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Abstract
A total of 75 papers published in 2017 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, and engineered nanoparticles 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, Fate and Occurrence, Pharmaceutical Metabolites, Anthelmintics, Antibiotic Resistance Genes, and Engineered Nanomaterials.

Keywords: pharmaceuticals, steroid hormones, anthelmintics, analytical methods, antibiotics, resistance genes, water and wastewater, agricultural environments.

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 clean– up 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 2017 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, and antibiotic resistance genes in bacteria. Studies on pesticides and flame retardants are not reviewed unless they were evaluated in the same study. A new section this year is a review of the literature on engineered nanomaterials in agricultural environments.

Analytical methods

New developments in analytical methods permit more rapid, sensitive, and simplified analysis of emerging contaminants in agricultural environments. Refinement of extraction, purification and detection methods can support research in the fate, transport and biological effects of these substances. There seems to be more emphasis on comprehensive screening methods for a wider variety of contaminants. For example, Aparicio et al. (2017) investigated the extraction of organic contaminants from environmental water using stir bar sorptive extraction (SBSE) with liquid chromatography tandem mass spectrometry (LC/MS/MS) detection. PDMS and EG– silicone stir bar coatings were tested for recovery efficiencies for both polar and non–polar pollutants. Other conditions for the extraction and desorption of analytes from 8 different contaminant groups were optimized which resulted in detection limits ranging from 7.0 ng/L to 177 ng/L. Percent recoveries were calculated to be between 61% and 130%. The method was applied to surface and tap water samples where surface water detections of surfactants ranged from 35 ng/L to 2326 ng/L.

A method utilizing online solid phase extraction (SPE) with LC/MS/MS has been developed by Axel et al. (2017) for the determination of 17 selected antibiotics and carbamazepine in water. Detection limits of less than 10 ng/L were achieved for most analytes. Downstream river water with effluent from two wastewater treatment plants were studied using the method. Results obtained were comparable to previous studies and detected carbamazepine as well as 7 other target antibiotics at concentrations up to 81 ng/L.

Comtois–Marotte et al. (2017) developed a multi–residue method with solid phase extraction pre–concentration and clean–up for the determination of 31 emerging contaminants in water, wastewater, and solid samples. Optimized MS/MS and full scan methods were compared to determine the best analysis suitability for each matrix. Contaminant concentrations obtained from the application of the method to WWTP effluents are presented. Filtered wastewater samples were also subjected to a yeast estrogen screen (YES) assay for comparison to results obtained from the LC/MS/MS analysis and ranged from 4.4 to 720 ng eq E2/L.

Solid phase extraction of tetracyclines from water samples utilizing magnetic silica magnetite nanoparticles was the focus of a method developed by Kaewsuwan et al. (2017). The synthesis of the nanoparticles and optimization results of various parameters are discussed. Detection limits of less than 10 µg/L were obtained. The results of analyzing real spiked water samples revealed recoveries between 82% and 88% for concentrations between 20 and 200 µg/L.

A multi–residue method for the determination of ten emerging contaminants in soil was presented by Lee et al. (2017) utilizing SPE and HPLC/MS/MS. The optimized soil extraction utilized a modified QuEChERS extraction with acetate and acetic acid to improve the extraction efficiency and analyte stability. Detection limits ranged from 0.05 µg/kg to 10 µg/kg with most recoveries between 60% and 120%. Real soil samples from the Korean Peninsula were evaluated with the method. Detections of clopidol, sulfathiazole, sulfamethazine, tiamulin, and tylosin were observed at concentrations below 10 µg/kg.

Li et al. (2017b) present a method for the determination of 82 veterinary drugs in swine lagoons using LC/MS/MS. Solid phase extraction (SPE) concentration and clean–up with Oasis PRiME HLB was superior to other tested C18 and HLB polymeric SPE cartridges. Most detection limits were less than 1 µg/kg with recoveries between 60% and 110%. Analysis of sludge samples from 3 swine lagoons showed maximum contamination concentrations of 2826 µg/kg for chlortetracycline and 1456 µg/kg for sulfamonomethoxine, with detections for other contaminants below 266 µg/kg.

A multi–residue SPE and HPLC/MS/MS method for the analysis of 63 pharmaceutical compounds in natural water has been developed by Mokh et al. (2017). The optimized method used acetonitrile:water (60:40) to elute the analytes from HLB SPE cartridges which were used to extract acidified samples followed by electrospray ionization mass spectrometry. Detection limits ranged from 2.3 ng/L to 94 ng/L with recoveries between 68% and 134%. Application of the method to water samples taken from sources in Lebanon detected caffeine and erythromycin at concentrations in excess of 2000 ng/L. Correlation data to bacteria contamination is also presented.

A multi–residue method for the analysis of phytoremediated micropollutants from wetlands has been developed by Petrie et al. (2017). The analytes were extracted by microwave accelerated extraction (MAE) from *Phragmites australis*, which had absorbed the pollutants in a constructed wetland setting. Extraction temperature was determined to be the most influential factor on recoveries. Recoveries of 80–120% were obtained with detection limits below 5 ng/g. Concentrations of pollutants ranged up to 200 ng/g in the plant extracts. Several metabolites were also observed which indicated that metabolism in the plant was possibly occurring.

A method for the extraction of tetracyclines (TCs) in water and milk using *in situ* SPE combined with HPLC analysis has been developed by Phiroonsoontorn et al. (2017). The TCs were extracted using precipitated hydroxide salts of magnesium and aluminum in alkaline conditions. The analytes were subsequently eluted for HPLC analysis by acidification of the separated precipitate. Enrichment factor optimization is discussed. Detection limits of 0.76 µg/L were obtained with recoveries of 81, 108%, and 55 89% for water and milk, respectively.

Rubirola et al. (2017) describe a multi–residue method for the determination of 24 pesticides, hormones, and pharmaceuticals in drinking water, surface water, and wastewater. The method utilized an automated on–line solid phase extraction protocol coupled to HPLC separation and MS/MS detection. Optimization of various parameters is discussed, including SPE cartridge type and volumes used for sample size and cartridge washing. Detection limits of 0.3 ng/L to 4.8 ng/L were obtained with recoveries greater than 85%. The method was applied to environmental waters from WWTP and DWTP sites in Spain.

The detection of endocrine disruptor contaminants (EDCs) in river water was the focus of a SPE/GC/MS method presented by Sghaier et al. (2017). The method was optimized for derivatization reaction conditions using BSTFA and gas chromatography mass spectrometry (GC/MS). Detection limits between 1 ng/L and 10 ng/L were obtained for 13 EDCs with recoveries of 52–71%. The method was applied to waters from six northern Europe rivers. High detections of bisphenol A and estrone were observed in two of the sampled rivers.

Wei et al. (2017) describe a method using ultrasound assisted dispersive liquid–liquid microextraction (UA–DLLME) method with LC/MS/MS detection for the determination of 23 endocrine disrupting contaminants in environmental and food samples. The compounds of interest were derivatized *in situ* with 4′–carbonyl chloride rosamine to enhance the electrospray ionization efficiencies during analysis. The optimized derivatization parameters are discussed. Recoveries of 83–116% were obtained with detection limits of 0.05–0.40 ng/L for environmental samples and 0.03–0.25 ng/g (dry wt.) for food samples.

A method for the determination of fluoroquinolones in fish biofluids and tissues as well as environmental waters has been described by Ziarrusta et al. (2017). Optimized extraction and clean–up protocols are discussed for each matrix. Recoveries between 80% and 126% were obtained. The method was utilized to study fluoroquinolone contamination in water samples taken from WWTP effluent, a downstream estuary, and seawater. Bioaccumulation in fish livers was also observed. Fluoroquinolones were detected up to a concentration of 278 ng/L in water and 4 ng/g in fish liver.

Bioassays

Biological endpoints can be used to screen samples for both measured and unknown contaminants. Neale et al. (2017) present an evaluation of small stream contamination by wastewater effluent by combining SPE with LC/MS/MS and bioassay screening. Four hundred and five compounds were analyzed by the analytical method to obtain concentration data. The same extracts were also subjected to eleven different bioassays to assess the environmental impact of the chemical contamination. The authors presented their conclusions on the importance of evaluating the effects from WWTP effluents by both biological and chemical factors.

Kunz et al. (2017) evaluated five in vitro bioassays for the estrogenic activity differences obtained from each assay. Various levels of estrogenic contamination were studied, from high levels to lower levels which required concentration with SPE and intra– day and inter– day variabilities were obtained. Coefficients of variation (CV) of 32% were found for the E2 equivalent results from all water samples and assays. The study found that the ERα–CALUX assay had the best repeatability and precision of the assays tested.

In a nationwide study by Conley et al. (2017), *in vitro* estrogen, androgen and glucocorticoid receptors were analyzed in stream water from 35 sites across 24 states and Puerto Rico. *In vitro* estrogen activity was detected in all the sites with concentration range of 0.054–116 ng/L. A strong linear correlation was reported between *in vitro* estrogen activity and steroidal estrogen after in vitro potency correction. Concentration of androgenic compounds and glucocorticoid receptor active compounds were mostly undetected (<25 %). The authors suggested that *in vitro* bioassays could be potentially used as a first–tier screen in environmental monitoring to identify chemical in environmental mixtures through their receptor activities.

Fate and occurrence

The literature in 2018 continues to provide clues to the environmental fate, occurrence and transport of emerging contaminants in agricultural environments. Papers published include studies of veterinary antibiotics, steroid hormones and other biologically active substances.

Veterinary Antibiotics

Transport of oxytetracycline, chlortetracycline and ivermectin from manure to irrigated pastures by surface runoff was studied by Bair et al. (2017), in the Sierra Foothills of Northern California. Less than 0.1% of the pharmaceuticals applied to manure were found in the runoff water with concentration range of 0.001–1.3 µg/L. In comparison to that, pharmaceuticals were strongly sorbed to manure and accumulated in the upper 5 cm of soil directly underneath the manure, with a concentration range of 24–175 µg/kg. There was no significant change in pharmaceutical runoff with increased irrigation flow or length of vegetative filter strip.

Out of eighteen antibiotics detected by Ding et al. (2017) in the Poyang Lake, China, sulfadiazine, oxytetracycline and doxycycline had the maximum concentrations ranging from 39.7–56.2 ng/L with greater than 50% detection frequency. The authors suggested that these high concentrations were related to the veterinary related agricultural use in the surrounding areas. Roxithromycin had the highest detection frequency ranging from 87.5–100% in each sampling period though its lowest concentrations resulted from dilution effects of high water flow during the peak periods. The risk quotients of these antibiotics were calculated to be below 0.01, indicating minimal ecological risks.

Twenty–five antibiotics, including 10 sulfonamides, 4 macrolides, 5 fluoroquinolones and 6 chloramphenicols, were measured in the coastal region of China, bordering South Yellow Sea by Du et al. (2017a) with concentrations up to 1349 ng/L. Fluoroquinolones and sulfonamides were most abundant with detection frequency of 50–70%. Trimethoprim was found in all samples. The distribution of antibiotics had a seaward decreasing trend with attenuation rate ranging from 0.07–0.19 km^{-1}. The authors concluded that dissolved organic carbon (DOC), salinity and seawater dilution contributed to the fate and transport of antibiotics in this region.

Tong et al. (2017) detected sixteen antibiotics in different alluvial sediment aquifer layers from breeding areas such as pig farms, chicken houses, fishponds and riverbanks in Jianghan Plains, China. Tetracyclines and fluoroquinolones had the highest concentrations ranging from 54–71 ng/g at detection frequencies of 82%. Samples collected from the river bank had the highest antibiotic concentrations followed by fish pond, pig farm and the lowest from the chicken houses. The concentrations were not found to decrease by depth, but increased between 0.6 and 1 m. Most of the antibiotics were retained within 8 m from the surface and only sulfadiazine and chlortetracycline were detected below 20 m of depth.

In another study done by Sun et al. (2017) in the Yangtze River Delta, China, 13 antibiotics were detected in agricultural soils with total concentrations ranging from 4.55 to 2,010 ng/g with quinolones having the highest mean concentration of 48.8 ng/g, followed by tetracyclines and sulfonamides with a mean concentration of 34.9 ng/g and 2.35 ng/g, respectively. High concentrations of antibiotics were detected in sites near manure application and wastewater irrigation that were the main sources of antibiotic inputs in the region. Antibiotic resistance genes were detected in 15 soil samples that had significant correlation with quinolones and tetracyclines. From the risk assessment studies, the authors concluded that doxycycline and ciprofloxacin could have severe ecological effect in agricultural soils.

Jaffrezic et al. (2017) found a predominance of veterinary and mixed–use pharmaceuticals including quinolones, tetracyclines, sulfonamindes and penicillin, over human specific pharmaceuticals, in Haute Rance, France with concentration ranging from 11–350 ng/L. Veterinary pharmaceuticals were only detected during runoff events from field sites where animal manure had been land applied. Mixed use and human–only pharmaceuticals were predominant in larger watersheds when run–off decreased.

In one of the first studies in Bangladesh, Hossain et al. (2017) found sulfamethoxazole, trimethoprim and tylosin to be the predominant antibiotics in both shellfish and finfish aquaculture water, with concentrations ranging from 7–42 ng/L. Preliminary ecological risk assessment showed no adverse risks with a risk quotient of less than 1. In a joint two phase U.S. Geological Survey and U.S. Environmental Protection Agency study reported by Furlong et al. (2017), treated water from 25 drinking water treatment plants with probable wastewater inputs were collected and analyzed. The treatment processes were reported to reduce the pharmaceutical concentrations from the source water to finished water. Carbamazepine, bupropion, cotinine, and metoprolol were more persistent with a median concentration of 113 ng/L.

A rainfall simulation study by Biswas et al. (2017), was conducted over 30 days in a continuous corn field with manure application rate of 170–193 Mg/ha followed by tillage treatments. The manure was either composted or stockpiled with a portion coming from hormone treated cattle. There was no statistically significant difference in hormone concentrations of manure from treated and untreated cattle in both stockpiled and composted manure. 4–androstenedione, estrone and progesterone were detected with concentration range of 0.7–6.8 ng/g in both composted and stockpiled manure irrespective of hormone treatment. In the runoff samples, estrogen and estrogenic substances were most commonly detected, with estrone and estriol, both metabolites of 17β-estradiol, occurring in 9% of the samples after the 30 days interval rainfall event. Overall there was a very low detection of hormones in runoff samples. The study concluded that detectable hormone levels could be found in surface runoff regardless of tillage and manure treatment practices. Timing of rainfall, hydrological events, tillage relative to manure application and soil properties were found to be important factors in hormone exports in runoff.

Surface water of four Midwestern national parks were collected and analyzed by Elliott and VanderMeulen (2017) for pharmaceuticals, hormones, personal care products, flame retardants and pesticides. Pesticides such as atrazine, simazine and metolachlor were detected in higher concentrations than other chemicals groups with simazine exceeding 1000 ng/L. Two of the four parks with greater urban influence had overall higher concentrations and larger number of the chemicals detected. Most chemicals were detected below permissible limits, except hydrochlorothiazide, simazine and estrone.

The occurrence and concentrations of antibiotics comprised from members of 6 chemical groups in shallow groundwater in China were studied by Chen et al. (2017a). Lincosamides were detected with the highest frequency but the results did not show a distribution pattern for the groups studied. Highest individual concentrations of 1200 ng/L and 861 ng/L were observed for ofloxacin and lincomycin, respectively. Antibiotics were detected in 73 of 74 monitoring wells sampled in the study.

Pharmaceutical metabolites

Significant progress has been made over the last 10 years with regards to improving our understanding of the presence of antibiotics and other pharmaceuticals in agro–ecosystems, however this body of work has primarily focused on the pharmaceutical parent compounds with limited effort to understand the fate and uptake of potential metabolites and transformation products.

This trend is changing, and a number of studies have confirmed the presence of pharmaceutical metabolites in treated wastewater used for irrigation and in WWTP sludge which can be used as a soil amendment.

Occurrence and fate

A review by Yin et al. (2017) summarizes the occurrence of pharmaceuticals and their transformation products in WWTP by–products (effluent and sludge) and soils highlighting the importance of not neglecting the presence of pharmaceutical transformation products in the environment. Taking advantage of the increasing sensitivity in mass spectrometry instruments, a simple and rapid analytical method to detect 88 pharmaceuticals and transformation products was published (Campos–Manas et al. 2017). Using this method, carbamazepine 10, 11–epoxide was detected in treated wastewater samples sampled from an urban WWTP in Almeria with concentrations in the range of 217–384 ng/L.

Biodegradation and biotransformation play an important role in the fate of pharmaceuticals in agricultural soils. The transformation of three antibiotics (clindamycin, sulfamethoxazole, and trimethoprim) in twelve different soils with contrasting properties was studied by Koba et al. (2017). The parent compounds were degraded in all soils and resulted in the formation of five metabolites. Interestingly, the formation and degradation of all detected metabolites was strongly correlated to the soil type. Clindamycin was almost completely degraded in all soils and resulted in the largest number of identified and detected metabolites, with clindamycin sulfoxide being the main metabolite of clindamycin at concentrations <2000 pmol/g. Only one metabolite was found in both the sulfamethoxazole and trimethoprim exposures, namely N4–acetyl sulfamethoxazole, and hydroxy trimethoprim respectively. Almost all of the formed metabolites were persistent in the soils, with the exception of N4–acetyl sulfamethoxazole.

The effect of exogenous organic matter (sewage sludge and farmyard manure) on sulfamethoxazole transformation was investigated by Goulas et al. (2017). Very low concentrations of sulfamethoxazole transformation products (N4–acetyl–sulfamethoxazole, 3–amino–5–methylisoxazole, aniline) were quantified after a three–month long incubation in this study. Transformation into metabolites and sorption to soil organic matter were concluded to be the key reasons behind the low environmental availability of sulfamethoxazole.

The degradation kinetics of sulfamethoxazole was also investigated by Zhang et al. (2017b), in addition to another antibiotic, sulfadiazine, under a range of incubation conditions. Sulfadiazine had a quicker dissipation rate and shorter half–life than sulfamethoxazole. After 49 d metabolites were identified in both of the antibiotic exposures with further analysis elucidating that reaction types including S–C bond cleavage, C–N bond cleavage, S–N bond hydrolysis, ring open and hydroxylation/oxidation were the key reactions resulting in the formation of transformation products. The degradation of these two antibiotics was found to increase after the application of manure to the soil system (<20%) with differences in mode of applying the manure (e.g. single or repeated) having a strong effect on the degradation rate.

Additional studies have reported significant degradation of pharmaceuticals in agricultural soils (Hurtado et al. (2017), however they did not identify the presence of specific metabolites or transformation products.

Plant Uptake of Metabolites

If metabolites and transformation products are present in soil systems there is the potential for these chemicals to be taken up and accumulate in plant material. Montemurro et al. (2017) irrigated lettuce plants with tap water containing 13 contaminants including two metabolites (acridone and valsartan acid) spiked at a concentration of 200 µg/L. All chemicals, including the two metabolites, were taken up by the lettuce after irrigation, resulting in average concentrations below 30 ng/g (dw) for acridone and valsartan acid.

Research has also demonstrated the active in–plant transformation of pharmaceutical parent compounds taken up from the soil, including work by Riemenschneider et al. (2017a); Riemenschneider et al. (2017b). Application of the method developed to analyze a broad range of contaminants, including nine metabolites of carbamazepine in plant tissues the authors re–analyzed samples from a previous study by Goldstein et al. (2014) to investigate the presence of additional carbamazepine metabolites. A total of seven metabolites were identified in the tomato plant and four metabolites in the cucumber plant – indicating plant specific metabolism. 2–OH–carbamazepine was identified and quantified as one of the main metabolites in addition to epoxy–carbamazepine and trans–Di–OH–carbamazepine in tomato leaves. This study demonstrated that the presence of metabolites should not be neglected when considering accumulation in plants as the concentration of carbamazepine and its metabolites was 2–fold (for cucumber) and 3.5–fold (for tomato) higher compared to carbamazepine concentrations alone.

Riemenschneider et al. (2017b) also explored carbamazepine transformation in tomato plants grown hydroponically where a total of 11 transformation products (mainly phase–I) were quantified. Whilst metabolites were detected in all plant parts including roots, stems, leaves, immature and mature fruits the ratio of carbamazepine metabolites to carbamazepine parent compound was highest in fruits (up to 2.5) and leaves (0.5), suggesting an intensive transformation of carbamazepine in these compartments. A further 10 novel transformation products (phase–I and II) were identified by LC–high resolution mass spectrometry screening. This led to a proposed transformation pathway for carbamazepine that was comparable with the metabolism of carbamazepine in humans.

Even with the scientific advancements documented in this review there is still paucity of knowledge concerning transformation product pathways in agro–ecosystems and their potential fate and uptake into crops with a majority of research focusing a small number of chemicals, in particular the carbamazepine metabolite, carbamazepine 10–11, epoxide and the transformation products of sulfamethoxazole (Klatte et al. 2017).

Anthelmintics

The interest related to the occurrence, and removal of anthelmintics in the environment has increased during the past few years. Kim et al. (2017) investigated the occurrence trends and effects of 30 human and veterinary pharmaceuticals, including antibiotics, anthelmintics, anti–inflammatory drugs, and β–blockers on seawater, sediment, cultured fish, and their feed collected from coastal and fish farm areas. Seven anthelmintics (albendazole, fulbendazole, thiabendazole, fenbendazole, fenbendazole–SO, fenbendazole–SO2, and prazoquantel) were analyzed. In seawater samples collected from coastal areas and fish farm areas, anthelmintics accounted for approximately 5% of the total concentration of the investigated compounds. Their total concentration ranged between 7.49 and 24.7 ng/L in coastal areas and between 5.91 and 29.0 ng/L in fish farm areas. Among the seven anthelmintics investigated, fenbendazole (1.3–11.6 ng/L) and praziquantel (2.78–22.7 ng/L) showed the highest concentrations in fish farms seawater samples and in coastal areas seawater samples, respectively. Albendazole, flubendazole, and fenbendazole–SO2 were not detected in seawater samples throughout the study (Kim et al. 2017). In contrast with the seawater results, anthelmintics were dominant in sediment samples collected from coastal areas and fish farm areas, accounting for 60% and 50%, respectively, of the total pharmaceuticals. Thiabendazole showed the highest concentration in fish farm sediments (20.7–697 ng/g) as well as in coastal area sediments (0–240 ng/g). Fenbendazole–SO2 was not detected in sediment samples throughout the study.

No anthelmintics were detected in sludge samples from three swine farms in Shandong Province, China (Li et al., 2017a). Similarly, no anthelmintics were detected in raw milk from dairy farms in Hebei Province, China (Han et al., 2017).

The ability of conventional activates sludge treatment (Čizmić et al., 2017a), advanced oxidation processes (Čizmić et al., 2017b) and biodegradation (Marsik et al. 2017); Raisová et al. 2017) to remove of anthelmintic compounds has been evaluated. For example, Čizmić et al. (2017a) investigated the occurrence and removal of 22 pharmaceuticals, including three anthelmintics (febantel, levamisole, and praziquantel) in a municipal WWTP that serves 1.2 million inhabitants, with maximum capacity of 330,080 m^3 per day with full mechanical and biological treatment based on conventional activated sludge treatment. Preziauntel and levaminole were detected in the influent (1110 and 229.8 ng/L, respectively) as well as in the effluent (112 and 176 ng/L, respectively). Praziquantel was below the analytical detection limit throughout the study. Removal efficiency ranged between 23% (levamisole) and 90% (febantel).

Čizmić et al. (2017b) investigated the ability of different treatments, including direct photolysis, photocatalysis, UV radiation, TiO_2 film, and hydrogen peroxide (H_2O_2), to remove praziquantel. The degradation of praziquantel followed the first order kinetic throughout the study. UV–C radiation with the TiO_2 film as a catalyst and H_2O_2 as an additional oxidant represented the most efficient experimental configuration. The photo degradation was inhibited in the presence of methanol. Five degradation products of praziquantel were observed during the photolytic and photocatalytic degradation processes. The two main degradation pathways include: amide bond cleavage inside the central tetrahydro–pyrazine ring and cyclohexane side–ring cleavage to the isopropyl group.

Marsik et al. (2017) evaluated the plant potential to remove, accumulate and/or degrade praziquantel in laboratory conditions, using Phragmites cell suspension and *in vitro* cultivated plants, and tested the results in a constructed wetland. The uptake and biotransformation was impacted by the starting concentration of the anthelmintic compounds. The biotransformation started rather slow and the decrease in the medium was less than 10% after 10 days when high concentration (200 mg/L) was used. A lower starting concentration (20 mg/L) and a longer incubation time (21 days) led to a 90% reduction in the medium (Marsik et al. 2017). The decrease of praziquantel concentrations within the medium of plant cell suspensions was also observed, and indicated its metabolic conversion. The accumulated anthelmintic compound was partly metabolized, and twenty–one compounds were identified. Praziquantel was completely removed and/or accumulated before the outflow point of the constructed wetland.

Raisová et al. (2017) tested the uptake and biotransformation of albendazole in cell suspension and in the whole ribwort plantain (*Plantago lancelota*), a common meadow plant, which can come into contact with this anthelmintic through the excrements of treated animals in pastures. Eighteen albendazole metabolites were detected in the ribwort plantain (*Plantago lancelota*), and most of them can be considered detoxicant. A substantial portion of the metabolites are unstable and can easily be transformed back to albendazole. Faster and massive uptake of albendazole was achieved in cells in the suspension cells compared with the uptake achieved in the roots of regenerates. The slower uptake in the roots was due to their defense mechanisms which limit the entry of xenobiotics. In the regenerates, albendazole and its metabolites were transported relatively slowly from the roots to the leaves probably due to their lipophilicity.

Puckowski et al. (2017) conducted an ecotoxicological examination of the effect of individual and mixtures of flubendazole and fenbendazole on *D. magna*. The mixtures demonstrated a tendency to be stronger than the additive toxicity towards the test animals. However, exposure to a single substance also showed high toxicity towards *D. magna*.

Antibiotic resistance genes

The occurrence of genetic indicators of antibiotic resistance continues to be a widely studied topic in agricultural environments and food production systems. For example, Zhu et al. (2017) investigated the abundance and diversity of ARGs and the microbial communities in conventionally– and organically–produced lettuce (CPL and OPL). Eight lettuce samples from each group were collected at the point of retail. Results based on high throughput quantitative polymerase chain reaction (HT–qPCR) showed that the absolute abundance of ARGs was 8 times higher in the phyllosphere of organically produced lettuce than in conventionally produced lettuce. In comparison, the abundance of ARGs from endophytes did not significantly differ between OPL and CPL. The microbial communities of the phyllosphere and endophytes differed significantly between OPL and CPL. The composition of microbial community accounted for 52.3% of the variation in ARG profiles, suggesting changes in bacterial community to be a potential driver for the emergence and dissemination of ARGs in OPL. In conclusion, plants grown in organic farms can contribute to the migration of ARGs into the food chain.

Zhang et al. (2017a) determined the temporal changes of antibiotic resistance genes (ARGs) in agricultural soils following the amendment of poultry, cattle and swine manure. Manure and manure spiked with tylosin were used in the study. Soil microcosms, including untreated soil, soil amended with manure, and soil amended with tylosin–spiked manure, were sampled eight times over 130 days. Overall, manure spiked with tylosin enriched the abundances and diversity of ARGs in soil. Among all manure types, tylosin–spiked cattle manure harbored the lowest diversity of ARGs. Poultry and swine manure showed stronger selection pressure on soil resistome than cattle manure. The relative abundances of ARGs in poultry manure treated soils increased and remained elevated. In contrast, the relative abundance of ARGs in other manured soils declined over time, particularly in swine manure treated soils. The slow decline of ARGs in soil amended with tylosin–spiked manure suggested the selective pressure exerted by antibiotics could prolong the persistence of the corresponding resistance genes.

The long–term impacts of manure application on the prevalence and abundance of ARGs in soils were recently assessed by Peng et al. (2017). Pig manure (PM), cow manure (CM), and low– or high–levels of wheat straw residues were combined with chemical fertilizers (NPK) and then added to soil. This 30–year study included six plots: four combinations, NPK only, and a control plot that received no amendment. The soil samples were taken either after the harvest of wheat in summer or soybean in fall. In general, tetracycline resistance genes were significantly more abundant in the soils exposed to PM+NPK than in the other amended and control soils. Moreover, the concentrations of heavy metals (e.g., Cu, Zn, and Pb) increased in manure treated soils (i.e., PM+NPK and CM+NPK) and the abundance of the class I integron–integrase gene (*intI1*) increased in PM treated soils. Both the heavy metals and the *intI1* gene showed a strong positive correlation with the abundance of ARGs. Application of wheat straw did not have significant effects on ARGs, heavy metals, or the *intI1* gene. The main conclusion is that the long–term application of manure can lead to elevated levels of ARGs in manure–amended soils.

The ability of two heavy metals (Zn and Cu) and an antibiotic (tetracycline) to (co)select for tetracycline resistance in agricultural soil was investigated by Song et al. (2017a). Soil was collected from an experimental farm in Denmark to establish soil microcosms. Five different concentrations of Cu, Zn, or tetracycline were added to the soil microcosms. Results showed that environmentally relevant levels of Cu (≥365 mg/kg) and Zn (≥264 mg/kg) caused significant increase in tetracycline resistance. In contrast, even unrealistically high levels of tetracycline (up to 100 mg/kg) did not cause increase of tetracycline resistance. Results also show that strong, initial metal– induced inhibition on microbial growth is a good predictor for selection of community resistance to tetracycline. This finding may be partially explained by the longer bioavailability of metals in soil. The authors concluded that toxic metals may exert a stronger selection pressure for resistance to an antibiotic than the specific antibiotic itself.

Zhou et al. (2017) evaluated the impact of the repeated applications of manure–based commercial organic fertilizers (COFs) in mitigating antibiotic and ARG contamination in soil. Chicken or swine manure–based COFs were applied to soils for 4 months. Soils were sampled at 0, 60, 61, 121 days after fertilizer application. The overall accumulation of antibiotics was observed in soils following repeated COF applications. The relative abundance of ARGs in COF treated soil increased after the first application and remained steady. In contrast, there was no significant changes to the relative abundance of the *intI1* gene in COF–amended soils between the first application and the repeated applications. Altogether, the work suggested the repeated use of manure–based COF in soils could enhance the dissemination of antibiotics and ARGs. The authors recommend land application of COF at least 60 days before crop harvest to prevent the spreading of ARGs in soil.

A microcosm experiment was conducted to investigate the impacts of manure–borne and indigenous soil microbial communities on the spread of ARGs in soil over a period of two months Chen et al. (2017b). To assess the effects of manure–born microbial communities on the spread of ARGs, soil with pig manure (S + M) and γ– irradiated soil with pig manure (RS + M) were used. Manure noticeably increased the abundance of ARGs in soil (S + M and RS + M). On the other hand, to assess the effects of indigenous soil microbial community on the dissemination of ARGs, soil (S) and soil with γ–irradiated pig manure (S + RM) were used. The diversity and abundance of ARGs in soil (S) did not vary significantly with the irradiated manure sample (S + RM). Hence, the results showed that bacterial communities in manure contributed to the elevation of ARGs, whereas indigenous soil microbial communities may resist the spread of ARGs. It was demonstrated that the presence of diverse indigenous microorganisms in conjunction with the inactivation of manure–born microorganisms led to reduced spread of ARGs in soil.

The effect of antibiotic administration in beef production on the emergence of ARGs was investigated by Vikram et al. (2017). A total of 719 fecal samples were collected from 36 lots of "raised without antibiotics" (RWA) and 36 lots of "conventional" (CONV) beef cattle over a 12–month period. Four methods (i.e., metagenomics, culture, qPCR, qPCR array) were employed in the study. In general, ARG levels were similar in the two production systems. The levels of Erythromycin–resistant (*ERYr*) Enterococcus sp. were significantly higher in CONV than in RWA, as were levels of ARGs *aadA1, ant(6)–I, blaACI, erm(A), erm(B), erm(C), erm(F), erm(Q), tet(A), tet(B), tet(M), and tet(X)* genes. Resistant *E. coli* concentrations were influenced more by season than by production systems. According to the qPCR array, the prevalence of other ARGs was: *aadA1* (91.7% in CONV vs 19.4% in RWA), *erm(A)* (41.7% on CONV vs 2.8% in RWA), *erm(C*) (52.8% in CONV vs. 2.8% in RWA). In general, most of the differences in resistance occurrence between the two production systems involved specific macrolide– lincosamide–streptogramin B (MLS) or tetracycline resistance genes and resistant bacteria. The authors concluded that restricted use of antibiotic alone would not be enough to inhibit the dissemination of all resistance classes. However, limiting in–feed chlortetracycline and tylosin administrations can prevent the spreading of corresponding ARGs.

Another recent study (Lu et al. 2017) examined the effects of diet (i.e., feed and grain) on the ARG profiles in pig manure. Twelve manure samples were collected from 6 piglets and 6 adult pigs that were fed either feed or grain. The number of ARGs detected in the manure from pigs receiving feed was more than 2–fold higher than in the manure of the grain–fed pigs. The concentrations of antibiotics and heavy metals in manure showed similar trends. Furthermore, because more additives were added to piglet feed than to adult pig feed, the concentrations of antibiotics and heavy metals in piglet manure were higher, resulting in higher diversity of ARGs. However, the relative abundance of ARGs in pig manure was higher than that of ARGs in piglet manure. In conclusion, the ARG pollution from pig manure is pertinent to ingredients in the food that pigs received.

Microbial fermentation bed (MFB), septic tank (ST), biogas digester (BD) and natural drying are four commonly used methods to treat waste manure. Ben et al. (2017) assessed the effectiveness of these four on–farm waste treatment methods to eliminate seven target ARGs. In swine manure and soils, tetracycline resistance genes (*tet(M), tet(O)*, and *tet(W)*) and sulfomonide resistance genes (*sul1* and *sul2*) were detected in high relative abundances. After treatment processes, ARG abundances were reduced by 0–1.81 logs by MBF, whereas the other treatment processes (i.e., ST, BD, and ND) showed low removal efficiency. The relative abundance of *tet(M)* increased by 0.47–1.31 logs after the ST and BD treatments. Similarly, the relative abundances of *tet(C), tet(G), sul1* and *sul2* increased after ST, BD and ND treatments by 0.74–3.90 logs. In comparison, the number of unique bacterial species in MFB was much higher than the other processes, suggesting that the evolution of bacterial communities in MFB reduced the chance of horizontal gene transfer and reduced ARGs.

Tien et al. (2017) investigated the potential of four different manure treatments to reduce the spread of ARGs with manure application. The four manure treatments included raw manure, anaerobic digestion, mechanical dewatering and composting. Application of raw, digested and dewatered manure all resulted in increases of the likelihood of detecting ARGs in soil. In contrast, composted manure resulted in the lowest abundance of target ARGs in soil following land application, e.g., 100 to 10,000–fold less than digested manure. Moreover, a dramatic drop in the abundance of some ARGs (i.e., *sul1, aadA, strB, erm(B)*, and *erm(F)*) occurred 93 days after the application of composted manure. Finally, composting was the only treatment whose resulting manure did not raise the levels of target ARGs on vegetable at harvest. The authors recommended at least 90 days between manure application and vegetable harvest to avoid ARG contamination.

Song et al. (2017b) examined the impact of wheat straw amendment in the anaerobic digestion on the fate of ARGs in swine manure. Three mass ratios of swine manure to wheat straw (i.e., 3:7, 5:5, and 7:3) were tested in three reactors (i.e., C1, C2, and C3). The authors monitored the biogas production, ARGs variations, and microbial community during anaerobic digestion over 55 days. In general, C3 (7:3) showed better performance in removing ARGs than did C1 and C2. After anaerobic digestion, the removal efficiency of the absolute abundance of all ARGs and *intI1* in C3 was 82.2%. In contrast, the removal efficiencies of ARGs in C1 and C2 were low (53.9% and

0.5%, respectively) and some ARGs *(tet(W), tet(C), ermX,* and *ermQ*) increased by 0.01–1.03 logs. Analysis of the evolution of bacterial communities indicated that C3 had the most diverse microbial community after AD. In addition, network analysis showed positive correlations between different ARGs and the same host bacteria. The authors suggested that variation in the bacterial community had major effects on the dissemination and/or dissipation of ARGs.

Muurinen et al. (2017) demonstrated that restricted antibiotic use on animals can significantly reduce the risks of ARG propagation following manure application. Fresh manure, stored manure, and unfertilized soil were sampled from two dairy farms and two swine farms. The same farms were also sampled for manure fertilized soil and ditch water at 0, 2 and 6 weeks after manure application. HT–qPCR results show that fresh manure had the highest diversity of ARGs, followed by stored manure and manured soils, while unfertilized soil showed the lowest diversity of ARGs. Furthermore, manure storage enriched the relative abundance of ARGs more than 4–fold for 41 genes and more than 2–fold for 62 genes, possibly due to cold stress, antibiotic residue–induced horizontal gene transfer, and the community shifts during storage. The relative abundance of ARGs and MGEs significantly decreased during the 4 weeks following land application, by more than 4–fold for 34 genes and more than 2–fold for 46 genes. The authors attributed the temporary elevation of ARGs in manured soil to the Finnish limited antibiotic use during animal production.

Engineered nanomaterials

The use of engineered nanomaterials (ENMs) continues to increase as fine–tuning and functionalization has continued to generate particles with applications in the electronics, medicinal, communications, textiles, and agricultural sectors among others. The growing production and use of ENMs in the past decade have led to increasing concerns about the intentional and unintentional exposure of these materials in the environment. In the agroecosystem in particular, studies published in the previous year have continued to focus on understanding the results of ENM exposure on plant and soil health as well as to synthesize recent research efforts resulting in a number of important critical reviews. Relevant to the agroecosystem, studies have focused on both soil microbial function as well as plant development and productivity.

Increasing recognition of the important interactions between soil microbes and plant development has contributed to the priority of the study of the effects of ENMs in the agricultural soil environment as well as their direct toxicity to plants. Investigating the effects of TiO_2 on soil grown wheat, Moll et al. (2017) showed that while no direct impacts on wheat performance or mychorrizal root colonization were detected, prokaryotic community structures were significantly impacted from exposure. Also studying the wheat production system, Adams and co–authors found the CuO nanoparticles (NPs) resulted in inhibition of root elongation, root hair proliferation and shortening of the zones of division and elongation. Their findings suggest that dissolution of CuO NPs increased Cu exposure in the rhizosphere affecting root colonizing bacteria and subsequent hormone signaling, specifically indole acetic acid (IAA), that otherwise would be responsible for promoting root growth.

The phytotoxicity of two other metal oxide NPs, CeO_2 and ZnO, were studied by Priester et al. (2017). Exposure to CeO_2 resulted in increased reactive oxygen species (an indicator of oxidative stress), lipid peroxidation, and genotoxicity which manifested in effects on leaf, pod, and stem production and to root nodule N_2 fixation potential. ZnO exposure resulted in leaf damage whereby Zn uptake was related to Zn complexes, resultant from dissolution, rather than the transport of the nanomaterial. Three ENPs (nAg, Al_2O3, and SiO_2) were investigated by McGee et al. (2017) where they showed that soil dehydrogenase and urease activity were especially sensitive to Ag ENMs.

Experimental designs that focused on elucidating the impacts of specific parameters of NPs as well as the agricultural environment have been developed to identify trends to help describe ENM toxicity. Asadishad et al. (2017) investigated the impact of ENM particle size (5, 50 and 100 nm) and surface coatings (PVC and citrate) on the enzymatic activity and bacterial community structure of agricultural soils using gold NPs (nAu) as the model contaminant. They found that particle size only impacted soil enzymatic activity at low ENM concentrations and only for PVC–coated nAu. Additionally, citrate coating increased enzymatic activity compared to PVC coatings. In general, nAu exposure increased the abundance of important soil bacterial groups and these increases were more pronounced with citrate coated nAu.

Du and co–authors examined the concomitant effects of increasing CO_2 and ENM toxicity using TiO_2 in rice and soil microbes (Du et al. (2017b). Increased CO_2, above current ambient concentrations, significantly increased the toxicity of TiO_2 on rice resulting in reduced biomass and grain yield. In addition, high CO_2 and TiO_2 exposures, increased accumulation of metals while reducing fat and sugars in grains. Exposures also impacted the functional composition of soil microbial communities.

Attempts to use frameworks and modelling to evaluate exposure and risk of ENM exposure in the agroecosystem have also emerged as tools to better understand ENM fate and toxicity. Keller et al. (2017) developed a systematic approach to investigate the fate and toxicity of copper NPs. This approach synthesized literature estimating release of these compounds into the environment, environmental fate, and toxicity assessed in aquatic and terrestrial environments. Resultant toxicity rankings were determined to be Cu^{2+} > nCu > nCu≈nCu$(OH)_2$ > µCu≈µCuO. The NanoFate model was developed and described by Garner and co–authors to predict the time–dependent accumulation of metallic ENMs throughout different environmental compartments. Modelled results predict that traditional ENMs (TiO_2 and ZnO) as well as soluble metallic oxides may accumulate above toxic thresholds in surface waters and soils. The model also reveals the influence of weather conditions and release scenarios on predicted concentrations (Garner et al. 2017).

While the study of ENMs has been an active area in past few years, compiling and summarizing the progress made in the study of ENM toxicity in the agricultural environment was a significant and necessary priority in 2017, which resulted in a number of important critical reviews. Rizwan and co–authors reviewed relevant studies looking at the effects of engineered metal and metal oxide nanomaterials on agricultural crops at the biochemical, physiological, and molecular levels. Their synthesis reveals the complex nature in describing the behavior of these NPs in the environment, resulting in both promotion and degradation of crop production. In addition, they highlight studies that characterize the uptake of these compounds into edible plant parts which are most likely to result in food chain exposures (Rizwan et al. 2017).

Similarly, Zuverza–Mena et al. (2017) focused on the physiological and biochemical effects in crops resulting from exposure to both carbon– and metal–based ENMs. In agreement with Rizwan et al. (2017) authors highlight both positive and negative effects on growth, physiological and biochemical traits, production and food quality that have been recently reported. They note that effects of ENM exposures are concentration, exposure media, and plant species dependent and a lack of experimental standardization makes drawing general conclusions about the impacts of ENMs in plants challenging.

Du et al. (2017c) reviewed the recent literature relating to metal oxide NP fate and toxicity in higher order terrestrial plants. Importantly, the authors note research gaps relating to long–term exposures, transgenerational phytotoxicity, need to identify genotype specific sensitivities, and addressing combined mixture toxicities including contaminants concomitantly occurring with ENMs.

The fact that NPs have been functionalized for use in the agricultural environment as pesticides and to deliver fertilizers contributes to their role as both a promotor and antagonist of crop development. This was highlighted by Pradhan and Mailapalli who provided a critical review that assessed the beneficial and adverse effects of the class of ENMs used as nanofertilizers in the agricultural environment. Their review emphasizes the existence of a paucity of regulatory action that is necessary to ensure the safe use of these products that incorporates specifics related to their individual fate in the environment. The authors note that significant work remains in characterizing the effects of these materials on target plants as well as the surrounding biota (Pradhan and Mailapalli 2017).

References

Aparicio, I.; Martin, J.; Santos, J. L.; Malvar, J. L.; Alonso, E. (2017) Stir bar sorptive extraction and liquid chromatography–tandem mass spectrometry determination of polar and non–polar emerging and priority pollutants in environmental waters. *J. Chromatogr. A* 1500, 43–52.

Asadishad, B.; Chahal, S.; Cianciarelli, V.; Zhou, K.; Tufenkji, N. (2017) Effect of gold nanoparticles on extracellular nutrient–cycling enzyme activity and bacterial community in soil slurries: role of nanoparticle size and surface coating. *Environmental Science: Nano* 4 (4), 907–918.

Axel, M.; Ewelina, K.; Jenny–Maria, B.; Leif, K. (2017) An online SPE LC–MS/MS method for the analysis of antibiotics in environmental water. *Environ. Sci. Pollut. Res.* 24 (9), 8692–8699.

Bair, D. A.; Popova, I. E.; Parikh, S. J.; Popova, I. E.; Tate, K. W. (2017) Transport of oxytetracycline, chlortetracycline, and ivermectin in surface runoff from irrigated pasture. *J Environ Sci Health B* 52 (9), 631–640.

Ben, W.; Wang, J.; Pan, X.; Qiang, Z. (2017) Dissemination of antibiotic resistance genes and their potential removal by on–farm treatment processes in nine swine feedlots in Shandong Province, China. *Chemosphere* 167, 262–268.

Biswas, S.; Kranz, W. L.; Shapiro, C. A.; Snow, D. D.; Bartelt–Hunt, S. L.; Mamo, M.; Tarkalson, D. D.; Zhang, T. C.; Shelton, D. P.; van Donk, S. J.; Mader, T. L. (2017) Effect of rainfall timing and tillage on the transport of steroid hormones in runoff from manure amended row crop fields. *J. Hazard. Mater.* 324, Part B, 436–447.

Campos–Manas, M. C.; Plaza–Bolanos, P.; Sanchez–Perez, J. A.; Malato, S.; Aguera, A. (2017) Fast determination of pesticides and other contaminants of emerging concern in treated wastewater using direct injection coupled to highly sensitive ultra–high performance liquid chromatography–tandem mass spectrometry. *J. Chromatogr. A* 1507, 84–94.

Chen, L.; Lang, H.; Liu, F.; Jin, S.; Yan, T. (2017a) Presence of Antibiotics in Shallow Groundwater in the Northern and Southwestern Regions of China. *Groundwater*, Ahead of Print.

Chen, Q.–L.; An, X.–L.; Li, H.; Zhu, Y.–G.; Su, J.–Q.; Cui, L. (2017b) Do manure–borne or indigenous soil microorganisms influence the spread of antibiotic resistance genes in manured soil? *Soil Biol. Biochem.* 114, 229–237.

Čizmić, M.; Babić, S.; Kaštelan–Macan, M. (2017a) Multi–class determination of pharmaceuticals in wastewaters by solid–phase extraction and liquid chromatography tandem mass spectrometry with matrix effect study. *Environmental Science and Pollution Research* 24 (25), 20521–20539.

Čizmić, M.; Ljobas, D.; Ćurković, L.; Škorić, I.; Babić, S. (2017b) Kinetics and degradation pathways of photolytic and photocatalytic oxidation of the anthelmintic drug praziquantel. *J. Hazard. Mater.* 323, 500–512.

Comtois–Marotte, S.; Chappuis, T.; Vo Duy, S.; Gilbert, N.; Lajeunesse, A.; Taktek, S.; Desrosiers, M.; Veilleux, E.; Sauve, S. (2017) Analysis of emerging contaminants in water and solid samples using high resolution mass spectrometry with a Q Exactive orbital ion trap and estrogenic activity with YES–assay. *Chemosphere* 166, 400–411.

Conley, J. M.; Evans, N.; Cardon, M. C.; Rosenblum, L.; Iwanowicz, L. R.; Hartig, P. C.; Schenck, K. M.; Bradley, P. M.; Wilson, V. S. (2017) Occurrence and In Vitro Bioactivity of Estrogen, Androgen, and Glucocorticoid Compounds in a Nationwide Screen of United States Stream Waters. *Environ. Sci. Technol.* 51 (9), 4781–4791.

Ding, H.; Wu, Y.; Zhang, W.; Zhong, J.; Lou, Q.; Yang, P.; Fang, Y. (2017) Occurrence, distribution, and risk assessment of antibiotics in the surface water of Poyang Lake, the largest freshwater lake in China. *Chemosphere* 184, 137–147.

Du, J.; Zhao, H.; Liu, S.; Xie, H.; Wang, Y.; Chen, J. (2017a) Antibiotics in the coastal water of the South Yellow Sea in China: Occurrence, distribution and ecological risks. *Sci. Total Environ.* 595, 521–527.

Du, W.; Gardea–Torresdey, J. L.; Xie, Y.; Yin, Y.; Zhu, J.; Zhang, X.; Ji, R.; Gu, K.; Peralta–Videa, J. R.; Guo, H. (2017b) Elevated CO2 levels modify TiO_2 nanoparticle effects on rice and soil microbial communities. *Sci. Total Environ.* 578, 408–416.

Du, W.; Tan, W.; Peralta–Videa, J. R.; Gardea–Torresdey, J. L.; Ji, R.; Yin, Y.; Guo, H. (2017c) Interaction of metal oxide nanoparticles with higher terrestrial plants: Physiological and biochemical aspects. *Plant Physiol. Biochem.* 110, 210–225.

Elliott, S. M.; VanderMeulen, D. D. (2017) A regional assessment of chemicals of concern in surface waters of four Midwestern United States national parks. *Sci. Total Environ.* 579, 1726–1735.

Furlong, E. T.; Batt, A. L.; Glassmeyer, S. T.; Noriega, M. C.; Kolpin, D. W.; Mash, H.; Schenck, K. M. (2017) Nationwide reconnaissance of contaminants of emerging concern in source and treated drinking waters of the United States: Pharmaceuticals. *Sci. Total Environ.* 579, 1629–1642.

Garner, K. L.; Suh, S.; Keller, A. A. (2017) Assessing the Risk of Engineered Nanomaterials in the Environment: Development and Application of the nanoFate Model. *Environmental Science & Technology* 51 (10), 5541–5551.

Goldstein, M.; Shenker, M.; Chefetz, B. (2014) Insights into the Uptake Processes of Wastewater–Borne Pharmaceuticals by Vegetables. *Environmental Science & Technology* 48 (10), 5593–5600.

Goulas, A.; Bourdat–Deschamps, M.; Nélieu, S.; Jimenez, J.; Patureau, D.; Haudin, C.–S.; Benoit, P. (2017) Development of a soft extraction method for sulfamethoxazole and transformation products from agricultural soils: Effects of organic matter co–extraction on the environmental availability assessment. *Sci. Total Environ.* 607–608, 1037–1048.

Han, R.–W.; Yu, Z.–N.; Zhen, T.–Y.; Wang, J. (2017) Survey of Veterinary Drug Residues in Raw Milk in Hebei Province, China. *J. Food Prot.* 80 (11), 1890–1896.

Hossain, A.; Nakamichi, S.; Habibullah–Al–Mamun, M.; Tani, K.; Masunaga, S.; Matsuda, H. (2017) Occurrence, distribution, ecological and resistance risks of antibiotics in surface water of finfish and shellfish aquaculture in Bangladesh. *Chemosphere* 188, 329–336.

Hurtado, C.; Montano–Chávez, Y. N.; Domínguez, C.; Bayona, J. M. (2017) Degradation of Emerging Organic Contaminants in an Agricultural Soil: Decoupling Biotic and Abiotic Processes. *Water, Air, & Soil Pollution* 228 (7), 243.

Jaffrezic, A.; Jarde, E.; Soulier, A.; Carrera, L.; Marengue, E.; Cailleau, A.; Le Bot, B. (2017) Veterinary pharmaceutical contamination in mixed land use watersheds: from agricultural headwater to water monitoring watershed. *Sci. Total Environ.* 609, 992–1000.

Kaewsuwan, W.; Kanatharana, P.; Bunkoed, O. (2017) Dispersive magnetic solid phase extraction using octadecyl coated silica magnetite nanoparticles for the extraction of tetracyclines in water samples. *J. Anal. Chem.* 72 (9), 957–965.

Keller, A. A.; Adeleye, A. S.; Conway, J. R.; Garner, K. L.; Zhao, L.; Cherr, G. N.; Hong, J.; Gardea–Torresdey, J. L.; Godwin, H. A.; Hanna, S.; Ji, Z.; Kaweeteerawat, C.; Lin, S.; Lenihan, H. S.; Miller, R. J.; Nel, A. E.; Peralta–Videa, J. R.; Walker, S. L.; Taylor, A. A.; Torres–Duarte, C.; Zink, J. I.; Zuverza–Mena, N. (2017) Comparative environmental fate and toxicity of copper nanomaterials. *NanoImpact* 7, 28–40.

Kim, H.–Y.; Lee, I.–S.; Oh, J.–E. (2017) Human and veterinary pharmaceuticals in the marine environment including fish farms in Korea. *Sci. Total Environ.* 579, 940–949.

Klatte, S.; Schaefer, H. C.; Hempel, M. (2017) Pharmaceuticals in the environment – A short review on options to minimize the exposure of humans, animals and ecosystems. *Sustain. Chem. Pharm.* 5, 61–66.

Koba, O.; Golovko, O.; Kodešová, R.; Fér, M.; Grabic, R. (2017) Antibiotics degradation in soil: A case of clindamycin, trimethoprim, sulfamethoxazole and their transformation products. *Environ. Pollut.* 220, 1251–1263.

Kunz, P. Y.; Simon, E.; Creusot, N.; Jayasinghe, B. S.; Kienle, C.; Maletz, S.; Schifferli, A.; Schonlau, C.; Ait–Aissa, S.; Denslow, N. D.; Hollert, H.; Werner, I.; Vermeirssen, E. L. M. (2017) Effect–based tools for monitoring estrogenic mixtures: Evaluation of five in vitro bioassays. *Water Res.* 110, 378–388.

Lee, Y.–J.; Choi, J.–H.; Abd El–Aty, A. M.; Chung, H. S.; Lee, H. S.; Kim, S.–W.; Rahman, M. M.; Park, B.–J.; Kim, J.–E.; Shin, H.–C.; Shim, J.–H. (2017) Development of a single–run analytical method for the detection of ten multi–class emerging contaminants in agricultural soil using an acetate–buffered QuEChERS method coupled with LC–MS/MS. *J. Sep. Sci.* 40 (2), 415–423.

Li, W.; Duan, H.; Li, C. (2017a) The occurrence of antibiotics and their ecological risk assessment in surface waters of China. *Fresenius Environ. Bull.* 26 (1a), 607–617.

Li, X.; Guo, P.; Shan, Y.; Ke, Y.; Li, H.; Fu, Q.; Wang, Y.; Liu, T.; Xia, X. (2017b) Determination of 82 veterinary drugs in swine waste lagoon sludge by ultra–high performance liquid chromatography–tandem mass spectrometry. *J. Chromatogr. A* 1499, 57–64.

Lu, X.–M.; Li, W.–F.; Li, C.–B. (2017) Characterization and quantification of antibiotic resistance genes in manure of piglets and adult pigs fed on different diets. *Environ. Pollut.* 229, 102–110.

Marsik, P.; Podlipna, R.; Vanek, T. (2017) Study of praziquantel phytoremediation and transformation and its removal in constructed wetland. *J. Hazard. Mater.* 323, 394–399.

McGee, C. F.; Storey, S.; Clipson, N.; Doyle, E. (2017) Soil microbial community responses to contamination with silver, aluminium oxide and silicon dioxide nanoparticles. *Ecotoxicology* 26 (3), 449–458.

Mokh, S.; El Khatib, M.; Koubar, M.; Daher, Z.; Al Iskandarani, M. (2017) Innovative SPE–LC–MS/MS technique for the assessment of 63 pharmaceuticals and the detection of antibiotic–resistant–bacteria: A case study natural water sources in Lebanon. *Sci. Total Environ.* 609, 830–841.

Moll, J.; Klingenfuss, F.; Widmer, F.; Gogos, A.; Bucheli, T. D.; Hartmann, M.; van der Heijden, M. G. A. (2017) Effects of titanium dioxide nanoparticles on soil microbial communities and wheat biomass. *Soil Biol. Biochem.* 111, 85–93.

Montemurro, N.; Postigo, C.; Lonigro, A.; Perez, S.; Barceló, D. (2017) Development and validation of an analytical method based on liquid chromatography–tandem mass spectrometry detection for the simultaneous determination of 13 relevant wastewater–derived contaminants in lettuce. *Analytical and Bioanalytical Chemistry* 409 (23), 5375–5387.

Muurinen, J.; Stedtfeld, R.; Karkman, A.; Pärnänen, K.; Tiedje, J.; Virta, M. (2017) Influence of manure application on the environmental resistome under Finnish agricultural practice with restricted antibiotic use. *Environmental science & technology* 51 (11), 5989–5999.

Neale, P. A.; Munz, N. A.; Ait–Aissa, S.; Altenburger, R.; Brion, F.; Busch, W.; Escher, B. I.; Hilscherova, K.; Kienle, C.; Novak, J.; Seiler, T.–B.; Shao, Y.; Stamm, C.; Hollender, J. (2017) Integrating chemical analysis and bioanalysis to evaluate the contribution of wastewater effluent on the micropollutant burden in small streams. *Sci. Total Environ.* 576, 785–795.

Peng, S.; Feng, Y.; Wang, Y.; Guo, X.; Chu, H.; Lin, X. (2017) Prevalence of antibiotic resistance genes in soils after continually applied with different manure for 30 years. *J. Hazard. Mater.* 340, 16–25.

Petrie, B.; Smith, B. D.; Youdan, J.; Barden, R.; Kasprzyk– Hordern, B. (2017) Multi–residue determination of micropollutants in Phragmites australis from constructed wetlands using microwave assisted extraction and ultra–high–performance liquid chromatography tandem mass spectrometry. *Anal. Chim. Acta* 959, 91–101.

Phiroonsoontorn, N.; Sansuk, S.; Santaladchaiyakit, Y.; Srijaranai, S. (2017) The use of dissolvable layered double hydroxide components in an in situ solid–phase extraction for chromatographic determination of tetracyclines in water and milk samples. *J. Chromatogr. A* 1519, 38–44.

Pradhan, S.; Mailapalli, D. R. (2017) Interaction of Engineered Nanoparticles with the Agri–environment. *J. Agric. Food. Chem.* 65 (38), 8279–8294.

Priester, J. H.; Moritz, S. C.; Espinosa, K.; Ge, Y.; Wang, Y.; Nisbet, R. M.; Schimel, J. P.; Goggi, A. S.; Gardea– Torresdey, J. L.; Holden, P. A. (2017) Damage assessment for soybean cultivated in soil with either CeO 2 or ZnO manufactured nanomaterials. *Sci. Total Environ.* 579, 1756–1768.

Puckowski, A.; Stolte, S.; Wagil, M.; Markiewicz, M.; Łukaszewicz, P.; Stepnowski, P.; Białk-Bielińska, A. (2017) Mixture toxicity of flubendazole and fenbendazole to Daphnia magna. *International Journal of Hygiene and Environmental Health* 220 (3), 575–582.

Raisová, L.; Podlipná, R.; Szotáková, B.; Syslová, E.; Skálová, L. (2017) Evaluation of drug uptake and deactivation in plant: Fate of albendazole in ribwort plantain (Plantago laceolata) cells and regenerants. *Ecotoxicology and Environmental Safety* 141, 37–42.

Riemenschneider, C.; Seiwert, B.; Goldstein, M.; Al–Raggad, M.; Salameh, E.; Chefetz, B.; Reemtsma, T. (2017a) An LC–MS/MS method for the determination of 28 polar environmental contaminants and metabolites in vegetables irrigated with treated municipal wastewater. *Analytical Methods* 9 (8), 1273–1281.

Riemenschneider, C.; Seiwert, B.; Moeder, M.; Schwarz, D.; Reemtsma, T. (2017b) Extensive Transformation of the Pharmaceutical Carbamazepine Following Uptake into Intact Tomato Plants. *Environmental Science & Technology* 51 (11), 6100–6109.

Rizwan, M.; Ali, S.; Qayyum, M. F.; Ok, Y. S.; Adrees, M.; Ibrahim, M.; Zia–ur–Rehman, M.; Farid, M.; Abbas, F. (2017) Effect of metal and metal oxide nanoparticles on growth and physiology of globally important food crops: A critical review. *J. Hazard. Mater.* 322, 2–16.

Rubirola, A.; Boleda, M. R.; Galceran, M. T. (2017) Multiresidue analysis of 24 Water Framework Directive priority substances by on–line solid phase extraction–liquid chromatography tandem mass spectrometry in environmental waters. *J. Chromatogr. A* 1493, 64–75.

Sghaier, R. B.; Net, S.; Ghorbel–Abid, I.; Bessadok, S.; Le Coz, M.; Hassan–Chehimi, D. B.; Trabelsi–Ayadi, M.; Tackx, M.; Ouddane, B. (2017) Simultaneous Detection of 13 Endocrine Disrupting Chemicals in Water by a Combination of SPE–BSTFA Derivatization and GC–MS in Transboundary Rivers (France–Belgium). *Water, Air, Soil Pollut.* 228 (1), 1–14.

Song, J.; Rensing, C.; Holm, P. E.; Virta, M.; Brandt, K. K. (2017a) Comparison of metals and tetracycline as selective agents for development of tetracycline resistant bacterial communities in agricultural soil. *Environmental Science & Technology* 51 (5), 3040–3047.

Song, W.; Wang, X.; Gu, J.; Zhang, S.; Yin, Y.; Li, Y.; Qian, X.; Sun, W. (2017b) Effects of different swine manure to wheat straw ratios on antibiotic resistance genes and the microbial community structure during anaerobic digestion. *Bioresour. Technol.* 231, 1–8.

Sun, J.; Zeng, Q.; Tsang, D. C. W.; Zhu, L. Z.; Li, X. D. (2017) Antibiotics in the agricultural soils from the Yangtze River Delta, China. *Chemosphere* 189, 301–308.

Tien, Y.–C.; Li, B.; Zhang, T.; Scott, A.; Murray, R.; Sabourin, L.; Marti, R.; Topp, E. (2017) Impact of dairy manure pre– application treatment on manure composition, soil dynamics of antibiotic resistance genes, and abundance of antibiotic– resistance genes on vegetables at harvest. *Sci. Total Environ.* 581, 32–39.

Tong, L.; Qin, L.; Xie, C.; Liu, H.; Wang, Y.; Guan, C.; Huang, S. (2017) Distribution of antibiotics in alluvial sediment near animal breeding areas at the Jianghan Plain, Central China. *Chemosphere* 186, 100–107.

Vikram, A.; Rovira, P.; Agga, G. E.; Arthur, T. M.; Bosilevac, J. M.; Wheeler, T. L.; Morley, P. S.; Belk, K. E.; Schmidt, J. W. (2017) Impact of "Raised Without Antibiotics" Beef Cattle Production Practices On Occurrences of Antimicrobial Resistance. *Applied and Environmental Microbiology* 83 (22), e01682–01617.

Wei, N.; Zheng, Z.; Wang, Y.; Tao, Y.; Shao, Y.; Zhu, S.; You, J.; Zhao, X.–E. (2017) Rapid and sensitive determination of multiple endocrine–disrupting chemicals by ultrasound– assisted in situ derivatization dispersive liquid–liquid microextraction coupled with ultra–high–performance liquid chromatography/tandem mass spectrometry. *Rapid Commun. Mass Spectrom.* 31 (11), 937–950.

Yin, L.; Wang, B.; Yuan, H.; Deng, S.; Huang, J.; Wang, Y.; Yu, G. (2017) Pay special attention to the transformation products of PPCPs in environment. *Emerging Contaminants* 3 (2), 69–75.

Zhang, Y.–J.; Hu, H.–W.; Gou, M.; Wang, J.–T.; Chen, D.; He, J.–Z. (2017a) Temporal succession of soil antibiotic resistance genes following application of swine, cattle and poultry manures spiked with or without antibiotics. *Environ. Pollut.* 231, 1621–1632.

Zhang, Y.; Hu, S.; Zhang, H.; Shen, G.; Yuan, Z.; Zhang, W. (2017b) Degradation kinetics and mechanism of sulfadiazine and sulfamethoxazole in an agricultural soil system with manure application. *Sci. Total Environ.* 607–608, 1348–1356.

Zhou, X.; Qiao, M.; Wang, F.–H.; Zhu, Y.–G. (2017) Use of commercial organic fertilizer increases the abundance of antibiotic resistance genes and antibiotics in soil. *Environmental Science and Pollution Research* 24 (1), 701–710.

Zhu, B.; Chen, Q.; Chen, S.; Zhu, Y.–G. (2017) Does organically produced lettuce harbor higher abundance of antibiotic resistance genes than conventionally produced? *Environment international* 98, 152–159.

Ziarrusta, H.; Val, N.; Dominguez, H.; Mijangos, L.; Prieto, A.; Usobiaga, A.; Etxebarria, N.; Zuloaga, O.; Olivares, M. (2017) Determination of fluoroquinolones in fish tissues, biological fluids, and environmental waters by liquid chromatography tandem mass spectrometry. *Anal. Bioanal. Chem.* 409 (27), 6359–6370.

Zuverza–Mena, N.; Martínez–Fernández, D.; Du, W.; Hernandez–Viezcas, J. A.; Bonilla–Bird, N.; López–Moreno, M. L.; Komárek, M.; Peralta–Videa, J. R.; Gardea–Torresdey, J. L. (2017) Exposure of engineered nanomaterials to plants: Insights into the physiological and biochemical responses–A review. *Plant Physiol. Biochem.* 110, 236–264.