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Daniel D. Snow

University of Nebraska at Lincoln, dsnow1@unl.edu

Shannon L. Bartelt-Hunt

University of Nebraska-Lincoln, sbartelt2@unl.edu

Shannon Devivo

University of Nebraska-Lincoln

Samuel Saunders

University of Nebraska-Lincoln

David A. Cassada

University of Nebraska at Lincoln, dcassada1@unl.edu

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Detection, Occurrence, and Fate of Emerging Contaminants in Agricultural Environments

Daniel D. Snow¹, Shannon L. Bartelt-Hunt²,
Shannon Devivo³, Samuel Saunders³, and David A. Cassada⁴

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Frequently studied environmental contaminants in agricultural systems include 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. Less well-known are environmental impacts of newer classes of contaminants such as pharmaceuticals, steroids, antibiotic-resistance genes and prion proteins. 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 often has 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 research on 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 2008 evaluating the detection, fate, and occurrence of emerging contaminants, with a particular focus on emerging contaminants in agricultural systems. Relevant contaminants are EDCs (particularly hormones and anabolic steroids), antibiotics and other pharmaceuticals associated with wastewater, antibiotic resistance genes in bacteria and prions. Studies on

pesticides and flame retardants are not reviewed unless they were evaluated in the same study.

Analytical Methods for Emerging Contaminants

Reviews. Recent reviews have helped summarize developments in aquatic toxicity studies and sample preparation methods for emerging contaminants in water. Schuhmacher et al. (2008) provided an overview of developments in liquid chromatography tandem mass spectrometry (LC/MS/MS) for analysis of organic contaminants. They review trends and improvements in the design of triple quadrupole, ion trap and quadrupole time of flight (Q-TOF) instrumentation for trace level quantitative analysis. This review also discusses electrospray matrix effects, multi-residue methods, and confirmation of target compounds using Q-TOF instrumentation.

Farré et al. (2008) describe what is known about the environmental fate of pharmaceuticals, hormones, perfluorinated compounds, disinfection by-products, sunscreens, and transformation products in aquatic systems. They indicate this is the first review specifically focused on what is known regarding transformation products of compounds such as veterinary pharmaceuticals, and point out that metabolites often are excreted in higher concentrations than the parent. While the toxicological profile of many emerging contaminants is poorly documented, transformation products may be completely unknown.

García-Galán et al. (2008) follow with a review of sulfonamide antimicrobials used in aquaculture, raising livestock, and in human medicine and what is known about methods for identification of their metabolites in

environmental samples. They indicate livestock will excrete 50–90% of the antimicrobial dose usually within several days with the parent drug making up 9–30% of the excreted compound. Acid conjugates comprise 5–60% of the excreted dose, although conjugates may revert back to the parent compound during storage as bacteria may cleave the acetyl moiety. They go on to summarize what is known regarding metabolic pathways for sulfas and potential biological degradation routes in manure. They list metabolites and degradation products of sulfonamide antimicrobials identified in the literature under different environmental conditions, as well as analytical considerations using liquid chromatography-mass spectrometry (LC/MS).

Passive Samplers. New methods for sampling surface water for emerging contaminants include polar organic contaminant integrative samplers (POCIS) using polymeric sorbent and sorbent mixtures contained in a hydrophilic membrane. Alvarez et al. (2008) screened estrogenicity of POCIS extracts using the yeast estrogen assay. A lack of estrogenic response in POCIS extracts was attributed to prevalence of atrazine sampled from the surface waters. Arditoglou and Voutsas (2008) compare two POCIS materials for recovery of selected endocrine disrupting compounds, including alkyphenols, bisphenol A, 17 β and 17 α -estradiol. Samplers were calibrated in the laboratory using static renewal and 7, 14 and 28 day equilibration periods. Both types of samplers were tested for field deployment in river water and seawater and results compared to grab samples collected during the same period. Alkyphenols were detected in both the grab samples

and POCIS with measured concentrations comparable to those obtained using uptake rates.

Methods for pharmaceuticals. New methods for analysis of a variety of antimicrobials and veterinary pharmaceuticals continue to be developed as research projects evaluate the environmental fate of these compounds. A high throughput multi-residue method was developed for 51 pharmaceuticals and steroid hormones by Hao et al. (2008) using polymeric solid phase extraction (SPE) and electrospray ionization (ESI) LC/MS/MS. Isotope dilution was demonstrated to be effective for ionization suppression for compound with labeled analogues. Several sample preservation approaches were tested for drinking water and wastewater. Separation and detection was achieved using acidic, neutral and basic LC mobile phases in both positive and negative ionization modes. Method detection limits ranged from 0.005 to 0.068 g/L. Thirty five of the target compounds were detected in treated wastewater and river water.

Batt et al. (2008) describe a method using mixed mode polymeric solid phase extraction, ultraperformance liquid chromatography, and triple quadrupole mass spectrometry to analyze 48 active prescription ingredients and 6 selected metabolites. Detection limits ranged from 0.001 to 0.051 g/L with recoveries ranging from 80% to 125%. The method was applied to seven wastewater effluents and one surface water sample with detections observed for 38 of the 54 analytes at concentrations up to 2.95 µg/L in the effluent samples.

Weiss et al. (2008b) develop a method for extraction and analysis of sulfamethazine and the

antiparasitic drug flubendazole and their metabolites in swine manure and seepage water from test plots fertilized with manure. Polymeric styrene divinylbenzene extraction cartridges were used to extract filtered seepage water samples, while liquid manure was diluted with water or a mixture of water and methanol prior to extraction. Extracts were analyzed by LC/MS/MS and detection limits were estimated near 0.02 g/L for water samples. Both compounds and their metabolites were detected in manure samples and in leachate from fields fertilized with the manure.

Ben et al. (2008) describe a method for analysis of antimicrobials used in swine facilities including five sulfonamides, three tetracyclines, and tiamulin in swine wastewater. Polymeric solid phase extraction cartridges were used to extract acidified wastewater with sodium EDTA added to complex metals. Extracts were analyzed using liquid chromatography-mass spectrometry ESI on a single quadrupole instrument. Ion suppression effects were evaluated by analysis of matrix-matched standards. Method detection limits were estimated and ranged from 0.005 to 0.091 g/L. Samples of swine wastewater from near Beijing (China) were analyzed by the method showing a concentration range of 0.62–32.6 g/L.

Pedrouzo et al. (2008) describe a method for polymeric SPE and analysis of five sulfonamide antimicrobials, three macrolides, omeprazole, ranitidine, and trimethoprim in water using ESI LC/MS with a single quadrupole system. Raw and treated wastewater, tap water and river water were fortified and extracted using 500 mg Oasis HLB cartridges and recoveries compared with

differing volumes of water and eluting solvents. Detection limits were estimated at 0.010 g/L. Three sulfonamide compounds, omeprazole and ranitidine were detected in raw wastewater at concentrations up to 1.82 g/L.

Watanabe et al. (2008) describe analysis of the veterinary pharmaceutical monensin in surface and ground water near a dairy operation using polymeric SPE with liquid chromatography tandem mass spectrometry. Sample extracts were analyzed using a single quadrupole ESI LC/MS with selected ion monitoring of the dehydrated sodium adduct ion. Monensin was detected at concentrations ranging up to 0.39 µg/L in ground water samples impacted by dairy wastewater.

Li et al. (2008) examine the fate of oxytetracycline and several degradation products in wastewater from a tetracycline production plant in China. LC/MS with ESI on a single quadrupole instrument without preconcentration of analytes. Water and sludge samples were fortified with a citric acid buffer as a complexing agent. Loading and removal efficiencies for each compound were estimated from measured concentrations and flow rates. Several hundred g/L of oxytetracycline and lower concentrations of all degradation products were measured in river water immediately downstream from the wastewater input. River sediments were also found to be heavily contaminated with oxytetracycline residues.

Loftin et al. (2008) examined the degradation rates of several tetracycline and sulfonamide antimicrobials, lincomycin, tylosin, and trimethoprim under varying temperature, pH, and ionic strength conditions in the laboratory. Solutions were analyzed using LC/MS ESI.

Pseudo first-order transformation rate constants were determined and tetracyclines shown to degrade relatively rapidly (half-lives from 6 hour to ~10 weeks), while the sulfonamide antimicrobials, tylosin, lincomycin, and trimethoprim were much more stable.

Though electrospray ionization is a sensitive and versatile interface for LC/MS, matrix suppression continues to hamper reproducible quantitation of emerging contaminants. Improvements in extract purification can help improve detection of these compounds. Chico et al. (2008) evaluated cleanup using restricted access materials (RAM) constructed from alkyl diol silica. These porous chromatographic supports are designed for removal of larger molecules and partially based on a size-exclusion chromatography. An in-line RAM column was used to remove interferences for detection of tetracycline antibiotics in polymeric SPE extracts from river water samples. Fluorometric detection with HPLC and RAM columns enabled detection of low concentrations extracted from river water.

In a 2-part paper, De Zan et al. (2008) propose solving matrix effects for analysis of 8 tetracyclines in wastewater using multivariate curve resolution and standard addition with polymeric SPE and HPLC ultraviolet detection. A model for baseline correction was used to reduce interferences and 3-level piecewise standard addition, with a multivariate calibration model, improved peak resolution and compound detection. García et al. (2008) follow this paper and compare noise reduction and peak detection with a newer algorithm (unfolded partial least squares) using diode array detection.

Hu et al. (2008a) identify two photodegradation products of the veterinary pharmaceutical tylosin A using HPLC and NMR. They also determined the stability and cross-reactivity of degradates and other forms of tylosin using enzyme linked immunoassay with HPLC analysis of water.

Methods for Steroid Hormones. Chang et al. (2008) present an ultra-performance liquid chromatography-tandem mass spectrometry method that uses solid-phase extraction with silica cleanup to analyze 18 androgens and progestogens in various water matrices. Detection limits ranged from <0.001 to 0.050 g/L for influent samples, for effluent samples, and surface water samples with recoveries ranging from 78% to 100%. Results of application of the method to wastewater and surface water samples from Japan are presented.

A method using a programmable-temperature vaporizer inlet for large volume injection gas chromatography with mass spectrometric detection (GC-MS) is described by Hu et al. (2008b) for the analysis of estrogens. Optimization of the initial inlet temperature and liner configuration is shown to be important for increased sensitivity of the analytes. Estimated detection limits of 0.031-0.046 µg/L were obtained for estrone, 17-estradiol, and 17-ethynylestradiol.

Kinani et al. (2008) used ultrasonication extraction coupled with solid-phase extraction cleanup, trimethylsilyl derivatization and gas chromatography-ion trap mass spectrometry detection to analyze 20 estrogenic chemicals in river sediment from five French rivers. Limits of Quantitation (LOQs) ranged from 0.01 to 0.60 ng/g in

matrix samples. Detection efficiencies for each analyte were also compared between EI or PCI modes of ionization and between SIS or MRM acquisition modes.

Matejíček and Kubán (2008) describe an LC ion-trap MS/MS method for estrogens which utilizes an on-line pre-column derivatization step to enhance the sensitivity for the analytes. Polymeric SPE (OASIS HLB) is followed by a solid-phase cleanup (Envi-Florisil) to prepare river water samples for analysis. Detection limits for the derivatized estrogens were estimated below 0.001 g/L for 17-estradiol, 17-estradiol, estrone, ethynylestradiol and estriol. HPLC column and mobile phase optimization, mass spectrometric parameters and results from the analysis of river water samples collected near a wastewater treatment plant are also presented.

Nieto et al. (2008) describe a pressurized liquid extraction method with liquid chromatography-tandem mass spectrometry detection to analyze estrogens and conjugated estrogens in sewage sludge. Optimized conditions of extraction enabled recoveries of greater than 81% for all analytes in the study. Detection limits of less than 26 ng/g were estimated for all analytes except for 17-estradiol, 17-estradiol, ethynylestradiol and estradiol 17-acetate which had values between 150 and 175 ng/g. Results from the application of the method to sewage sludge from treatment plants is presented showing determinations of estrogens up to a value of 406 ng/g obtained for estriol.

Tan et al. (2008) describe a method for the analysis of endocrine disruptive compounds using gas chromatography/mass spectrometry detection after stir-bar

sorptive extraction from wastewater and solids and subsequent thermal desorption. Recoveries of target compounds ranged from 44% to 128% with detection limits of 0.002 g/L for water samples and 0.02 ng/g for solid samples. Analysis of influent wastewater and solid samples from an Australian wastewater treatment plant indicated that high levels of phthalates, alkylphenols, and estrogens were present. Significantly reduced levels were observed after anaerobic, aerobic and anoxic treatment at the plant.

A method utilizing a panel of human cell derived CALUX reporter gene bioassays is described by van der Linden et al. (2008) for the estrogen, androgen, progesterone, and glucocorticoid receptor mediated transactivation activity in effluents from sewage treatment plants and tap and surface waters. Results indicate that estrogenic activity (as estradiol equivalents – EE) were consistent with previous studies with 0.0002-0.0005 g EE/L for surface water and 0.0004-0.001 µg EE/L for effluent water. The authors also obtained significant glucocorticoid activity as well as measurable androgen and progesterone activities in the effluent and surface water samples.

Vulliet et al. (2008) present a multi-residue method for the determination of natural and synthetic estrogens, progestagens, and androgens in water utilizing liquid chromatography with tandem mass spectrometry detection after solid-phase extraction. Recoveries of the analytes were greater than 80% with detection limits in the low ng/L range. Possible sensitivity losses due to matrix effects and ion suppression were evaluated for each analyte with the androgens most affected at 10%-20% losses in

response. Results from surface water and ground water samples analyzed by the method with concentrations are also presented with measured analyte concentrations below 0.010 g/L.

Zheng et al. (2008) utilized a gas chromatography/mass spectrometry method with solid-phase extraction and Florisil cleanup to analyze derivatized estrogens and progestagens in liquid and solid dairy waste. Recoveries ranged from 80% to 120% for all analytes except for medroxyprogesterone which exhibited low recovery. Detection limits ranged from 0.0003-0.017 µg/L in lagoon water, 0.050-0.210 µg/L in dairy wastewater, and 2-40 ng/g in solid wastes. Results from application of the method to the waste disposal pathway of a dairy farm are also presented.

Zorita et al. (2008) present a gas chromatography/mass spectrometry method coupled with hollow-fiber microporous membrane liquid-liquid extraction for the analysis of estrogens in tap and sewage water. The membrane extraction method minimizes organic solvent usage while producing precisions of better than 10% at 0.050 µg/L. Detection limits were between 0.002 and 0.010 µg/L for the derivatized target estrogens. Optimization results of various method parameters are presented.

Fate and Transport of Steroid Hormones

Agricultural practices contribute significantly to hormone loading to the environment. These hormones are often present in livestock waste, and reach the environment through runoff from feedlots and application of manure as a nutrient source. Understanding the occurrence and fate of

hormones in the environment is important in order to reduce the impacts of these contaminants on wildlife and humans.

Hormone Occurrence. Arikan et al. (2008) published a study presenting the results of a survey of 15 subwatersheds and 7 stations on the Choptank River in Maryland over four different seasons. The watershed, located on the Delmarva Peninsula of the Chesapeake Bay, contains 62% agricultural land, 33% forested land, and 2% wetlands, with 5% of land being developed. The peninsula is dominated by the poultry industry. Estriol, 17 α -ethinylestradiol, estrone, and progesterone were detected at concentrations ≤ 0.020 $\mu\text{g/L}$ in several subwatersheds. Testosterone was the only hormone detected at a river station at a concentration of 0.016 $\mu\text{g/L}$. This data suggests that hormones were not present in surface waters at significant levels.

Hormones have been detected at significant levels within animal manures. Zheng et al. (2008) investigated the concentrations of hormones within waste treatment systems containing dairy manure or lagoon water. In both the dairy wastewater and lagoon water, 17 α -estradiol, 17 β -estradiol and estrone were detected. In fresh dairy wastewater, concentrations of 17 α -estradiol were almost an order of magnitude higher than the other hormones, indicating that 17 α -estradiol is more prevalent in excrement than 17 β -estradiol and estrone. The data showed a steady decrease in 17 α -estradiol accompanied by a steady increase in estrone along the disposal pathway of the dairy wastewater, suggesting 17 α -estradiol may readily oxidize to estrone in the wastewater. Total hormone

concentrations in the lagoon water were much lower than those in dairy wastewater, possibly due to dilution, biodegradation, photodegradation, sorption, residence time, and settling of hormone-associated manure particles.

Within three sequencing lagoons, the total concentrations in the second and tertiary lagoons were almost 2 orders of magnitude less than in the primary lagoon, possibly due to longer retention times and thus more degradation and settling of particles.

The same study also evaluated hormones present in solid manure from dairy cattle. 17 α -estradiol, 17 β -estradiol, estrone, and progesterone were detected at concentrations up to 1000 ng/g, with 17 α -estradiol accounting for the largest percentage of the total hormone on a dry weight basis in the fresh manure. However, in piled manure after two weeks, estrone was detected at the highest concentration (697 ng/g). This correlates with data obtained from the wastewater treatment system indicating that 17 α -estradiol may readily degrade to estrone. The total concentration of hormones in the piled manure was about half of that of the fresh manure, indicating steady biodegradation of the hormones. Settled solid wastes were collected from three slotted dams, and 17 α -estradiol, 17 β -estradiol and estrone were detected at concentrations significantly less than those in the fresh or piled manure.

Hormone Fate. Because recent studies have indicated hormones occur in fresh and treated manures, it is important to determine if hormones may leach from agricultural waste treatment systems into groundwater. Arnon et al. (2008) collected soil and groundwater samples below a dairy-farm wastewater lagoon, and compared

hormone concentrations to a reference site located upgradient of the farm. Testosterone was detected in sediments at a depth of 45 m, while estrogen was detected at 32 m. Groundwater samples also contained higher concentrations of testosterone and estrogen compared to the reference site. Advection, dispersion, and sorption modeling could not explain the migration of the hormones to the depths at which they were found, indicating that other transport mechanisms, such as preferential flow paths, may lead to enhanced hormone transport. Improved management of waste treatment systems may be needed to reduce leaching of these hormones to groundwater.

After land-application of manure, there are several factors influencing loading of hormones to the environment, including precipitation and tillage techniques. To determine the effects of rainfall and tillage, Jenkins et al. (2008) conducted a study of transport of estradiol and testosterone from a Cecil sandy loam. The soil had been managed since 1991 under no-till and conventional tillage, with either poultry litter or conventional fertilizer applied as nutrient sources. Rainfall was simulated on 2 by 3-m field plots at a constant rate in 2004 and variable rate in 2005, and samples were taken to determine flow-weighted concentrations of the hormones of interest. Testosterone was detected at higher concentrations in runoff from no-till plots with poultry litter for both rainfall intensities. Estradiol concentrations were not affected by tillage method, fertilization treatment, or rainfall simulation pattern. The authors concluded rainfall immediately following application of poultry litter has little potential for contaminating surface waters with hormones.

One factor affecting the runoff concentrations of hormones is the sorption affinity of the hormones to the soil. Several studies were conducted in 2008 to determine sorption of estrogenic and androgenic compounds. Sarmah et al. (2008) performed batch sorption experiments for 17 β -estradiol and 17 α -ethinylestradiol on New Zealand soils collected from dairy farming regions. Estrone was formed during the equilibration of 17 β -estradiol with the soil. In Manawatu and Horotiu soils, sorption of steroid hormones followed the order of 17 β -estradiol < estrone < 17 α -ethinylestradiol. In Pukekohe soils, sorption differed in that estrone < 17 α -ethinylestradiol < 17 β -estradiol and the log K_{oc} was 3 ($\pm 1 - 0.2$ log units). Based on this study there is moderate to high potential for soils to retain hormones. The concentrations used in this study were significantly higher than those normally detected in the environment due to analytical constraints. In the environment, hormones are generally encountered sub g/L and sorption rates are likely to be very slow. The ability of these hormones to leach through the vertical profile would be limited, except in the case where macropore flow exists.

The sorption of 17 β -estradiol to Groseclose loam, Myatt sandy loam, and Cecil loam soil from Virginia using a series of batch equilibrium experiments was determined by Kozarek et al. (2008). Continuously shaken, soil-water mixtures were created using 250 mL glass bottles with Teflon-lined caps. Each mixture contained a mass of soil and a background solution with 17 β -estradiol. Sodium azide was added to minimize biodegradation, and mixtures were covered to minimize photolysis. Sampling was conducted at 24 h through 9 to 10 days to ensure

equilibrium was reached. Samples were analyzed using gas chromatography-mass spectrometry. Samples were analyzed for estrone using standards to obtain relative peak responses for estrone and 17 β -estradiol. Linear, Freundlich, and Langmuir isotherms were developed for the aqueous 17 β -estradiol concentrations adjusted for degradation to estrone. Equilibrium was reached within 24 hours, which is similar to the results reported in previous studies. The linear isotherm model provided a good fit to model the sorption of 17 β -estradiol to agricultural soils, and the sorption was correlated to the organic content of each soil with log K_{oc} ranging from 2.90 to 3.99 - comparable to values determined for the New Zealand soils in the Sarmah et al. (2008) study.

Fan et al. (2008) developed a model for the degradation, sorption, and transport of 17 β -estradiol in undisturbed soil. Batch experiments were conducted to determine the sorption of 17 β -estradiol to natural soils. Three concentrations of 17 β -estradiol were used to represent the varying concentrations detected in animal manure. The aqueous concentration of ^{14}C decreased over time for all concentrations, possibly due to transformation or sorption processes. Controlled batch experiments using clear and amber vials with autoclaved sterile soil were also conducted to determine the possibility of photodegradation of 17 β -estradiol. From these experiments it was concluded that photodegradation was not significant.

Soil column experiments were also conducted using 15 cm long saturated columns Fan et al. (2008). Calcium chloride was used as a tracer to determine transport of a conservative, nonsorbing solute in the

column. A pulse of [4- ^{14}C]-17 β -estradiol in 300 mL of 0.01 M $CaCl_2$ -estradiol solution was applied to the column, and then eluted with >17 L of 0.01 M $CaCl_2$. Thin-layer chromatography (TLC) was used to determine any 17 β -estradiol metabolites in the effluent. Due to low ^{14}C mass recovery from the first column experiment, a second experiment was conducted, accounting for volatile metabolites and halting biotransformations at the end of the experiment. Soil samples were taken from the columns for both experiments and analyzed using TLC. Mass recovery of the ^{14}C from both column effluents was only about 6%, with estrone and a higher polarity unidentified metabolite accounting for nearly all of the effluent ^{14}C ; no 17 β -estradiol was detected in the effluent from either column. Recovery of $^{14}CO_2$ was only about 0.01%, indicating that 17 β -estradiol was resistant to mineralization. Analyses of the column experiments showed that the ^{14}C was 47-51% irreversibly sorbed and 22-25% reversibly sorbed, which is consistent with earlier incubation experiments. Analysis of the resident soil extracts from the reversible sorption sites indicated that 55%, 20%, and <2% of the ^{14}C was recovered as the polar metabolite, estrone, and 17 β -estradiol respectively, with most of the ^{14}C being retained in the 5-10 cm depth of the column.

Casey et al. (2008) conducted a field lysimeter study to determine the transport of 17 β -estradiol and testosterone. Pentafluorobenzoic acid (PFBA) was used a conservative tracer, and hormone profiles compared with the PFBA. Both 17 β -estradiol and testosterone were detected in the effluent earlier than the PFBA indicating antecedent presence of the hormones, analytical

nonspecificity, and/or facilitated transport. Mass recoveries of 17 β -estradiol and testosterone were 0.46% and 0.02% respectively, which may be attributed to nonextractable hormones still bound to the soil or degradation into metabolites that were not detected using the methods of the study. Based on soil analysis, the most significant factors contributing to the fate and transport of hormones in the field were soil-water status, organic matter content, and colloidal facilitated transport.

Sarmah and Northcott (2008) determined degradation rates of 17 β -estradiol, 17 α -ethinylestradiol, bisphenol-A, and 4-n-nonylphenol in both river water-sediment and groundwater-aquifer material under anaerobic and aerobic conditions. Within the first 2 to 4 days, over 90% of all 4 compounds had degraded in both media under both conditions, with the degradation rate slowing significantly for the remaining period. Only minor differences were observed between the dissipation times (DT₅₀ and DT₉₀) for both media under aerobic conditions for all four hormones. However, under anaerobic conditions in the groundwater-aquifer matrix, DT₉₀ values for 17 α -ethinylestradiol and bisphenol-A ranged from >1000 d to >300 d respectively. Under anaerobic conditions in the river water-sediment, 17 α -ethinylestradiol and bisphenol-A DT₉₀ values were 5.9 d and approximately 4.9 d, respectively. Sulfate-, nitrate-, and iron-reducing conditions, as well as abiotic factors, contributed to the degradation of the 4 compounds under anaerobic conditions.

Xuan et al. (2008) investigated the degradation of 17 β -estradiol in a silt loam soil, using different mixtures of

untreated and sterilized soils. In untreated soil, 17 β -estradiol degraded with a half-life of 0.17 d, with the degradation rate constant proportional to the percentage of non-sterilized soil. The relationship indicates that microorganisms play a major role in the degradation of 17 β -estradiol in soil. It was also determined that the degradation kinetics followed a simple first-order model with respect to temperature, moisture, and a coexisting antibiotic (sulfadimethoxine). The authors also compared the degradation rates and products of 17 β -estradiol, 17 α -estradiol, estriol, and estrone. They concluded that 17 β -estradiol degraded to estrone, but not to 17 α -estradiol as determined by other studies that used dairy manure. Estriol was a degradation product of 17 α -estradiol, but it did not accumulate and was present for only a short period. Estriol was present for a short period of time in the degradation of estrone. The degradation rates of the 4 hormones follow the order 17 β -estradiol > estriol > 17 α -estradiol > estrone, with all four half-lives below 3 days in a 20% nonsterilized soil mixture.

Scherr et al. (2008) evaluated deconjugation and degradation rates of estrone-3-sulfate (Ea-3S) to estrone. Three topsoils were collected from three geographic regions of New Zealand. E1-3S degraded rapidly in all soils, with degradation increasing with increasing temperature. Dissipation times (DT₅₀ and DT₉₀) ranged from a few hours to several days. It was also determined that biological activity plays a significant role in the deconjugation of E1-3S to estrone. Estrone may persist longer than a few hours, with DT₉₀ values >10 days. While most of the previous studies focused only on

estrogenic compounds, Khan et al. (2008) conducted experiments to determine the degradation of 17 α - and 17 β -trenbolone and trendione in agricultural soils. Aerobic degradation rates in clay loam and sandy soil were measured. Degradation half-lives for both isomers to trendione ranged from a few hours to 0.5 days with concentrations ≤ 1 mg/kg. Rates were similar with and without application of manure. Trenbolone degradation was dependent on concentration, with rates decreasing with increasing applied concentrations. Trendione persisted longer than trenbolone with a half-life ranging from 1 to 4 days. There was also conversion of trendione back to 17 β -Trenbolone and of the 17 α - isomer back to the 17 β - isomer. All of these studies suggest that while hormones may be present in livestock waste at concentrations that may cause adverse effects in humans and wildlife, sorption and degradation kinetics will reduce the load placed on the environment from agricultural practices.

Veterinary Antibiotics and Resistance Genes

It is now recognized that the heavy use of antibiotics by humans and agriculture has led to the ubiquitous detection of these chemicals in water environments across the globe (Snow et al. 2008). Studies published in 2008 continued to refine and supplement current knowledge of antibiotic occurrence, adsorption, transport, and degradation in agriculturally-impacted water, manure, and manure-amended soils. Others continued to highlight the occurrence and fate of antibiotic resistance genes (ARGs). Finally, a number of 2008 studies sought to bridge the gaps between antibiotic occurrence, ARG

occurrence, and changes in environmental microbial communities.

Occurrence of the ionophore monensin was observed in lagoons and shallow groundwater from two dairy farms in California (Watanabe et al. 2008). Monensin is the only feed additive permitted for use in the US in lactating cows. Kemper et al. (2008) failed to detect a wide range of antibiotics in manure and leachate from two conventional and two organic dairy farms in northern Germany, but monensin was not tested. Aust et al. (2008) found sulfamethazine (up to 9990 ng/g) and chlortetracycline (400 ng/g) but did not detect tylosin in manure and soil from two Canadian feedlots administering those antibiotics

Dolliver and Gupta (2008b) monitored antibiotic runoff losses from manure and manure-amended agricultural land in Wisconsin in two studies. Losses of chlortetracycline, monensin, and tylosin from beef manure stockpiles subjected to two rainfall events were 0.2-1.8% and primarily a function of water loss. Runoff and seepage losses of the same antibiotics from manure-amended silt loam soil were <5% of the total applied, with 99% of the losses during the non-growing season (Dolliver and Gupta (2008b)). Weiss et al. (2008a) simulated a heavy rainfall after land application of manure from pigs treated with sulfamethazine and flubendazole (an antiparasitic drug). Losses from arable cropping seepage water were around 3% for both drugs (including metabolites), whereas losses from permanent grassland were over 10%. Larsbo et al. (2008) applied the dual-permeability model MACRO to simulate transport of sulfadimine in surface runoff and soil.

The model performed well at the microplot scale but had poor results at the field scale.

Adsorption of antibiotics remained a research focus in 2008. Sanders et al. (2008) studied adsorption of sulfadimethoxine and ormetoprim to sand and two soils. Adsorption increased with increasing organic matter and clay content, but the antibiotics were not co-introduced with manure, limiting the applicability of the results. Gu and Karthikeyan (2008) found significant decreases in tetracycline adsorption to hydrous Al oxide when humic acid was present. Another study found significant hysteresis effects for adsorption of sulfadiazine to five different soils in the presence of manure. Overall adsorption was low, but the adsorbed fraction strongly resisted desorption (Sukul et al. (2008)). Finally, two studies investigated cosorption of tetracycline and copper (II) to montmorillonite (Wang et al. (2008)) and two whole soils (Jia et al. (2008)) as affected by pH.

Antibiotic degradation during manure composting and anaerobic digestion was also studied in 2008. Thermophilic composting of turkey litter spiked with antibiotics was performed for 35 d under three management conditions: frequently mixed piles, vessel composting, and undisturbed piles (Dolliver and Gupta (2008a)). Sulfamethazine was not reduced at all, whereas chlortetracycline was 99% reduced and monensin and tylosin were 54-76% reduced. Compost pile management did not significantly affect antibiotic degradation, suggesting that simple manure stockpiling is as effective at removing antibiotics as intensely managed composting. Arikan (2008) operated anaerobic digesters with manure

from beef calves medicated with chlortetracycline. A 75% decrease in chlortetracycline was observed after 33 d with a corresponding increase in water-soluble 4-epi-chlortetracycline and iso-chlortetracycline. Also in 2008, Loftin et al. (2008) measured degradation half-lives for a wide range of antibiotics in sterile buffers as a function of pH, ionic strength, and temperature.

Antibiotic Resistance Genes. The occurrence and fate of antibiotic resistance genes (ARGs) was the subject of a number of 2008 studies. Rahman et al. (2008) detected the tet(M) tetracycline resistance gene in up to 96% of resistant isolates from marine sediments off Japan. Bacillales was the most dominant order possessing the gene. The sulfonamide resistance genes *sul1*, *sul2*, and *sul3* were detected in shrimp ponds, a city canal, and fish ponds receiving wastewater from swine farms in Vietnam (Hoa et al. (2008)). The genes were most often found on *Acinetobacter* plasmids. Another study found 55% of *E. coli* isolates from poultry slaughterhouses in Portugal had multidrug resistance (Martins da Costa et al. (2008)). Castiglioni et al. (2008) measured resistance to a wide range of antibiotics in isolates from northern Italy rivers and consistently detected the *marA* resistance gene. The fate of six tetracycline resistance genes in field-scale water columns was monitored for 14 d by Engemann et al. (2008). Gene disappearance coefficients were always higher in sunlight than darkness, and some genes readily migrated into biofilms. Another study found evidence of transposon-mediated selection of these tet ARGs (Knapp et al. 2008).

Other studies attempted to link antibiotic

occurrence to ARG occurrence or changes in in situ bacterial populations. Kotzerke et al. (2008) observed reduced microbial activity (as measured by cell respiration) in soils amended with manure containing sulfadiazine (SDZ), whereas pure manure increased activity. However, manure was applied only once, and SDZ levels were much higher than practical in situ values. Another study amended two soils with manure and SDZ at much lower doses and observed decreases in total phospholipid fatty acids and bacteria:fungi ratios and changes in DGGE patterns (Hammesfahr et al. 2008). Heuer et al. (2008) investigated the fate of SDZ administered to pigs. Over 96% of the SDZ and its metabolites were recovered after 10 d in the manure (Heuer et al. 2008). During manure storage, *sul1* and *sul2* resistance genes increased exponentially through 60 d but decreased greatly thereafter. Extractable amounts of SDZ decreased exponentially in soil, and *sul1* and *sul2* genes were also reduced over time.

Another study found no long-term persistence of pollution-induced community tolerance (as measured by leucine incorporation) in soil spiked with tylosin (Demoling and Baath 2008). In this study, bacteria growth was only inhibited at a high tylosin dose (1500 mg/kg). Cermak et al. (2008) monitored changes in the bacterial communities of two soils spiked with lincomycin by cell culture, T-RFLP diversity profiles, and clone-sequencing of 16S rDNA and the *lmrB* resistance gene. No increase in resistant strains was seen in cultivable microbes after spiking, but significant shifts in bacterial diversity were observed after lincomycin spiking for a high pH (7.6) soil. In another study, levels of macrolide-lincosamide-

streptogramin B (MLS_B) resistant bacteria increased substantially during the first three months in an anaerobic sequencing batch reactor fed with swine waste containing tylosin (Angenent et al. (2008)). Thereafter, MLS_B resistance averaged 45%, while the swine waste feed averaged only 18%.

Fate of Prions in the Environment

Investigations into the fate of prions in the environment continued in 2008. Prion diseases, also called transmissible spongiform encephalopathies (TSEs), are a group of fatal neurodegenerative diseases and include bovine spongiform encephalopathy (BSE or 'mad cow' disease), scrapie of sheep and goats, chronic wasting disease (CWD) of deer, elk and moose, and Creutzfeldt-Jakob disease in humans. Strong evidence suggests that the sole infectious agent of prion diseases is comprised of PrP^{Sc} (i.e. the prion protein), an abnormally-folded isoform of a normal cellular protein (PrP^c). The misfolded conformation of PrP^{Sc} conveys distinct biological and physicochemical properties to PrP^{Sc}, including resistance to proteolysis and inactivation. Saunders and colleagues recently reviewed all aspects of prions in the environment, including occurrence, fate, and mitigation, with a special focus on prion interactions with soil (Saunders et al. (2008a)).

It is known that prions enter the environment through mortalities and are shed in blood and saliva. Two papers published in 2008 established that prions can also be shed in feces. One reported PrP^{Sc} in infected-mouse stools out to 48 h post-oral inoculation but not at terminal disease

(Maluquer de Motes et al. (2008)). Safar et al. (2008) demonstrated infectivity in feces from prion-infected hamsters throughout the entire incubation period, with the highest infectivity during the first 7 days post-oral inoculation.

Of critical importance to the study of prions in the environment is establishing the most environmentally-relevant form of the prion protein. The N-terminal of PrP^{Sc} is known to affect prion adsorption (Saunders et al. (2008a)). Saunders et al. (2008b) determined that the N-terminal of PrP^{Sc} is lost between 1 week and 30 d upon incubation in brain homogenate at 22 or 37°C. This indicates that most PrP^{Sc} entering the environment in prion mortalities will lack the N-terminal, which could significantly impact prion fate in the environment. This report also found significant differences in PrP^{Sc} degradation between CWD-elk and hamster brain homogenates, indicating that rodent prion models may not be accurate simulations of natural prion fate.

The fate of prions in wastewater treatment processes was investigated in two 2008 studies. Maluquer de Motes et al. (2008) incubated prion-infected brain homogenates in municipal sewage, seawater, and PBS buffer. Scrapie and BSE PrP^{Sc} were completely degraded after 28 d and 84 d, respectively, in sewage, but remained intact longer in PBS buffer. PrP^{Sc} associated with the sewage solids. Hinckley et al. (2008) determined that PrP^{Sc} can survive aerobic activated sludge treatment, partition into the sludge solids, and retain infectivity after anaerobic digestion. These studies suggest that prions entering wastewater will persist after treatment and

potentially enter the environment through biosolids land application or landfilling. However, prions are not expected to enter wastewater in large quantities and would be highly diluted in the process.

Two 2008 studies explored the interactions of recombinant PrP (recPrP) with organic matter. Polano et al. (2008) found a large increase in recPrP adsorption to kaolinite with the addition of humic acid. Pucci et al. (2008) reported sorption capacities of 330-1000 µg/mg for soil organic matter. However, the results of these two studies using recPrP may not correlate well to actual adsorption of the infectious prion protein, because recPrP is likely a poor model of in vivo PrP^{Sc}.

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