Detection, Occurrence and Fate of Emerging Contaminants in Agricultural Environments

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Abstract

A total of 79 papers published in 2016 were reviewed ranging from detailed descriptions of analytical methods, to fate and occurrence studies, to ecological effects and sampling techniques for a wide variety of emerging contaminants likely to occur in agricultural environments. New methods and studies on veterinary pharmaceuticals, steroids, antibiotic resistance genes, cyanotoxins, and potential effects of biochar use in agricultural environments continue to expand our knowledge base on the occurrence and potential impacts of these compounds. This review is divided into the following sections: Introduction, Analytical Methods, Steroid Hormones, Anthelmintics, Antibiotic Fate and Occurrence, Antibiotic Resistance Genes, Cyanotoxins, and Implications of Biochar in Agricultural Environments.

Keywords

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INTRODUCTION

Water resources in agricultural environments are impacted by a wide variety of contaminants including nutrients, sediments, and pesticides. These groups of contaminants typically occur at easily measured concentrations in surface run–off in agricultural watersheds. Nutrients, especially nitrogen, and pesticides have also been shown to impact ground water quality in areas susceptible to contamination. The impacts of newer contaminant classes such as pharmaceuticals, steroids, antibiotics and antibiotic–resistance genes of bacteria are less well-known. These "emerging" contaminants clearly have potential to enter the environment and cause known or suspected adverse ecological or human health effects. Release of these contaminants to the environment has very likely occurred for quite some time, but methods for their detection at environmentally–relevant concentrations have only recently become available.

Evaluating the environmental fate and effects of emerging contaminants includes compounds such as surfactants, antibiotics and other pharmaceuticals, steroid hormones and other endocrine–disrupting compounds (EDCs), fire retardants, sunscreens, disinfection byproducts, new pesticides and pesticide metabolites, and naturally–occurring algal toxins. Detection of these contaminants in environmental matrices (water, wastewater, soils and sediments) is particularly challenging because of the low detection limits required, the complex nature of the samples, and difficulty in separating these compounds from interferences. New extraction and cleanup techniques, coupled with improvements in instrumental technologies provide the needed sensitivity and specificity for accurate measurement.

The objective of this paper is to review the literature published in 2016 evaluating the detection, fate, and occurrence of emerging contaminants, with a particular focus on those contaminants likely to be found in agricultural systems. Relevant contaminants are EDCs (particularly hormones and anabolic steroids), antibiotics and other pharmaceuticals associated with wastewater, antibiotic resistance genes in bacteria. Studies on pesticides and flame retardants are not reviewed unless they were evaluated in the same study. New sections this year include a review of the literature on cyanotoxins and the implications of biochar use in agricultural environments.

ANALYTICAL METHODS

New developments in analytical methods permit more rapid, sensitive, and simplified analysis of emerging contaminants in agricultural environments. For example, Chung et al. (2016) describes an LC/MS/MS method for the analysis of several classes of veterinary antibiotics in surface water from the Yeongsan River in China. Sample concentration using Oasis™ HLB solid-phase extraction produced method detection limits between 0.1 and 74 ng L^{-1}, and recoveries ranging from 71 to 120% in reagent water. Results indicated that lincomycin, sulfamethazine, sulfamethoxazole, and sulfathiazole were the most frequently detected antibiotics with maximum concentrations greater than 307 ng L^{-1}.

A multiresidue screening method for mixtures of pesticides and drugs was published by Cotton et al. (2016) to quickly characterize contaminant concentrations in water. The fully automated method utilizes solid phase extraction (SPE) and ultrahigh pressure liquid chromatography (UHPLC) with high resolution mass spectrometry (HRMS) to measure over 500 different analytes at detection limits ranging between 0.1 and 1,000 ng L^{-1}. Application of the method to samples of tap water in Paris, France led to identification of 34 different organic contaminants at concentrations below the European Union drinking water limit of 0.1 μg/L.

Gao et al. (2016a) developed a method for measurement of several classes of veterinary antimicrobial drugs in water and in livestock feces and urine. Optimization of extraction and clean-up conditions, including adjustment of pH, solvent, and solid-phase extraction media, are presented for each class of drug. Method detection limits ranged between 0.01 – 0.05 μg L^{-1} for water, between 0.5 – 1 ng g^{-1} for feces and urine were reported with recoveries falling between 85 – 110%. Analysis of agricultural wastewater and nearby river waters indicated occurrence of quinolones, sulfonamides, and tetracyclines up to 56.8 μg/L in the wastewater samples.

A method combining solid-phase extraction with dispersive liquid-liquid microextraction (SPE-DLLME) was reported by Liang et al. (2016b) for concentrating several classes of antibiotics in wastewater for analysis by ultra-high pressure liquid chromatography-tandem mass spectroscopy (UHPLC/MS/MS) analysis. Optimization of extraction phases, pH, flow rates, solvents and solvent volumes are presented. Detection limits between 0.08 and 1.67 ng g^{-1} were reported with recoveries between 64 and 100% at concentrations fortified to 500 ng g^{-1}. Results from analysis of a variety of wastewater samples using the methods are presented.

Measurement and uptake of four classes of antibiotics in food crops irrigated with wastewater was investigated by Sallach et al. (2016). Evaluation of four approaches to plant tissue extraction are presented with optimization of detection limits, recoveries, and preparation times. The best overall method was used to extract antibiotics from lettuce tissue irrigated with synthetic wastewater. Method detection limits in plant tissues were generally < 100 ng g^{-1}, though sonication produced more variability and higher detection limits.

Analysis of veterinary antibiotics used in swine production and their degradation products is the focus of a method described by Solliec et al. (2016). Soil and manure samples were equilibrated with an aqueous buffer prior to concentration and cleanup using solid phase extraction. Water samples were filtered and acidified with a similar aqueous citric acid and EDTA buffer before extraction. HPLC coupled with high resolution mass spectrometry reportedly produced detection limits between 2.0 and 27 ng L^{-1} for tile drainage water, 1.0 – 7.4 ng g^{-1} in soils, and 3.6 – 12 ng g^{-1} for manure with recoveries between 40 and 120% for tetracyclines and selected degradation products. The method was used for analysis samples from a swine production facility, and results indicated that the degradation products often occurred at significantly higher concentrations (Solliec et al. 2016).

Off-line extraction combined with on-line SPE and LC/MS/MS by Tlili et al. (2016) was used for determination of antibiotics and other drugs in water and suspended solids from French wastewater treatment plant (WWTP) influent and effluent, aerated lagoons, and river waters. Pressurized liquid extraction (PLE) protocols were optimized for three residue classes before combining for the final extracts. Detection limits near 0.1 ng L^{-1} were reported for most analytes, except for sulfadiazine (0.9 ng L^{-1}) and florfenicol (0.36 ng L^{-1}) with recoveries between 50% and 102%.

Tandem SPE for measurement of multiple classes of antimicrobials from water was described by Tran et al. (2016) for wastewater samples analyzed by UHPLC and tandem mass spectrometry. The tandem extraction system used both polymeric and ion exchange SPE cartridges at pH = 3 to maximize recoveries of analytes. Optimization of mass spectroscopic parameters combined with isotope dilution compensated for analyte losses due to extraction efficiency and matrix effects. Detection limits of < 5 ng L^{-1} were reported for surface water, < 10 ng L^{-1} for treated wastewater, and < 15 ng L^{-1} for raw wastewater. Reported recoveries ranged from 85% to 106% for most analytes. Results obtained from the optimization of the method and from the application of the method to wastewater samples from WWTP effluents and influents are presented.

Van den Meersche et al. (2016) describe a method using UHPLC/MS/MS for analysis of veterinary antibiotics extracted from swine manure. Analytes were extracted using a mixture of acetonitrile and trichloroacetic acid. Optimization of extraction and instrumentation conditions are described. Recoveries between 94% and 106% were obtained with detection limits ranging from 1 to 20 ng g^{-1}.

Kaufmann et al. (2016) propose a novel instrumental method using interpretation of ion abundance ratios to elucidate the structures of unknown compounds. Using differences in daughter ion intensities obtained from fragmenting isotopic parent ions (masses A and A+1) at narrow and wide isolation windows, losses of the heavier isotopes during fragmentation can be observed. This "Product-ion isotopologue pattern" (PIIP) technique is reported by the authors to assist in the identification of the number of carbons lost during fragmentation for several classes of antibiotics. Comparisons of the PIIP technique to identification of unknowns using conventional relative isotopic abundances are described.

STEROID HORMONES

The occurrence and fate of steroid hormones in agricultural environments continues to be of interest. For example, Noguera-Oviedo and Aga (2016) investigated the changes of concentrations and estrogenic activities of free and conjugated estrogens through a full scale anaerobic co-digestion system. Free estrogens analyzed by gas chromatography-mass spectrometry (GC/MS) included 17β-estradiol (β-E2), 17α-estradiol (α-E2), estrone (E1), and estriol (E3), and their sulfate- and glucuronide-conjugates were measured by LC/MS/MS. Results showed that the total estrogen concentrations in manure were not significantly changed after digestion while the composition was changed. The predominant species α-E2 (65%) in the untreated manure was mostly converted to E1 during digestion, making E1 dominant in the digested manure (72%). Conjugated estrogens were detected at

very low levels in the untreated manure and mostly deconjugated after digestion. Estrogenicity estimated from estrogen concentrations and their relative potencies did not show a dramatic change. The results of this study indicate that mesophilic anaerobic digestion cannot provide an effective removal of estrogens and endocrine disrupting activities.

Zhang et al. (2016e) evaluated the impact of stereoselectivity and co-occurrence on the biotransformation of estradiol and trenbolone isomers in a sandy and a silt loam sediment. Both α- and β-isomers of E2 or TB were added to saturated sediment microcosms individually or together. Attenuation rates and biotransformation products were monitored periodically using derivatization gas chromatography–mass spectrometry. Results showed that in both sediment types, β-isomers generally dissipated more rapidly than α-isomers, indicating the significance of stereoselective degradation of E2 and TB isomers. However, the interaction of co-occurring isomers was sediment type-specific. In the sandy sediment, the dissipation rates of both α- and β-isomers decreased when they were present together compared with the dissipation rates of individual isomer, whereas the changes were not significant in the silt loam sediment. Estrone and trendione were primary metabolites of E2 and TB isomers, respectively. The formation and decay of estrone were similar in both sediments while less dissipated α-TB was converted to trendione relative to β-TB in the sandy sediment. The abundance of organic carbon and nutrients were suggested by the authors to be a possible explanation for this sediment-specific behavior. These results indicate that co-occurrence of stereoisomers could prolong steroid persistence and thus pose greater environmental risk.

Zhang et al. (2016d) investigated the impact of sediment particle size on the attenuation rates and metabolite formation of 17β-estradiol (E2) and 17β-trenbolone (TB). A sandy and a silt loam sediment were fractionated into sand and fine (silt, clay or mixed silt and clay) fractions using wet sieving and repeated sedimentation. Microcosms were established by amending saturated whole sediments and different fractions with E2 or TB. It was found that the attenuation of parent compounds followed a first order kinetics in the coarse fraction while a biphasic pattern was observed in the fine fractions. In the second phase following the initial rapid decay phase, the residues of E2 and TB associated fine particles were more persistent than those in the sand fraction. Estrone and trendione were primary metabolites for E2 and TB, respectively. Although no clear correlation was observed between sediment particle size and the formation or degradation rates of the daughter compounds, the authors unveiled that the dissipation rates of estrone and trendione associated with the fine fractions were not statistically different from those with the corresponding whole sediment. These results indicate that fine particles may play an important role in influencing the persistence of and the potential risk posed by steroid hormones in the aquatic systems.

Yang et al. (2016a) performed a first attempt to evaluate the distribution and fate of 17 micropollutants in drain fields receiving septic tank effluents over an eight-month period. Drain fields were simulated by lysimeters constructed using pressure treated wood, commercial sand and natural soil collected from the A and A/E horizons. The 17 micropollutants of interest included steroid hormones, pharmaceuticals and personal care products (PPCPs), plasticizers and wastewater markers. Sucralose, caffeine, acetaminophen,

carbamazepine, ibuprofen, sulfamethoxazole, estrone, triclosan, triclocaban, butyl paraben, ethyl paraben, methyl paraben, propyl paraben, and bisphenol-A were detected in the septic tank effluents, while butyl paraben and ethyl paraben were missing in the leachate from the drain fields. Most contaminants (85%) were retained or removed by the drain fields via sorption or microbial degradation so that their concentrations in the leachate were below 200 ng L^{-1}. Median monthly total concentrations of hormones and PPCPs in the leachate varied between 30 and 86 ng L^{-1}, indicating septic systems are still important sources for micropollutants to enter the environment. Sucralose was more stable than caffeine in the drain fields and was suggested by the authors as a better indicator of septic tank effluent.

Fairbairn et al. (2016a) monitored 26 emerging contaminants including herbicides, pharmaceuticals and personal care products (PPCPs) in a mixed-use watershed in Minnesota over a 7-month period in 2012. Water samples were collected from wastewater treatment plant (WWTP) effluent, upstream and downstream sites on the Zumbro River. Sampling events took place to catch snowmelt, the first precipitation after corn plantation, late summer baseflow, and postharvest flows. Sixteen compounds were detected in the watershed, among which herbicides such as atrazine, acetochlor, metolachlor, and mecoprop, and PPCPs such as caffeine, DEET, acetaminophen, trimethoprim, and carbamazepine were of high detection frequency (>50%). 4-nonylphenol, erythromycin, sulfamethoxazole, and carbamazepine were detected at the greatest concentrations (median >100 ng L^{-1}). Agrochemicals entered the watershed primarily from upstream and peaked during high flow conditions. Input of trimethoprim, mecoprop, nonprescription pharmaceuticals, and personal care products were from mixed sources and pathways with peaks also under high flow conditions. WWTP effluent was found to be a relatively stable sources of carbaryl, 4-nonylphenol, and prescription pharmaceuticals regardless of flow conditions. They suggested that mass balance analysis may be a powerful tool for emerging contaminants source apportionment.

The authors have also conducted a longer period (2011–2012) monitoring of the 26 contaminants in the same watershed (Fairbairn et al. 2016b). It was found that the concentrations and loadings of the detected contaminates were closely related to land use and flow conditions. Similar trends as reported in the 7-month monitoring were observed for WWTP-contributed compounds and agrochemicals. However, several compounds such as carbaryl, carbamazepine, trimethoprim, and cotinine which were considered to come from WWTP effluent may also leach from septic systems or land-applied biosolids.

Shappell et al. (2016) investigated the estrogenic activity of runoff from agricultural lands post-application of various types of animal waste to frozen ground, the effect of vegetation on estrogenic activity of runoff, the potential correlations between measured estrogenic activity, and various nutrients/ions that might be used as an indicator for the presence of estrogenic activity. The study was conducted between 2009 and 2011 at the former North Appalachian Experimental Watershed (Coshocton, OH). Six gages small watershed were used in 2009, while three watersheds were used in 2010 and 2011. During the first year, six small watersheds used to produce corn were evaluated, treatments: two no-manure controls, two liquid swine manure with 30-m setbacks, and two turkey litter with 30-m setbacks. In addition, beef manure was applied to six frozen plots of forage. During the following two years, applications were repeated on the swine manure watersheds and one control

watershed. The measured estradiol equivalents (E2Eqs) and nutrient concentrations generally peaked in the first runoff event after application. The highest measured E2Eq (5.6 ng L^{-1}) was in the first event after swine manure application and was less than the Lowest Observable Effect Concentration (LOEC) for aquatic species (8.9 ng L^{-1}) and well below the concentrations measured in other studies using enzyme linked immunosorbent assays (ELISAs) to measure hormone concentrations. No runoff occurred from plots planted with forage, indicating low risk for environmental impact. During year 2 and year 3, estrogenic activity never exceeded the Predicted No Effect Concentrations for E2 (2 ng L^{-1}). When post-application runoff contained high estrogenic activity, strong correlations (R^2 0.86 to 0.96) of E2Eq to Ca^{+2}, Mg^{+2}, and K^+ concentrations were observed, indicating under some condition these cations might be useful surrogates for E2Eq measurements.

ANTHELMINTICS

Although anthelmintic drugs are widely used for veterinary treatment, few studies have investigated their occurrence in the environment. In an attempt to elucidate the environmental fate of anthelmintic drugs, Kumirska et al. (2016) investigated the occurrence of two benzimidazoles (flubendazole [FLU] and fenbendazole [FBZ]) and one avermectin (doramectin [DOR]) in water, sediment and fish tissue samples collected along the River Reda (northern Poland). Regardless of the compartment, FLU, FBZ, and DOR were detected at least once. In water samples, FLU was the most frequently detected anthelmintic compound (12/13) followed by FBZ (11/13) and DOR (4/13). FLU and FBZ were constantly below the method quantification limit (MQL) while DOR ranged between 196.7 ng L^{-1} and < MQL. A similar trend (FLU > FBZ > DOR) was observed in the sediment and fish samples. However, measured concentrations were consistently below the MQLs.

Environmental risk

Bundschuh et al. (2016) assessed the acute toxicity (between 24 and 96 h) of five antibiotics including three anthelmintic drugs (FBZ, FLU, and ivermectin [IVE]) for nine freshwater macroinvertebrate species. FBZ, FLU and IVM caused substantial acute toxicity in most of the tested freshwater macroinvertebrates. *Daphnia magna* was the most sensitive test species for IVM and FBZ, while *Tubifex tubifex* and *Dugesia gonocephala* were slightly more sensitive towards FLU. The sensitivity of the freshwater macroinvertebrates deviated several orders of magnitude (acute median effective concentrations ranged between 0.59 and > 8000 μg L^{-1}). Among the three anthelmintic drugs, IVM represented the biggest environmental threat for freshwater macroinvertebrates species.

Eichberg et al. (2016) investigated the effects of anthelmintic Cydectin and its active pharmaceutical ingredient Moxidectin on seed germination using three wide-spread plant species of temperate grasslands (*Centaurea jacea, Galium verum*, and *Plantago lanceolate*). Cydectin and Moxidectin had adverse effects on seed germination. A two third reduction in terms of reseeding number was observed and a 12 d delay of germination occurred when Moxidectin was applied at 10 mg L^{-1}. Moxidectin acted more strongly on seeds if administered in formulation (Cydectin) than if administrated solely. Moxidectin may impact

plant regeneration not only indirectly (reduced breakdown of feces) but also directly through toxic effects.

Gao et al. (2016b) investigated the combined subacute toxicity of Copper (Cu) exposure and albendazole (ABZ) in earthworms (*Eisenia*) using three methods: the chronic growth and reproduction, antioxidant enzyme activity, and earthworm Cu residue. Various levels of Cu (0 to 160 mg Kg^{-1}) and ABZ (0 to 9 mg Kg^{-1}) were tested. No mortalities were found for the earthworms in all of the treatments after a 28 d exposure. The chronic reproduction method showed that among the five reproductive parameters used (cocoon numbers, cocoon weight, cocoon hatching success, juvenile numbers, and the biomass of the juvenile and cocoon) only cocoon weight was not affected by the Cu concentration in the absence or presence of ABZ. The concentrations of ABZ highly impacted the subacute toxicity of exposure to Cu on earthworm reproduction (decreased with low concentrations [3 mg Kg^{-1}], increased with high concentrations [9mg Kg^{-1}]). The antioxidant enzyme activities (including CAT, SOD, and GSH-PX) showed contrasting results depending on the enzyme type, exposure time, and exposure concentration. For example, the CAT activity had a different trend from SOD activity during the 28-day exposure period. After exposure of 7 days, the activity was significantly induced at the low Cu concentration of 80 mg kg^{-1} with the presence of ABZ, but not in the absence of ABZ. ABZ was not found to influence the Cu residues in adult earthworms, and with the increasing of the Cu exposure concentrations, the internal concentrations tended to level off, which was consistent with the above responses of the earthworms' reproduction and enzyme activity to Cu exposure.

Rath et al. (2016) evaluated the acute toxicity of IVE, its degradation products and UV/TiO2 and UV/TiO2/H2O2 by-products on *Daphnia similis*. No acute toxicity to *D. similis* was observed throughout the study. The toxicity of the solutions submitted to the photocatalytic processes decreased over time and it was completely eliminated after 10 minutes.

Stuchlíková et al. (2016) investigated the phytotoxicity and biotransformation of the benzimidazole anthelmintic drugs (ABZ, FBZ, and FLU) in a meadow plant (harebell, *Campanula rotundifolia*) grown in pastures. ABZ, FBZ, and FLU were not found to be toxic for harebell cells. FLU, ABZ, and FBZ were transformed by harebell cells into 18, 24, and 29 metabolites, respectively. The transformation rates were different among the three anthelmintic drugs. After 24-h incubation, 98%, 84%, and 16% of parent ABZ, FBZ, and FLU were transformed into metabolites, respectively. The phase I biotransformation was dominated by S-oxidation, hydroxylation, carbonyl reduction and hydrolysis. During phase II, many various glucosides, acetylglucosides, and glucosylglucosides were formed.

Sorption and degradation

Havlíková et al. (2016) investigated the photocatalytic degradation and the kinetics of the degradation of two widely used anthelmintic drugs (IVE and praziquantel [PZQ]) under different TiO2 concentration (0.25 to 2.5 g L^{-1}) and pH levels (3 to 9). Degradation pathways under different conditions were also investigated. The degradation efficiency increased for both compounds with the increase in the TiO2 concentration from 0.5 to 2.0 mg/L, and then remained constant. The estimated k-values ranged between 0.36 and 0.64 h^{-1} for IVE and between 0.29 and 0.47 h^{-1} for PZQ, respectively. The degradation rate

remained constant regardless of the pH of the aqueous dispersion for both compounds. The photo degradation was about 90% for both compounds after 5 h of irradiation and it was inhibited in the presence of iodide anion and isopropyl alcohol. IVE and PZQ were completely removed after 7 h of irradiations. The contribution of hydroxyl radicals and holes was 92.1 % for IVE and 93.2 % for PZQ, respectively. IVE was degraded to five degradation intermediates and PZQ to six intermediates.

Rath et al. (2016) investigated the sorption and desorption of IVE in two Brazilian soils (sandy and clay soil) using batch sorption and column experiments. Photo degradation in aqueous solutions was also investigated. Adsorption and desorption coefficients were higher in the clay-rich soil compared to sandy soil. IVM showed a strong interaction with the binding sites in both soils, suggesting a low potential for groundwater leaching. The dissipation rate (DT50) was higher in the clay soil, which also presented a higher biomass content compared to the sandy soil (11.5 and 15.5 d, respectively). IVM showed a degradation efficiency rate > 85% in aqueous solution regardless of the TiO_2 concentrations ranging between 10 and 120 mg L^{-1}. The degradation rate was higher during the first seconds of the reaction and lower after 60 s. pH did not influence the reactivity efficiency.

ANTIBIOTIC FATE AND OCCURENCE

A growing number of studies are investigating the fate and occurrence of antibiotics in agricultural environments. Burke et al. (2016) investigated the occurrence of 26 veterinary compounds belonging to four groups, macrolides (MLs), sulfonamides (SAs), tetracyclines (TCs), and penicillins (PNs) at an agricultural intensively used drinking water catchment in Northern Germany. A set of 24 sampling points, including nine surface water sampling points and 15 shallow groundwater observation wells, was examined. In addition to the field investigation, a column study was conducted to elucidate the sorption behavior of trimethoprim. Eight antimicrobial compounds (sulfadiazine, sulfapyridine, sulfamethoxazole, trimethoprim, dehydrato-erythomycin, sulfadimidine, tylosin, and tetracycline) were detected in surface water, while only trimethoprim was detected in groundwater. Higher concentrations were observed in surface water (10 to 155 ng L^{-1}) compared to groundwater (5 to 12 ng L^{-1}). Trimethoprim showed a moderate sorption potential to the sandy aquifer material (linear adsorption coefficient: 1.45 L Kg^{-1}; retardation coefficient: 5.7) Burke et al. (2016).

Dong et al. (2016) investigated the seasonal and spatial variation of 12 antibiotics belonging to four groups, SAs, TCs, MLs, and quinolones (QNs), in three main tributaries of Liao River (Jilin Province, Northern China). Water and sediment (top 10-cm layer) samples were collected from seven sampling sites in summer (July 2015) and autumn (November 2015). Several antibiotics, except sulfamethizole, were quantified in soil and/or water samples. Eleven of twelve target compounds were detected in water samples with total concentrations ranging between 106 and 1346 ng L-1. Nine of twelve antibiotics were detected in sediments with total concentrations ranging between 1 and 1,190 ng g^{-1}. Among the four groups of antibiotics investigated, TCs had the highest concentrations in water and in sediments, while SA concentrations were generally lower. The number of antibiotics detected and the total antibiotic concentrations in water at each location were significantly higher in autumn than

in summer due to the higher water flow-through rate and enhanced microbial activity occurring during the summer (Dong et al. 2016).

Li et al. (2016b) investigated the seasonal and spatial occurrence of seven antibiotics belonging to two groups, SAs and TCs, in water samples from the Tiaoxi watershed (Northwest Zhejiang Province, East China). Twenty-three surface water samples were collected from eight sampling sites located in areas with different land use (i.e., agriculture, forest, grassland, wetland, etc.), percentage and density of variables (i.e., population, poultry, livestock, and aquaculture). Three sampling campaigns, September 2008, March 2009, and June 2010, were conducted. The target antibiotics were detected at the eight sites throughout the study. Their concentrations were in ng L^{-1} level except doxycycline and oxytetracycline in June 2010 (μg L^{-1}). Concentrations were highly dependent on seasonal effects. Maximum concentrations of all antibiotics, except chlortetracycline, occurred in June. Meteorological data revealed larger rainfall amounts in June compared to September and March. Li et al. (2016) argued that this unusual trend, high concentrations of antibiotics during wet season, was related to the different type of source pollution (nonpoint source vs. point source pollution). The occurrence of selected antibiotics was also linked to the land use types. For example, TCs showed positive correlation with area of developed in September (r = 0.93) and barren land in March (r = 0.87). Concentrations of doxycycline and oxytetracycline were significantly correlated with density of aquaculture (r = 0.74, 0.76, respectively, June 2010).

Zhang et al. (2016a) investigated the occurrence of seventeen target antibiotics belonging to four groups, TCs, SAs, MLs, and fluoroquinolones (FQs), in soil surface samples (0 to 20 cm) collected from protected vegetable farm lands as well as open farmlands (Jiangsu, Shanghai, and Yunnan province, China). The impact of vegetable planting durations and manure type applications was also elucidated. The seventeen target antibiotics were detected in the different soil samples. Their concentrations ranged between 0.1 and 8,400 ng g^{-1}. Tetracycline, norfloxacin, ofloxacin, enrofloxacin, and roxithromycin were the only antibiotics detected in all soils samples. Significantly (p > 0.05) higher concentration of the antibiotics were observed in the protected vegetable land compared to the traditional open farmlands due to the higher loading amount of organic amendments used. The occurrence of selected antibiotics was highly impacted by farming management (organic vs. conventional) and planting duration (short term [< 5 years], middle term [5–10 years], and long term [>10 years]). Concentrations of TCs in the soils of organic farms were lower than that in conventional farms, while the highest residual concentrations of FQs were measured in soils from organic farms. In terms of planting duration, TCs and FQs showed much higher residual concentrations during the short-term planting land, while SAs showed much higher residual concentrations during the middle-term planting land.

Zhang et al. (2016c) investigated the effects of soil texture and drought stress on the uptake of three groups of antibiotics, SAs, TCs, and lincosamides. The internalization of human pathogens into lettuce through root uptake following wastewater irrigation was also investigated. Synthetic wastewater containing sulfamethoxazole, lincomycin, and oxytetracycline, and one Salmonella strain was used. The effect of soil texture was elucidated by using three soils obtained by mixing sand into Sharpsburg silt clay (25:75,

50:50, 75:25 %). The impact of drought stress was achieved by growing lettuce plants for 6 weeks in soils (sand: silt clay = 50: 50) regularly irrigated (control), not irrigated for 3 days (mild drought) and 4 days (severe drought). The selected antibiotics were detected in all soils at concentrations ranging between 11 and 736 ng g^{-1}. In sand, lincomycin concentrations were significant higher than sulfamethoxazole and oxytetracycline. Sulfamethoxazole was the only antibiotic detected in lettuce samples and increased with the percentage of sand in the soil. The difference in the pathogens levels in soil was highly impacted by the initial level of Salmonella (5 vs 8 log CFU mL^{-1}), while the soil type was not significant. According to Zhang et al. (2016c), the effects of drought on antibiotic uptake were compound specific, because the drought-trigged alteration of root exudate might have different effects on the bioavailability of different antibiotics in soil. The internalization of Salmonella was negligible when the pathogen level in irrigation water was low, and high when the initial level was high.

Zhao et al. (2016) investigated the occurrence and temporal-spatial variation of 8 antibiotics belonging to three groups, TCs, FQs, and MLs, in the intertidal zones of the Yellow River Delta (China). The partitioning trends of two antibiotics between the surface water and sediments were also investigated. Seventeen surface water and sixteen sediment samples were collected from seven sampling sites in April 2014 and September 2014. Results showed that the selected antibiotics were constantly identified at ng L^{-1} level in surface water, and ng g^{-1} level in sediments. Among the three groups of antibiotics investigated, FQs and MLs had the highest and the lowest concentrations in water and in sediments. Norfloxacin and roxithromycin showed the highest and lowest concentrations in water (70.35 and 0.21 ng L^{-1}, respectively) and sediments (105 and 0.87 ng L^{-1}, respectively). Seasonal variations were observed for most antibiotics in water (p < 0.05), except for ciprofloxacin and erythromycin, while no significant seasonal variations were observed in sediments (p > 0.05). The properties of the sediments such as particle-size fractions, cation-exchange-capacity, and the content metal ions played crucial roles in the partition behaviors of norfloxacin and erythromycin (Zhao et al. (2016)).

ANTIBIOTIC RESISTANCE GENES

Xu et al. (2016) compared two management practices for beef cattle manure, stockpiling and window composting, in terms of their effectiveness on reducing antimicrobial resistance genes (ARGs). The levels of *sul*(1), *tet*(B), and *erm*(X) in the manure declined by 0.5, 1.6 and 2.8 log units per gram of dry matter, respectively, after 102 days. The concentration of the 16S rRNA gene reduced by 0.9 and 0.6 log units per gram dry matter during composting and stockpiling, respectively. Composting resulted in a greater decrease of these genes than stockpiling due to longer thermophilic periods of temperatures 55°C. Of the genes studied, *sul*(1) had the least reduction with both management practices, while *tet*(M), *tet*(W), *erm*(B), *erm*(X) and *sul*(2) were effectively reduced during composting. Overall, composting was found to be more effective in reducing ARGs in beef cattle manure than stockpiling.

Xie et al. (2016a) assessed the long-term effects of field application of sewage sludge on the antibiotic resistome of soil using high-throughput quantitative polymerase reaction (HT-qPCR). The method included primer sets for 213 ARGs, eight transposase genes, one class 1

integrase gene, and the 16S rRNA gene. Results show that the field application of sewage sludge increased the abundance of mobile genetic element (MGE) marker genes and ARGs in comparison to the control soil receiving no sludge. A total of 130 genes were detected in both soil and sludge and were divided into two subgroups: genes conferring resistance to multidrug classes, aminoglycoside, β-lactam, macrolide-lincosamide-streptogramin B (MLSB), and vancomycin (subgroup 1) and those conferring resistance to tetracycline, FCA, and sulfonamide (subgroup 2). Genes in subgroup 1 were detected with high abundance in soils, and with low abundance or no detection in sludges. Conversely, genes in subgroup 2 were more prevalent in sludge than in soil. Aminoglycoside and tetracycline resistance genes (*aphA*(1) and *tet*(M)) were attenuated following sludge application, likely resulting from the low ability of these genes to be horizontally transferred by MGEs into soil microbiome.

In a study by Duse et al. (2016), the occurrence and spread of quinolone resistant *Escherichia coli* (QREC) were investigated in the environment. The authors analyzed fecal samples from the farm environment, postpartum cows, and preweaned calves. The genetic diversity of QREC within farms was determined in relation to geographic distance between farms and the number of cattle purchased. It was also observed that QREC was more prevalent in areas where calves were kept than in areas where older cattle were kept. Clonal dissemination of QREC was observed between and within farms due to the circulation of similar strains of QREC in the farms, as indicated by genetic fingerprinting results. Farms within shorter distance had similar QREC strains. The on-farm diversity was very low as only two genotypes were found in the five farms analyzed, however the genetic diversity increased upon the introduction of new cattle carrying new QREC strains.

Luby et al. (2016) investigated the fate and transport of tylosin resistant enterococci and macrolide resistance genes (*erm* and *msr*(A) genes) in artificially drained agricultural fields following the land application of swine manure. The level of occurrence of antibiotic resistant bacteria and ARGs in samples from plots with or without manure application were evaluated under no-till and chisel plow tillage conditions. The highest concentration of enterococci was found in soil immediately after manure application, and this concentration reduced to background concentrations within six months. Manure samples had high concentrations of *erm* genes (> 107 copies g^{-1} manure). The most frequently detected ARGs across manure, soil and drainage water samples was *erm*(B). The concentration of the *erm* genes decreased to a level similar to the control plot during the first year after manure application. Comparing manured plots to control plots, *erm*(B) and *erm*(F) concentrations were significantly greater due to manure application. In drainage water samples, *erm*(C) had the highest concentration with a steady concentration regardless the land application method used.

A study by Fang et al. (2016) evaluated changes in soil microbial community during repeated treatment by carbendazim (CBD) and chlortetracycline (CTC). Different concentrations of CBD and CTC were applied to soil individually or in combination. Degradation of both CBD and CTC followed first order kinetics with CBD having faster degradation kinetics than CTC. The relative abundance of five genera (i.e., *Bacillus, Actinobacillus, Pseudomonas, Mycobacterium,* and *Corynebacterium*) in CTC treated soil increased with increased CTC treatment concentration and frequency. The relative

abundance of these five genera decreased with increased CBD treatment concentrations and frequency. Genes coding efflux pumps (e.g., *tet*(A) and *tet*(B)), ribosomal protection proteins (e.g., *tet*(M) and *tet*(O)), and enzymatic degradation (e.g., *tet*(X)) were identified to play major roles in accounting for resistance to the CTC in soil.

Nõlvak et al. (2016) investigated the effect of inorganic and organic fertilizer on the abundance and proportion dynamics of ARGs and integron-integrase genes (i.e., *intI*(1) and *intI*(2)) in agricultural grassland soils. Targeted genes encoding resistance to sulfonamides (*sul*(1)), tetracycline (*tet*(A)), cephalosporins (blaCTX-M), penicillin (blaOXA2) and flouroquinolones (*qnr*(S)) were analyzed as affected by mineral fertilizer application in comparison to cattle slurry and cattle slurry digestate. The non-fertilized grassland soil contained background concentrations of *sul*(1), blaCTX-M and *tet*(A). Results showed that the application of mineral fertilizer increased the abundance and proportion of tet(A) in soil but had no effect of blaCTX-M or *sul*(1) as their levels remained almost identical to non-fertilized controls. Soil amendment with cattle slurry and its digestate significantly enhanced the abundance and proportion of *intI*(1), *intI*(2), blaCTX-M, and *sul*(1) in grassland soil.

Another study by Xie et al. (2016b) investigated the dynamics of antibiotics and ARGs during commercial composting of wastes from cattle, poultry and swine, at different composting phases. All of the 15 antibiotics administered and a total of 161 ARGs were detected in all the samples. ARGs encoding resistance to aminoglycoside, tetracycline, MLSB and multidrug were most frequently detected. The level of fluoroquinolones in poultry and swine manure increased after the thermophilic phase (temperature > 60°C), possibly due to the release of adsorbed fluoroquinolone from mineralized organic matters. There was a reduction in the abundance of ARGs and MGEs during composting, partly because thermophilic composting might have killed most bacteria. The results also indicated a strong correlation between ARGs (*qac*(E 1), *aad*(A2), *erm*(X), and *cml*(A1)) and MGEs (*cintI*(1), *intI*(1), *tnp*(A04)). Multiple ARGs with class 1 integron cassettes were found in close relation to transposons, which was observed in both manure and compost samples. The study also reported high correlation between MGEs and norfloxacin and ofloxacin antibiotics in compost. The authors suggested that antibiotics may cause a selective pressure for ARGs.

Leclercq et al. (2016) investigated the diversity of tetracycline mobilome within a Chinese pig manure sample. The authors identified two new tetracycline resistance genes (TRGs), one encoding for efflux pump (*tet*(59)) and one for mosaic ribosomal protection (*tet*(W/N/W)). The authors identified 17 distinct TRGs by coupling fosmid tetracycline resistance large-insert library construction and next-generation sequencing. The new efflux pump encoding gene *tet*(59) was preceded by a homolog of the tetracycline repressor *tet*(R), which is typically found upstream of tetracycline genes encoding for efflux pumps. The new gene *tet*(W/N/W) shared 96% amino acid composition with *tet*(W) and matched the central region of *tet*(N), creating the *tet*(W/N/W) mosaic gene. This study also analyzed the genomic context of the TRGs in order to identify their mobility potential and found six new putative nonconjugative transposons: Tn6298, Tn6303, Tn6299, Tn62300, Tn62301 and Tn62302.

Sui et al. (2016) examined the distribution of ARGs during the process of anaerobic digestion (AD) followed by land application of swine wastewater. The ARGs of tetracycline (*tet*(G), *tet*(M) and *tet*(X)), sulfonamide (*sul*(1) and *sul*(2)), and macrolide (*erm*(B), *erm*(A), *ere*(A) and *mef*(A)) were detected in high abundance (>108 copies mL^{-1}) in swine wastewater and digested liquor. AD could reduce ARG levels by 0.21 to 1.34 orders of magnitude. The findings highlighted a significant difference in the ARG removal efficiency between the seasons. The copy numbers of *tet*(X), *sul*(1), *sul*(2), *erm*(B), *mef*(A) were significantly reduced in the winter. The results of the study also confirmed that when AD operation temperature was increased to 55°C, the removal rate of some genes (i.e., *tet*(A), *tet*(O), *tet*(X), *tet*(W) and *intI*(1)) was enhanced.

Background levels of antibiotic resistance in southeastern Nebraska soils was recently characterized by Durso et al. (2016). They sampled native Nebraska prairie soils not affected by human or food-animal waste production. Soil samples were collected from 20 sites, in five counties, enumerated on tetracycline and cefotaxime media, and screened for tetracycline-, sulfonamide-, β-lactamase, and macrolide-resistance genes. Selected sites were not grazed during the last 20 years. To minimize potential sources of variations, sites were selected based on geographic proximity, and all sample collections were performed within the same week. Phenotypically, all 100 native Nebraska prairies soil samples contained bacteria that were resistant to tetracycline and cefotaxime. Genotypically, carriage of tetracycline genes in bulk soil DNA extracts was common. Ninety-eight percent of the soil samples and all 20 prairies had at least one tetracycline gene. Despite the lack of human inputs at the selected sites, 91% of the samples showed the presence of sulfonamide genes. No correlations were found between either phenotypic or genotypic resistance and soil physical or chemical properties (Durso et al. 2016).

Graham et al. (2016) used historical data to identify which sector, agricultural versus medical antibiotic, had most influenced acquired antibiotic resistance (AR) on broad scales. Four broad-spectrum β-lactam AR genes (ARG; blaTEM, blaSHV, blaOXA, blaCTX-M) and class-1 integron genes (int1) in soils from manured (M) versus inorganic fertilized (IF) fields. The Askov Long-Term Experiment (LTE) Station in Denmark was selected due to the extensive information available since 1894. Total β-lactam ARG levels were higher in M versus IF in soil post-1940. Dominant individual ARGs varied over time. blaTEM and blaSHV were predominant between 1963 and 1974, while blaCTX-M became predominant since 1988. When non-therapeutic antibiotic use was banned in Denmark, blaCTX-M levels declined in M soils. Graham et al. (2016) suggested that a strong bridge between clinical and agricultural AR was apparent and to reduce globally increasing AR, antibiotic use and stewardship must improve across all sectors.

CYANOTOXINS

Cyanotoxins are often discussed as the potentially harmful byproducts of urbanization and agriculture due to their broad distribution in both marine and freshwater ecosystems. For example, Loftin et al. (2016) explored the distribution and prevalence of cyanotoxins in a nation-wide survey of 1161 lakes and reservoirs across the continental United States. Hepatotoxic microcystins (MC) were prevalent in 32% of the sampled lakes with a mean

concentration of 3.0 μg L^{-1}. Other cyanotoxins, including cylindrospermopsin, the neurotoxins saxitoxin, anatoxin-a, and nodularin-R were also detected in 4.0%, 7.7%, 15%, and 3.7% of the samples, respectively. The survey also noted that the co-occurrence of cyanotoxins was rare among the surveyed sites.

Cyanotoxins are not limited to surface waters. Global reports have noted the presence of MC in desert drylands (Chatziefthimiou et al. 2016) and movement into groundwater reservoirs (Yang et al. 2016b). Yet despite the widespread prevalence of MC and other cyanotoxins, the impact of harmful algal blooms is still debated due to a lack of congruency among survey data collected across multiple agencies (Brooks et al. 2016).

Microcystins are produced by a variety of cyanobacterial strains (e.g. *Microcystis spp.*). In order for a toxic bloom to occur, however, a population of cyanobacteria with the genetic capacity to produce toxins must exist within a specific set of environmental parameters. Marmen et al. (2016) evaluated the presence, distribution, and genetic diversity of potentially toxin-producing *Microcystis* in 58 Israeli surface waters using the genes *mcyA* and *mcy*D, two components of the genetic pathway required for the production of MC in the genus *Microcystis*. Using PCR amplification of the two genes, potentially-toxic *Microcystis* strains were identified in roughly 65% of the sampled locations. All those serving as aquaculture or irrigation waters were *mcyD* positive indicating the presence of potentially toxic *Microcystis* and suggesting a strong potential for crop-land contamination by cyanotoxins.

Recent reviews have further highlighted the role of cyanotoxins as emerging freshwater contaminants in agro-ecosystems primarily through toxin accumulation in plant tissues and yield reduction from irrigation with toxin-contaminated waters (Bouaïcha and Corbel 2016; Testai et al. 2016). Bioaccumulation of MC in food-crops including rice (Liang et al. 2016a), tomato (Corbel et al. 2016), lettuce (Bittencourt-Oliveira et al. 2016); and arugula (Kézia Cordeiro-Araújo et al. 2016) have illustrated that MC accumulation in plant tissues is influenced by a variety of factors relating to the species and developmental state of study plants as well as the type, exposure time, and concentration of the cyanotoxins. For example, Corbel et al. (2016) evaluated MC bioaccumulation in tomato (*Solanum lycopersicum*) tissues (root, stem, leave, and fruit) started from seed. Seedlings were exposed to 90 days of daily microcystin treatments ranging between 0 – 100 μg equivalents of microcystin-LR L^{-1}. MC-LR was detected in all tissues with the exception of the fruit at the time of harvest, but at very low concentrations that never exceeded 0.001% of the total MC quantity the plant was exposed to during the irrigation period.

Comparatively, in a study focused on the impact of contaminated irrigation water on rice (*Oryza sativa*) MC bioaccumulation, Liang et al. (2016a) irrigated seedlings with MC-contaminated water produced from freshly lyophilized cyanobacterial extracts. Plants were exposed to total MC concentrations ranging between 1 – 3000 μg L^{-1} for 7 days. One-third of the plants were harvested after the 7 d exposure, one third following a 7 d recovery without MC exposure, and the final third after maturation. MC significantly accumulated in the seedling roots and leaves during the initial 7 day exposure at 1000 μg L^{-1} and 3000 μg L^{-1} which was maintained through the recovery period. Roughly 10 % of the applied MC was

detectable within the roots of plants exposed to the highest MC treatment concentration. At the time of harvest, MC had aggregated in all plant tissues, including the grains, reflective of the treatment MC concentrations. Further, rice plants exposed to the higher treatment concentrations also had reduced growth and photosynthetic rates.

Microcystins are also likely to accumulate in soils (see Bouaicha and Corbel 2016 for review) and therefore, may also affect plant growth through effects on the soil microbial community. El Kalloufi et al. (2016) evaluated the effects of MC-contaminated waters on the rhizosphere growing in conjunction with the non-food crop alfalfa (*Medicago sativa*). Seedlings were exposed to 100 μg MC-LR L^{-1} isolated from a cyanobacterial extract every three days for a 30 day period. Microbial communities from the soils, rhizosphere, and roots between non-exposed and exposed treatments revealed compartment-specific results. MC exposure primarily influenced the relative abundance and diversity of various bacterial families in the bulk soil and most notably affected the relative abundance of *Pseudomonadaceae* and *Enterobacteriaceae* in the root and root-adhering communities.

Treatment with MC containing waters may also select for MC-tolerant bacterial strains that buffer the detrimental effects of MC on plant growth. For example, Lahrouni et al. (2016) demonstrated that a MC tolerant *Rhizobium* strain was able to maintain nodulation and nitrogen content of plants during sustained treatment with MC-containing irrigation water. Here, previously isolated *Rhizobium* strains with varying degrees of sensitivity to MC were grown with faba bean (*V. faba* L. var. Aguadulce) and exposed to 100 μg L^{-1} for a one month period. Nodulation in plants with the MC-tolerant strain decreased by roughly 10% when exposed to MC while plants with the MC-sensitive strain decreased by 20%. Given the available information, further work related to the impacts of compromised irrigation water on agricultural environments is needed to full assess the impact of freshwater cyanotoxins on food and non-food crops.

ACTIVATED CARBON AND BIOCHAR

Recently, carbonaceous geosorbent materials, namely biochar (BC) and activated carbon (AC), have been investigated for their use in agricultural applications. As a soil amendment, traditional benefits of BCs and ACs include increased carbon sequestration, increased soil fertility, and increased plant productivity. In addition, numerous other impacts of AC and BC soil amendments have been identified in studies published in the previous year. One of the most profound ancillary benefits of AC & BC amendments is their high sorption potential and resultant effects on the mobility of contaminants through impacted soils. Heavy metal contamination in agricultural soils remains a significant concern with impacts on plant productivity as well as potential for human exposure. In an experiment that monitored Cd and Cu levels in paddy soils over the course of three years following BC amendment, Li and co-authors showed that contaminant bioavailability to rice was reduced. Their comparison of two BC materials showed that characteristics of BCs impact how they age over time which in turn effect their longterm in-situ viability (Li et al. (2016a)).

A similar study compared amendments utilizing an AC and a BC on the phytoavailability and phytotoxicity of Cd, Pb, and Zn, on two plants, spinach and mustard. Brendova et al.

(2016) showed that both AC and BC amendments resulted in increased plant biomass. However, the effects on phytoavailability were contaminant specific, amendment specific, and plant specific.

In addition to metals, changes in compound mobility resulting from BC amendments were investigated for other chemical classes including pesticides, herbicides, and pharmaceuticals. Pesticide runoff is a significant concern of ecologists and motivated the study by Jin et al. (2016) to predict and confirm sorption capacity of different BC soil amendments. While results showed that BCs were effective in stabilizing pesticide contaminated soils, predicting sorption capacity was made increasingly complicated by cross-effects between BCs and soil. Comparing two BC materials, Bair et al. (2016) showed that sorption capacity varied between the two BCs and this difference was magnified by the concomitant addition of biosolids. They also note that for some compounds, namely agrochemicals, sequestration by BCs can limit their efficacy.

Impacts with native soil microbial communities by BC amendments has been the subject of significant study and the idea that BC may benefit microbiota by providing optimal microhabitats was the focus of Schnee et al. (2016). Their study of two BC materials with very different pore structures, showed that BC is capable of promoting microbial colonization; However, physical pore space characteristics were not adequate predictors for microbial habitat quality. Promotion of microbial activity resulting from BC amendments was not observed in arid and semi-arid soils at relevant BC application rates in a paper by Elzobair et al. (2016). This was in stark contrast to manure amendment which significantly impacted microbial communities and enzymatic activities in the same soils.

Soil amendments incorporating ACs and BCs do not provide only potential benefits, there are risks associated with their use as well. Noting that BC formation often results in the incorporation of polycyclic aromatic hydrocarbons and metals which are introduced into the soil environment along with the BC material, Visioli et al. (2016) used root phytoxicity bioassays to assess biochar ecotoxicity. They noted that metal contamination associated with biochar had the potential to effect root elongation but had little effect on seed germination.

The use of AC and BC is not limited to soil amendments. Composting of bio-waste is an emerging frontier for utilization of these materials. A BC material derived from straw was shown to accelerate the degradation and maturation of composted pig manure in a study by Zhang et al. (2016b). The BC amendment increased humidification, decreased dissolved organic content and NH4, increased conductivity and lowered the pH.

Jindo et al. (2016) found that biochar amendments to manure compost increased the C content of humic and fulvic acids in the manure with greatest impact on the stabilization of fulvic acids. They noted that sorption of humic substances by the BC likely protected them from further decomposition resulting in increased compost quality.

The interaction between BC and bio-waste was investigated at two major phases of the composting process in a study conducted by Vandecasteele et al. (2016). Adding BC amendments either at the start of composting or later prior to compost storage, researchers were able to determine specific impacts to the material compost. When added at the

beginning, faster rate of decomposition, reduced emissions of greenhouse gasses, reduced losses of N, and increases in readily available P were observed. When BC was added after composting, just prior to the storage period, an increase in C content and a reduction in P resulted. While the timing of BC addition impacted the condition of P in the resulting compost, field trials with ryegrass using the different compost conditions showed no clear impact on differences in P utilization by the plants.

Similar to soil amendments, when BCs are added to composting material the microbial community and function is influenced. Following the theory that heavy metal contaminants present in compost materials provide a selective pressure on bacterial populations which contribute to the proliferation of antibiotic resistance, Cui et al. (2016) investigated antibiotic resistance genes (ARG) in chicken manure compost following the addition of different biochars. Their study revealed that reductions in heavy metal bioavailability correlated with reduction in ARGs. However, these results were BC dependent with ARG, likely associated with non-pathogenic bacteria, increasing in the presence of one BC material even though metal concentrations were reduced.

The ability to engineer AC and BC materials for specific environmental applications represents an exciting technological frontier and was the topic for a recent review by Rajapaksha et al. (2016). They found that physical, chemical, impregnation, and magnetic processes could be used to create outcome-based biochar modifications with the potential to increase their use in remedial technologies. Ahmed et al. (2016) et al. examined the same basic concept of modified BCs as they relate to water and wastewater treatment and highlight studies that engineer surface functionality as well as nanomaterial impregnation to increase efficiency, capacity, and selectivity of contaminant sorption.

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