cu (Tang et al., 1999).

Chromium uptake by wheat was substantial; values ranged from 816.8 (NPK) to 1309 mg kg^{-1} ($CaSO_4$) with a mean value of 1090 mg kg^{-1} (Table 4). In the presence of the compost, $CaSO_4$, and control treatments, this species behaved as a hyperaccumulator. The threshold criterion for metal hyperaccumulators established by Baker (1981) is a tissue clover had hyperaccumulator characteristics: Cr content ranged from 1044.8 (control) to 1298 mg kg^{-1} (compost) with an overall mean of 1185.4 mg kg^{-1}. There were no significant differences in soil Cr concentrations among the plant and soil treatments ($p > 0.05$).

In a study of metal uptake by grasses (Pichtel and Salt, 1998), *Agrostis capillaris* took up 995 mg/kg (dw) and ryegrass (*Lolium perenne*) tissue accumulated 359 mg/kg Cr. Gough and Severson (1976) measured 500 mg/kg Cr in sagebrush from the vicinity of a P fertilizer factory. *Leptospermum scoparium* leaves were found to contain 2470 mg/kg Cr (ash dw) grown on a serpentine soil (Lyon *et al*., 1971), and *Sutera fodina* leaves contained 48,000 mg/kg Cr (ash dw) (Wild, 1974). These data demonstrate that several varied plant species are capable of tolerating Cr-rich soil and accumulating Cr without toxic effects.

The Cr content in plants is controlled mainly by the soluble Cr content of the soil (Kabata-Pendias, 2011), which is presumably a function of soil Cr speciation. The Cr(VI) form is highly soluble and plant-available compared to Cr(III) (Shahid et al., 2017). Chromium redox speciation was not conducted in this study, however.

Lead content of wheat ranged from 144.0 (control) to 836.8 mg kg^{-1} (biosolids) with an overall mean value of 523.5 mg kg^{-1} (Table 4). Lead content of clover ranged from 260 (biosolids) to 1372 mg kg^{-1} (compost) with a mean value of 790.8 mg kg^{-1}.

Tissue concentrations of Pb exceeded levels considered phytotoxic (> 5 mg kg^{-1}) by Markert (1992). However, Nan et al. (2002) found that wheat was able to grow on soil containing as much as 700 mg kg^{-1} Pb. In a study by Pichtel et al. (2000), Pb content in plants growing at a contaminated site were as high as 1467 mg kg^{-1}. Pichtel and Salt (1998) found that *P. pratense*, *A. capillaris* and *L. perenne* accumulated 141, 122 and 120 mg/kg, respectively, of Pb. Cannon and Bowles (1962) reported that certain grasses survived with tissue Pb concentrations as high as 3000 mg/kg dw. *Calluna vulgaris L. Hull* (common heather) and *A. vinealis* Schreber, contained 327 and 2932 mg/kg dw, respectively, in shoot tissue.

metal concentration > 1,000 mg kg^{-1} in shoots. Likewise,

The compost treatment clearly enhanced Pb uptake by clover (1372.8 mg kg^{-1}); in contrast, Pb content of clover in the biosolids treatment was markedly lower, i.e., 260 mg kg^{-1}. The difference in uptake is likely due to the fact that the compost was relatively young and contained substantial dissolved organic carbon (DOC) compounds. The biosolids, however, had been aged for over one year; as a result, the organic fraction is likely to be complex and relatively immobile in soil. Organic amendments may mobilize metals if they contain high DOC contents which form soluble complexes with metals in the soil solution (Khokhotva and Waara, 2010; Venegas et al., 2016). In a study by Houben et al. (2012), amendments with high dissolved organic carbon (DOC) content provoked an initial increase in Pb leaching; later, changes in Pb leaching corresponded with a decline in DOC content.

There were no significant differences in soil Pb concentrations among the plant and soil treatments ($p > 0.05$).

Based on the above data a number of green plants may possess the potential for phytoextraction of heavy metals from PW-contaminated soil.

Bioconcentration factor and metal uptake

The bioconcentration factor (BCF) reflects the progressive accumulation of metal from soil into a specific plant part (Branquinho et al., 2007). The process of phytoextraction generally requires the translocation of heavy metals to easily harvestable plant parts, i.e. shoots. By observing the BCF, we can compare the ability of different plants in taking up metals from soil and translocating them to shoots. Tolerant plants tend to restrict soil-to-root transfers and therefore accumulate little in biomass, while accumulators actively take up and translocate metals into above-ground biomass. Plants exhibiting BCF values less than one are unsuitable for phytoextraction (Fitz and Wenzel, 2002).

Wheat shoots had BCF values for Cu ranging from 1.0 (biosolids and CaSO$_4$) to 2.9 (compost); for Cr ranging from 13.1 (NPK) to 24.2 (CaSO$_4$); and for Pb from 0.25 (control) to 1.6 (NPK) (Table 5).

Table 5. Bioconcentration factors for Cu, Cr and Pb in wheat and clover shoots, growth chamber study.

		Na	**Cu**	**Cr**	**Pb**
Wheat					
	Compost	9.1	2.8	18.5	1.32
	Biosolids	10.7	1.0	21.2	1.35
	CaSO$_4$	9.0	1.0	24.2	0.40
	NPK	1.2	5.9	13.1	1.64
	Control	7.7	1.2	17.1	0.25
Clover					
	Compost	9.7	22.2	21.0	2.7
	Biosolids	7.6	9.6	19.2	1.1
	CaSO4	8.2	9.4	24.5	2.4
	NPK	-	-	-	-
	Control	6.6	1.5	30.6	1.3

Greatest metal uptake and accumulation in both plant species was either in the biosolids or compost treatment (Table 6). Wheat shoots had uptake values for Na ranging from 1905 (NPK) to 34,095 µg (compost); Cu from 5.1 (CaSO$_4$) to 169.8 µg (compost); Cr from 214.8 (control) to 2313.7 µg (biosolids); and Pb from 30.2 (NPK) to 1174 µg (compost).

Clover shoots had uptake values for Na ranging from 413 (control) to 11,767 µg (compost); Cu from 1.7 (control) to 62.4 µg (compost); Cr from 37.2 (control) to 816.8 µg (biosolids); and Pb from 4.3 (control) to 518.7 µg (compost).

The ability of wheat shoots to take up soil Pb was considerable (Table 6) – Pb concentrations in the compost and biosolids treatments were 1174 and 1051 µg, respectively.

This contrasts with Pb removal in the non-amended treatment, i.e., 32 µg.

The above data demonstrate the capability of wheat and/or clover, in combination with organic amendments, for possible phytotreatment of metal-enriched PW.

Table 6. Removal of Cu, Cr and Pb in wheat and clover shoots, growth chamber study. (*n* = 4)

Plant	Soil Treatment	Na	Cu	Cr	Pb
			µg		
Wheat					
	Biosolids	26342.1±12044.0	83.0±72.3	2313.7±1135.5	1051.4±1489.3
	Compost	34095.6±13367.4	169.8±76.7	1969.7±947.2	1174.9±1335.4
	NPK	1905.5±1352.4	26.6±24.7	165.7±135.6	30.2±41.5
	CaSO$_4$	2993.7±2317.8	5.1±7.7	1401.5±1134.7	356.6±543.7
	None	2694.0±2564.5	11.4±13.8	214.8±165.3	32.2±52.0
Clover					
	Biosolids	9457.5±8130.0	34.2±32.1	816.8±704.5	129.7±282.5
	Compost	11767.7±7740.6	62.4±46.7	744.9±631.7	518.7±917.9
	NPK	1111.2±801.7	18.3±19.4	105.4±88.0	14.2±22.9
	CaSO$_4$	1219.7±920.9	1.9±2.9	584.9±493.4	194.2±301.2
	None	413±101.2	1.7±1.5	37.2±7.6	4.3±6.3

Field Study

Soil properties

The pH of the PW-contaminated soil ranged from 4.5 (upper horizon, corn) to 6.8 (lower horizon, turf) (Table 7). The pH of the non-contaminated soil ranged from 6.4-7.3. The PW was highly acidic (pH 2.2; Table 1), which contributed to pH decline in the upper horizon of the PW-contaminated soil.

Metal concentrations in the PW-treated soil were substantially higher than those in the non-contaminated soil (Table 7) (p < 0.05). Highest soil Na occurred in the corn treatment upper and lower horizons (1688 and 1580.8 mg kg^{-1}, respectively). Lowest soil Na concentrations (102 and 108.2 mg kg^{-1}) were in the upper and lower horizons, respectively, of the non-vegetated plots. The synthetic PW was highly sodic (Na concentration = 2011.5 mg l^{-1}; Table 1).

Sodium from PW application was clearly mobile in the profile (Table 7) – in the corn treatment, Na concentrations in the upper and lower horizons were 1688 and 1580 mg kg^{-1}, respectively. The same effect was noted in the turf treatment, where Na concentrations in the upper and lower horizons were 1521 and 1392 mg kg^{-1}, respectively. Sodium is readily leached from the profile (FAO, 2017).

In the PW-treated plots grown to corn, soil Cu concentrations showed a distinct distribution by depth (Table 7): the upper horizon contained 323 mg kg^{-1} while the lower horizon contained 83.4 mg kg^{-1} (p < 0.05). The Glynwood soil in this experiment contained 3.9% TOC (Table 2), which provides 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).

Plant Response and Metal Accumulation

Corn plants experienced a 75% die-off within 7-10 days of PW application. The effect is likely due to the high salinity and Na concentration of the introduced PW. Toxicity symptoms included interveinal chlorosis; burning on leaf surfaces and margins was also evident. Leaf burn became more severe until defoliation and plant death occurred. These are common symptoms of Na toxicity (Stone and Downer, 2013). Sodium is required by plants in only minute quantities and can impart toxic effects when at high levels (typically > 200 mg/kg) (Legg, 2017). Sodium concentration in the corn tissue was 2220 mg kg^{-1} (Table 8). Excessive accumulation of Na in cell walls can lead to osmotic stress and cell death (Tabur and Demir, 2010). Chromium concentrations were low (< 14 mg kg^{-1}) for all treatments. Likewise, soil Pb concentrations were not excessive.

Table 7. Metal concentrations of field soil, upper and lower horizons. (*n* = 4)

Plant treatment	**Horizon**	**PW**	**pH**	**EC**	**Na**	**K**	**Cu**	**Cr**	**Pb**
				dS m^{-1}	----------mg kg^{-1}----------				
Corn									
	Upper	Y	4.51+0.28^a	17.9±6.2	1688.3±78.1^a	111.8±31.5^a	323.2±101.9^a	6.9±10.6^a	75.8±108.0^a
	Lower	Y	6.34+0.65^b	6.6±0.1	1580.8±150.8^a	54.2±22.9^a	83.4±69.1^a	7.7±15.4^a	133.6±176.0
	Upper	N	6.68+0.01^b	14.7±0.1	69.9±27.4^b	51.8±8.2^a	2.8±0.6^b	13.8±15.0	BDL$^{1, b}$
	Lower	N	6.1+0.22^b	9.7±4.1	39.7±46.4^b	20.2±4.8^{ab}	2.6±0.3^b	2.6±3.7^a	BDL^b
Turf									
	Upper	Y	6.62+0.20^b	1.5±0.6	1521.8±117.7^a	30.3±5.1^a	301.0±102.1^b	13.9±24.0	254.4±198.8
	Lower	Y	6.82+0.34^b	0.9±0.2	1392.2±75.2^a	8.0±0.4^b	3.1±1.0^b	7.5±12.6^a	276.5±228.7
	Upper	N	7.27+0.01^b	2.3±0.1	154.4±14.1^b	53.8±33.5^a	1.8±0.8^b	8.9±12.6^a	BDL^b
	Lower	N	6.84+0.01^b	2.1±0.1	180.6+14.4^b	26.0+12.9^{ab}	1.8+0.8^b	4.9+6.5^a	BDL^b
None									
	Upper	N	6.4+0.01^b	6.7±7.6	102.0+91.6^b	51.8+8.2^a	2.8+0.6^b	13.8+15.0^a	BDL^b
	Lower	N	6.5+0.50^b	2.2±0.8	108.2±112.9^b	20.2±4.8^{ab}	2.6+0.03^b	2.6±3.7^a	BDL^b

Means followed by the same number are not significantly different at $\alpha = 0.05$.

Excess Na^+ is frequently assumed to be largely responsible for reductions in growth and yield under saline conditions (Chi Lin and Huei Kao, 2001; Tsai *et al.*, 2004; Hong *et al.*, 2009). Soil Na concentration in the upper horizon of the corn treatment was 1688.3 mg kg^{-1} (Table 7). In a greenhouse study Miller et al. (1980) evaluated the effects of PW components on plant growth and found that NaOH and other compounds reduced yields of sweet corn (*Zea mays* L. var. succharata) and/or green beans (*Phaseolus vulgaris* L.). Six drilling fluids reduced yields of green beans and sweet corn when added to soil (Miller and Pesaran, 1980); high levels of soluble salts or high percentage exchangeable Na^+ were considered to be the main causes of reduced growth. Adams (2011) reported severe acute and chronic toxicity of mixed hardwood trees and ground vegetation (*Vaccinium* L., *Smilax rotundifolia* L., and *Kalmia latifolia* L.) that resulted in 56% vegetation mortality after two years of land application of hydraulic fracturing fluid. Soil Na^+ and Cl^- concentrations increased by approximately 50-fold as a result of land application of the fluids.

Lead accumulation by corn may also have imparted toxic effects to both plant treatments. Lead content in corn and turf tissue was 1201 and 1985 mg kg^{-1}, respectively (Table 8). Lead is known to induce a broad range of toxic effects to organisms, including those that are morphological, physiological, and biochemical in origin. Lead impairs plant growth, root elongation, seed germination, seedling development, transpiration, chlorophyll production, lamellar organization in the chloroplast, and cell division (Pourrut et al., 2011).

Huang and Cunningham (1996) measured Pb uptake in corn shoots as high as 375 mg kg^{-1} when grown in nutrient solution. Bricker et al. (2001) measured 2435 mg kg^{-1} Pb in corn shoots grown on contaminated soil.

The turf mixture survived the shock loading of PW. Approximately 50% of plants in the PW-treated plots experienced minor leaf burn and chlorosis; however, this effect was only temporary. Sodium and chloride may be directly toxic and cause characteristic leaf burn in susceptible species (Bernstein, 1965; Bernstein and Hayward, 1958). Sodium concentration in turf tissue was 3125 mg kg^{-1} (Table 8). Vymazal et al. (2007) found that reed canarygrass (*Phalaris arundinacea*) accumulated 20,376 mg kg^{-1} Na.

Lead content of the turf tissue was substantial – 1985 mg kg^{-1} was measured (Table 8). In a study by Pichtel et al. (2000), Pb content in plants at a contaminated site were as high as 1467 mg kg^{-1}. Cannon and Bowles (1962) reported that certain grasses survived with tissue Pb concentrations as high as 3000 mg/kg dw. Pichtel and Salt (1998) measured 141 mg kg^{-1} Pb in Timothy grass (*Phleum pratense*). In a greenhouse study ryegrass (*Lolium perenne* L.) was grown in soil containing synthetic hydraulic fracturing fluids (Nelson et al., 1983). The fluids increased soil EC and concentrations of total and extractable Cu, Pb, and other metals. Ryegrass yields may have been reduced by high soil Zn and EC levels.

Soil remediation

Remediation practices on PW-contaminated soil often tend to be straightforward (Pichtel, 2016). In-situ remediation involves: (1) removal of salts via leaching with irrigation or natural precipitation; (2) replacement of exchangeable Na^+ with Ca^{2+}; and (3) removal or immobilization of metals. Simple soil dilution may relieve salinity and sodicity problems following release of PWs. In a study by Wolf et al. (2015), where PWs occurred primarily at the soil surface, mixing of the less-contaminated deeper soil with surface soil resulted in dilution of contaminants. Addition of inexpensive amendments is often successful in treating soil salinity and sodicity problems. Both inorganic amendments (e.g., $CaSO_4$) (Anderson, 2015) and organic materials (de Jong, 1979) have proven successful.

Table 8. Metal concentrations in corn and turf tissue, field study.

Plant	PW	Na	K	Cu	Cr	Pb
				mg kg^{-1}		
Corn	Y	2220±1018.6^{a}	9765.3±4272.6^{a}	1294±1745.1^{a}	104.0±180.1^{a}	1201.3±766.7^{a}
	N	788.0±181.0^{b}	5080.0±1216.2^{a}	37.2±35.1^{b}	68.0±84.9^{a}	28.0±5.7^{b}
Turf	Y	3125.3±4370.7^{a}	21155.3±13714.9^{a}	197.3±245.0^{a}	156.7±245.8^{a}	1985.3±2216.0^{a}
	N	444.0±141.3^{b}	7712.0±3248.1^{b}	18.0±4.0^{b}	43.0±31.6^{a}	90.0±68.2^{b}

Means followed by the same number are not significantly different at $\alpha = 0.05$.

Phytoremediation is a cost-effective, low-technology process defined as the engineered use of green plants including vegetable crops, grasses and even annual weeds to extract, accumulate and/or detoxify environmental contaminants (Prasad, 2004; Alkorta et al., 2004; Garbisu et al., 2002). Phytoextraction involves the use of accumulating plants to transport metals from soil to concentrate them into roots and above-ground shoots. In certain cases contaminants can be concentrated thousands of times higher in the plant than in the soil (Pichtel, 2016). Following harvest of the extracting crop, the metal-rich plant biomass can ashed to reduce its volume, and the residue processed as an 'ore' to recover the contaminant metals.

Phytoremediation is useful for soils contaminated with metals to shallow depths. This technology can work well in low-permeability soils, where many technologies have a low success rate. It can also be used in combination with conventional cleanup technologies (e.g., 'pump and treat' of groundwater). Phytoremediation can be an alternative to harsher remediation technologies such as soil flushing (Pichtel, 2007).

In the clover treatment, the food waste compost provided for maximal uptake of Cu, Cr and Pb compared to all other treatments. In the field study, both corn and turf accumulated substantial quantities of soil Cu and Pb. Considering its resilience to toxic soil conditions, mixed turf may be effective for phytoremediation of PW-affected soil. The utilization of organic amendments has been found to improve the metal accumulating potential of plants, depending on species and amendment properties (Zubillaga et al. 2012; Wiszniewska et al. 2016). Several organic materials have been evaluated as supplements for phytoremediation (Gholami et al. 2012; Wang et al. 2013). In metal-contaminated soils, amendments have increased plant tolerance, altered rates of metal accumulation (Walker et al. 2004; Chaiyarat et al. 2011), and stimulated biomass production.

CONCLUSIONS

In growth chamber and field studies, several plant species were capable of tolerating the application of synthetic oil and gas production water. Furthermore, several species accumulated substantial quantities of metals from PW-affected soil. In the growth chamber, clover was the most efficient in accumulating Cu and Cr in shoots. Plant uptake of metals was enhanced by application of organic wastes, particularly biosolids and food waste compost, to soil.

The turf mixture (Kentucky bluegrass and perennial ryegrass) is considered a practical candidate for remediation of PW-affected soil due to robust biomass production over a short period, good adaptation to a wide range of soil types, and tolerance to stressed environments. By virtue of these qualities, this species mix is recommended for remediation of PW-contaminated soil. The results of this study demonstrate that specific crop and amendment combinations can significantly affect the efficiency of reclamation strategies of soils contaminated by oil and gas production water. The reported study may be of practical value to oil and gas production industries which generate large quantities of contaminated drilling wastewater.

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