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Land application of biosolid, livestock, and drilling wastes to US farmland: a potential pathway for the redistribution of contaminants in the environment

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In the United States (U.S.), waste byproducts generated from the treatment of municipal waste (biosolids), production of livestock (livestock waste), and drilling of oil and gas wells (drilling waste) are commonly applied to agricultural lands. Although this can be a cost-effective reuse/disposal practice, there is limited research on the potential for contaminant exposures and effects on ecosystems, wildlife, and human health from such land applications. In this study, we conducted extensive chemical, microbial, and toxicity analyses of biosolid, livestock, and drilling wastes just prior to land application on agricultural lands at 34 sites across the U.S. Twenty-two analytical methods were used to determine potential contaminant exposures profiles for 452 organic and 114 inorganic chemicals, nine microbial groups, estrogenicity, and cytotoxicity. Analytical results document unique and substantial chemical, microbial, and toxicity profiles for these land-applied wastes. Of the three waste byproducts, biosolids contained the greatest concentrations of household chemicals, pesticides, pharmaceuticals, per-/polyfluoroalkyl substances, calcium, and phosphorus. Livestock waste contained the greatest concentrations of total and leachable dissolved organic carbon, biogenic hormones, mycotoxins, plant estrogens, total inorganic nitrogen, and potassium. Drilling waste contained the greatest concentrations of BTEX compounds (benzene, toluene, ethylbenzene, and xylenes), polycyclic aromatic hydrocarbons, rare-earth elements, barium, strontium, and uranium–thorium series radioisotopes. Biosolid and livestock wastes had greater culturable heterotrophic bacteria, halophilic bacteria, *Escherichia coli* (*E. coli*), enterococci, and staphylococci concentrations, and greater microbial diversity than drilling waste. Bioassay analyses indicated that exposure to contaminants in livestock wastes and biosolids could result in estrogenic effects, whereas exposure to contaminants in drilling waste could result in cytotoxic effects. Our study documents that current reuse/disposal practices for biosolid, livestock, and drilling wastes on agricultural lands could provide a potential pathway for the redistribution of unique and complex contaminant mixtures into the environment that have bioactive, endocrine disrupting, and carcinogenic characteristics. Results of this study provide a snapshot of chemical compositions and concentrations that can be used to inform the development of best-management practices to help maximize beneficial reuse of these wastes and minimize risk to the environment and human health.

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Environmental significance

It is common practice for waste byproducts generated from the treatment of municipal waste, production of livestock, and drilling of oil/gas wells to be applied to farmland as a cost-effective means of reuse and disposal. Current reuse/disposal practices for biosolid, livestock, and drilling wastes provide a potential pathway for the redistribution of unique and complex contaminant mixtures into the environment that have bioactive, endocrine disrupting, or carcinogenic characteristics. Biosolids provide the greatest source of PFAS and designed-bioactive chemicals, whereas livestock waste provide the greatest source of endocrine-disrupting chemicals. Drilling waste provide the greatest sources of BTEX compounds (benzene, toluene, ethylbenzene, and xylenes), polycyclic aromatic hydrocarbons, rare-earth elements, barium, strontium, and uranium–thorium series radioisotopes.

1. Introduction

It is common practice for waste byproducts generated from the treatment of municipal waste (biosolids), production of livestock (livestock waste), and drilling of oil/gas wells (drilling waste consisting of spent drill fluids and cuttings) to be applied to farmland as a cost-effective means of reuse and disposal.[1–5] Based on an annual wet-weight basis in the United States (U.S.), ~53% (12.1 billion kilograms [B kg]) of all biosolids generated[6] and ~100% of livestock waste (~1270 B kg)[7,8] are applied to farmland as fertilizer to increase agricultural yields. In contrast, there is a substantial knowledge gap regarding the amount of drilling waste that is land applied annually in the U.S. The U.S. Environmental Protection Agency (USEPA) reported that ~24.6 B kg of drilling waste (mud, fluid, and cuttings) was generated from the drilling of oil and gas (OG) wells in 2016.[3] Of the top 20 energy-extraction and -production states, which accounted for approximately 82% of oil and 95% of gas production in 2016, 16 had regulations that allowed for land application of drilling waste. A recent study on land application of drilling waste in Oklahoma, reported that ~1.3 B kg of solid and liquid drilling waste was land applied on ~22 000 acres in 2016.[9] In 2016, Oklahoma only accounted for ~6% of the U.S. OG production,[3] indicating that the amount of drilling waste land applied at the national scale is likely in the 10s of billions of kg per year applied on 100 000s of acres.

Biosolids and livestock wastes are beneficial sources of organic matter and nutrients to replenish soils[5,7] as well as documented sources of excessive nutrients and metals[10–13] and a variety of contaminants of global concern (CGC), including per-/polyfluoroalkyl substances (PFAS),[14–16] pharmaceuticals,[17–20] pesticides,[21–24] and endocrine-disrupting chemicals.[25–28] PFAS are a group of tens of thousands of synthetic chemicals. Since initial production in the mid-1950s, PFAS have been distributed globally in the environment from industrial manufacturing processes, consumer use, and disposal of PFAS-containing products.[29,30] PFAS are largely resistant to biotic transformations due to their extremely strong carbon–fluorine bonds. PFAS and many other CGCs, exhibit bioaccumulation potential, and/or have been shown to cause deleterious biological effects and disruption to key cellular functions in animals and humans.[29,31–39] Antibiotics and other CGC in land-applied biosolids and livestock waste can be transported away from application sites during rain-induced infiltration and runoff events, resulting in environmental soil and water-quality degradation.[40–42] Increased use, release, and biotic exposure of antibiotics in the environment can contribute to the development of antibiotic-resistant bacteria (ARB) and antibiotic-resistant genes (ARG)[43,44] and affect aquatic[45,46] and terrestrial[47] ecosystems. Antibiotic resistant bacterial infections are estimated to be responsible for 700 000 global deaths annually, which is predicted to increase to 10 million deaths per year by 2050.[48] In addition, there is evidence for potential unintentional human and animal exposures from consumption of food crops that have taken up CGCs such as chronic-disease medications,[17] antibiotics,[40,49,50] PFAS,[51,52] and pesticides.[53–55]

Agricultural producers commonly allow the disposal and application of drilling waste on pasture and rangeland,[1,2] yet there is limited research regarding such applications and their potential environmental, wildlife, and human health implications.[56,57] Drilling waste is generated during the exploration and installation of OG wells and is composed of drilling fluids and waste rock cuttings returning to the surface. Drilling fluids are used to cool and lubricate the drill bit, maintain the integrity of the borehole and geologic formation, and provide a transport mechanism to circulate and remove drill cuttings at land surface. Whereas drilling fluids are engineered for a specific use and geology at each well site;[3] they primarily consist of a slurry of liquids and solids that contain a complex mixture of inorganic and organic chemicals present in the base fluids (*e.g.*, water, diesel), additives (*e.g.*, barium, bentonite, zinc, plastics, mica flakes), formation water, and drill cuttings (*e.g.*, pulverized rock). Limited data indicate that drilling wastes are sources of toxic trace elements (*e.g.*, arsenic, chromium, lead, nickel, uranium),[3] BTEX compounds (benzene, toluene, ethylbenzene, xylenes),[3,58] PAHs (polycyclic aromatic hydrocarbons, such as acenaphthylene, chrysene, fluorene, phenanthrene, and pyrene),[59] and radioactive elements (*e.g.*, uranium-235 and -238, radium-226 and -228).[3,60] Environmental and human exposures to these chemicals have resulted in deleterious effects to biota and are recognized as a global human health issue.[35–38,61–63]

At the national scale, little is known about the magnitude of contaminant exposures resulting from the myriad of inorganic and organic chemicals present in biosolids, livestock, and drilling wastes that could be released during application/disposal to farmland. The potential for the redistribution of inorganic and organic contaminants (*e.g.*, designed bioactive chemicals, toxic heavy metals, known carcinogens, and endocrine-disrupting chemicals) to the environment from land application of waste byproducts can be evaluated by a comprehensive understanding of the potential contaminant exposure profiles and effects on the environment, wildlife, and human health. There are large data gaps related to the composition and concentrations of rare-earth elements (REEs) in these waste materials, including the potential of recycling REEs for use in the production of various technological devices.[64] To address these significant data gaps, the U.S. Geological Survey (USGS), in collaboration with municipalities and stakeholders within the animal food production and energy sectors, conducted a national-scale study that included extensive chemical and biological analysis of three commonly land-applied waste materials (biosolids, livestock wastes, and drilling wastes) prior to application to farmland. This article summarizes the analytical results of 452 organic chemicals (*e.g.*, hormones, PFAS, pharmaceuticals, pesticides, semivolatile and volatile organic chemicals) and 114 inorganic chemicals (*e.g.*, nutrients, trace and rare-earth elements, and radionuclides), as well as microbial community characterization (culturable bacteria enumeration and enrichment, and total community composition), total estrogenicity, and cytotoxicity present in land-applied waste materials collected from 34 locations in 14 states across the U.S. Our study provides useful first insights at the national scale into understanding the chemical composition and concentrations of land-applied wastes. The results can be used by stakeholders, resource managers, farmers, and the public to help develop best-management practices that can maximize beneficial reuse/disposal and minimize risk to the environment and human health.

2. Materials and methods

2.1 Description of sites

From June to December 2021, 34 samples of land-applied waste byproducts (*e.g.*, biosolid, livestock waste, and drilling wastes) were collected in 14 U.S. states (Fig. 1). In total, the sampling network consisted of 10 municipal wastewater treatment plants (WWTP), 11 animal feeding operations (AFO), and 13 OG well development/drilling sites (Table SI-1). The sites selected for sampling in this study are comparable to other WWTPs, AFOs, and OG drilling sites across the U.S. in terms of biological treatment methods and volume of waste generated, the number and type of animals on feed, and drilling operations that used water-based and/or oil-based drilling fluids. The biosolid samples included nine Class B (restricted use) samples and one Class AA (unrestricted use) sample.[65] Untreated livestock wastes included samples from five bovine, four poultry, and two swine AFOs. Spent drilling waste included six oil-based and seven water-based drilling waste samples from OG development sites at various stages of directional drilling in unconventional shale gas and tight oil formations. Aside from one Class AA biosolid sample, all sampled sites had permits that allowed application to farmland. For all sites, samples were collected 1 to 10 days prior to land application.

2.2 Sampling protocols

Prior to field sampling, all sampling equipment and composite-sample containers were: (1) cleaned using tap water and anionic detergent, (2) rinsed with tap water followed by reagent-grade blank water, and (3) air-dried and placed in bags made of 100% virgin low-density polyethylene film. At each of the 34 sites, a ∼14 L composite sample was collected in a ∼19 L high-density polyethylene container. Composite samples representative of the specific bulk-waste source at each site were collected by random subsampling (8–10 subsamples of ∼1.5 L). Composite samples

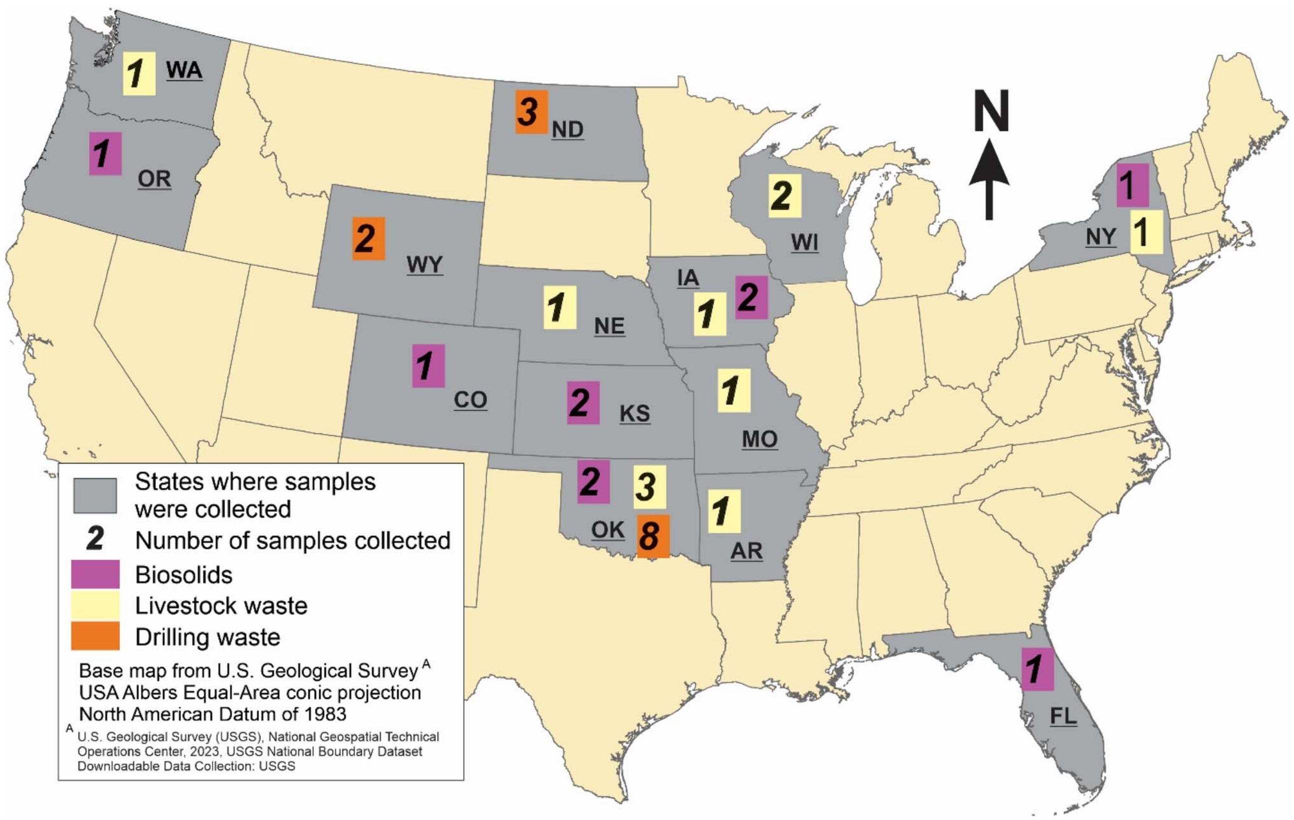

Fig. 1 Map of the United States where municipal biosolid, livestock, and drilling wastes samples were collected.

were secured (lid fastened and doubled bagged), placed into a cylindrical cooler (38 L), transported at ambient temperature to a USGS field station for processing, and split into 12 subsamples for specific laboratory analyses (Table SI-2).

Individual subsamples were obtained by dividing the composite sample into six individual piles arranged on a 1.5 meters squared clear low-density polyethylene sheet, followed by sampling each pile with the use of a 60 mL sterile high-density polyethylene scoop. For most sites (28 of 34 sites), the composite sample was split into subsamples at the USGS field station and shipped (overnight on ice) to receiving laboratories on the day of sampling. The exceptions to this procedure were six sites where the composite sample was shipped overnight at ambient temperature to a USGS field station for subsampling the day after collection and then shipped overnight on ice to receiving laboratories.

2.3 Analytical and statistical methods

Twenty-two analytical methods (Table SI-2) were used to determine individual concentrations of 452 target-organic chemicals; 114 inorganic chemicals; 9 bacterial groups (Table SI-3); bioluminescent yeast estrogen (BLYES) and bioluminescent cytotoxicity yeast reporter (BLYR) bioactivities;[66] total concentrations of anionic surfactants,[67] total organic carbon (TOC),[68] and nonvolatile dissolved organic carbon (NVDOC)[69] in the 34 waste samples. The total concentration of NVDOC, estrogenic compounds (estimated as 17β-estradiol equivalents [E2Eq] using BLYES), and BLYR were determined in blank-water leachate generated from biosolid, livestock, and drilling wastes as described in the SI Methods. Analyses of target-organic chemicals in solid samples included the quantification of 186 pesticides;[70] 93 pharmaceuticals;[71] 76 semivolatile[72] and volatile[73] chemicals; 44 hormone-related compounds (method in SI); 40 PFAS;[74] 10 antibiotics (OGRL LC-MS/MS antibiotics [method includes both human and veterinary-use pharmaceuticals], method in SI), and 3 glyphosate-based pesticides (method in SI). Analyses of inorganic chemicals and physical properties included 66 trace metals, major ions, and rare-earth elements;[75] 39 gamma emitting radionuclides;[76] 3 nutrients (ammonium, inorganic nitrogen, and nitrate + nitrite);[77,78] total cyanide;[79] total mercury;[80] and pH.[81] Throughout the manuscript we use the term heavy metals to refer to heavy elements, including metalloids. Bacterial cultivation and enumeration were performed using methods described in the SI Methods and Table SI-3. Microbial communities were characterized using Illumina 16S iTag sequencing, and data were analyzed using mothur v.1.47.0,[80–82] R v. 1.3.1,[83] and Prism GraphPad. Principal component analysis (PCA; factoextra version 1.0.7)[82] was used in R statistical software[83] to explore correlation patterns of inorganic and organic concentration results from the 34 waste samples. All analytical organic, inorganic, microbial, and toxicity results are provided in the SI and companion data releases.[9,84,85]

2.4 Quality assurance

Quality assurance (QA) samples consisted of laboratory reagent-water blanks (lab blanks) and spikes (lab spikes), three equipment field blanks, and one field duplicate (Tables SI-4 to SI-6). Out of all the organic chemicals analyzed, 6 pharmaceuticals and 1 NVDOC were detected above the established minimum detection level (MDL) or long-term reporting level (RL) in one or more lab and/or field-blank samples (Table SI-4), with a total of 13 raised RLs. For environmental samples that had detections in a blank sample, the concentrations were reported as a non-detection and the RL was set at 3 times the greatest concentration measured in the blank sample. Environmental sample concentrations for amitriptyline, caffeine, ciprofloxacin, cocaine, DEET, sertraline, and NVDOC that were <10 times the adjusted RL, were retained and used in interpretation in this paper and coded "V" to indicate that the reported concentration may have been influenced by contribution occurring during collection or laboratory analysis.

Whereas matrix interference was not exhibited for most of the target-organic methods, the AXYS liquid chromatography-tandem mass spectrometry (LC-MS/MS) pharmaceuticals method (Table SI-2) resulted in nonquantifiable results (NQ) for some individual pharmaceuticals in drilling and livestock waste samples and could not be used in interpretation (Table SI-9). Overall, the analysis of field duplicate samples indicated high levels of precision, reproducibility, and good sample representation during composite sampling (Table SI-5). However, the greatest relative percent differences (RPDs) were for metformin (144%), equol (138%), and cesium (125%) that could indicate limited precision, reproducibility, or sample preparation. Overall, recoveries for isotope-dilution standards and surrogate standards (Table SI-6) for QA and field samples ranged from 85–102% for pesticides (OCRL – LC-MS/MS pesticides); 95–110% for antibiotics (OGRL – LC-MS/MS antibiotics); 100–108% for glyphosate pesticides (OGRL – LC-MS/MS glyphosate); 93–109% for hormones (OGRL – LC-MS/MS hormones); 68–93% for gas chromatography-mass spectrometry (GS-MS) semivolatiles (RTI – GC-MS semivolatile organic chemicals); 92–103% for volatiles (RTI – GC-MS BTEX volatile organic chemicals), 69–100% for PFAS (AXYS LC-MS/MS PFAS); and 69–111% for pharmaceuticals (AXYS LC-MS/MS pharmaceuticals).

As multi-substrate adduction and cytotoxicity may both play a role in presumptive mixed inhibition in the analysis of bioluminescent yeast estrogen (BLYES) and bioluminescent cytotoxicity yeast reporter (BLYR) bioassay results, all values in this study were determined using back calculations from serial dilutions to minimize effects within the undiluted extracts. In solid-phase extractions based on blank water leachate created for bioassay analysis, 32 of 34 waste materials, irrespective of waste type, exhibited some level of photoinhibition which may have impacted assay results. Due to the observed pigmentation and turbidity (optical density > 0.1), and consequent mechanical photo-inhibition, all obtained back calculations of evaluated livestock and biosolid sample matrices are *de facto* underestimates of total bioreactivity. In contrast, drilling waste samples were neither turbid nor pigmented but potentially indicated underestimates due to cytotoxic effects.

2.5 Estimates of biosolid, livestock, and drilling waste loads and calculation of chemical loadings from land application

Land-applied biosolid estimates for the U.S. were obtained from the National Biosolids Data Project.[6] The reported estimate of beneficial use of land-applied biosolids (including agricultural, forestland, reclamation, and Class A land application) was 3 027 971 dry metric tons nationally in 2018. Using an estimated percent moisture of 75% for wet biosolids (Table SI-1), an estimated 12.1 B kg (wet weight) of biosolids were land applied across the U.S. in 2018. The livestock waste load was estimated using the total number of beef, swine, and chickens in the U.S. in 2018 and the estimated waste per day that each animal category generates (Table SI-7).[86,87] The estimated total of livestock waste generated in the U.S. was 1240 B kg. To estimate the waste load of drilling waste land applied nationally, an empirical approach based on reported land-applied drilling waste estimates for Oklahoma was used. Reported drilling waste volumes from 755 land-application permits in Oklahoma during 2018[9] were matched with the total depth of the source wells[88] using methods described in previous research.[89] Masses of drilling wastes were calculated using densities of 0.21 U.S. ton per barrel (ton/bbl) for liquid wastes and 0.23 U.S. ton per bbl for solid wastes.[3] Total estimated masses of drilling waste generated in 2018 were 5.82 and 56.5 B kg in Oklahoma and the U.S., respectively (Table SI-8). In 2018, 2.51 B kg of drilling waste was land applied in Oklahoma,[9] accounting for 43.1% of the total estimated mass of drilling waste generated in Oklahoma. Nationally, the percentage of drilling wastes being land applied is expected to be less than Oklahoma due to varying state regulations. Assuming that 25% of the total wastes generated are land applied gives an estimated 14.1 B kg of land-applied drilling wastes nationally in the U.S. in 2018 (Table SI-8). Detailed information on methods used to estimate biosolid, livestock, and drilling waste loads is provided in SI. The national waste load estimates for biosolids, livestock wastes, and drilling wastes were used with median chemical concentration data analyzed in our study to calculate estimates of annual chemical loadings for the U.S. (*i.e.*, chemical loading = waste load × median chemical concentration).

3. Results and discussion

3.1 Comparison of chemistries in land-applied waste materials

Of the 452 target-organic chemicals analyzed, 203 (45%) were detected in at least one of the 34 waste samples (Table SI-9), with 249 not detected in any sample (Table SI-10). The total number of individual target-organic chemicals detected varied substantially among biosolids (148 detected), livestock waste (101 detected), and drilling waste (35 detected) samples. Principal components analysis (PCA) revealed linear combinations of target-organic and -inorganic concentrations that resulted in distinct clustering of the individual waste types (Fig. 2). Four principal component dimensions (dimensions 1–4) account for ∼50% of the total matrix variation (Table SI-11). The strongest PCA contributions for biosolids came from prescription pharmaceuticals, PFAS, and pesticides, whereas the plant estrogens, antibiotics, nutrients, and mycotoxins were the strongest PCA contributions in livestock wastes (Table SI-12). For drilling waste, the rare-earth elements (REE), metals (including light metals, heavy metals, and toxic heavy metals), PAHs, and BTEX compounds provided the greatest PCA contributions.

Total organic carbon and leachable NVDOC were both measured at substantially greater concentrations in biosolids and livestock wastes when compared to drilling wastes (Table SI-9). Median total organic content in biosolids (34.4%) and livestock wastes (38.1%) was more than 5 times greater than in drilling wastes (6.2%). Overall, leachable NVDOC concentrations were greater in livestock waste (median 832 mg L^{-1} as carbon [C]) than in biosolids (median 174 mg L^{-1} C) and drilling waste (median 14.0 mg L^{-1} C). Leachable NVDOC is the most mobile fraction of organic carbon compounds and has important implications for the mobility of persistent organic contaminants (*e.g.*, PFOA, PFOS, metformin) and trace elements [*e.g.*, arsenic, copper (Cu), zinc (Zn)] due to the propensity of these contaminants to sorb onto NVDOC, thereby facilitating their transport.[90] A confounding factor in evaluating facilitated transport of contaminants by NVDOC, however, is the biodegradability of the leachable NVDOC once the materials are land applied. Previous research documented that a large portion of the dissolved organic carbon (DOC) leached from biosolid samples was rapidly biodegradable under aerobic conditions.[91] In our study, the sample with the greatest concentration of NVDOC was from the Class AA biosolid sample (Biosolid-FL-10) that had undergone an additional time-and-temperature treatment regime that occurred as part of a biosolid-pelletizer system. Additionally, the Class AA biosolid sample also had the greatest (maximum) concentrations of 15 individual PFAS across all samples (Table SI-9 and Fig. 3), possibly indicating that high-temperature treatment can result in the breakdown of the organic carbon into more leachable and persistent compounds. Previous research has documented greater PFAS production rates in activated sludge systems operating at longer retention times and greater temperatures.[92,93] Previous research has also documented greater concentrations of persistent DOC from biosolids that had undergone various additional treatments (*e.g.*, polymer thickening, dewatering, drying, and thermal treatment).[91]

The total number of target-organic chemicals (Tables SI-9) detected, as well as the organic compositions and concentrations measured at individual sites, varied substantially between the three waste types (Fig. 3). Of the total target-organic detections (1223 detections) across all sites, biosolids accounted for more than half (∼66%) of all detections, followed by livestock waste (∼24%) and drilling waste (∼10%). Although target-organic chemicals were detected more frequently in biosolids and livestock waste, the total target-organic concentration in a single drilling waste sample (200 000 ng g^{-1}, Water-DF-WY-4) was over 3 times greater when compared to biosolids (67 600 ng g^{-1}, Bio-FL-10) and livestock waste (50 200 ng g^{-1}, Bovine-NY-6).

3.1.1 Pharmaceuticals.

Prescription pharmaceuticals (P-Pharms) were detected more frequently and at greater concentrations in biosolids compared to livestock and drilling wastes (Fig. 3). In total, there were 53 individual P-Pharms (336 total detections) in biosolids, 23 P-Pharms (55 detections) in livestock waste, and only six P-Pharms (8 total detections) in drilling waste (Table SI-9). The number of P-Pharms detected in

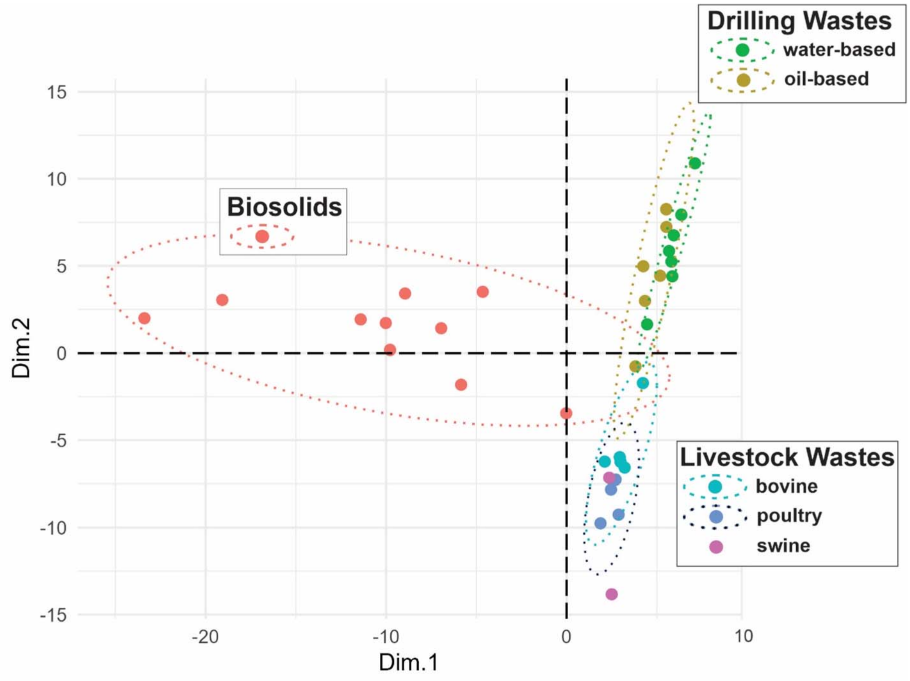

Fig. 2 A principal components analysis (PCA) scatterplot across a two-dimensional plane (Dim-1 and Dim-2) showing linear combinations that result in distinct clusters for municipal biosolids, livestock wastes (bovine, poultry, and swine), and drilling wastes (oil-based and water-based) samples. Ellipses drawn represent a 95% confidence level for a multivariate t-distribution.

individual samples ranged from 21 to 38 for biosolids, 1 to 11 for livestock waste, and 0 to 1 for drilling wastes. Of the total P-Pharms detections and concentration across all samples, biosolids accounted for 84% of all P-Pharms detected and 92% of the total P-Pharms concentration (Fig. SI-1).

Nineteen prescription chronic-disease medications (CDMs)—commonly used to treat asthma, diabetes, epilepsy, cholesterol, heart disease, and hypertension—were the most frequently detected type of P-Pharms in biosolids (Table SI-9), accounting for almost half (~48%) of all detected P-Pharms in biosolids. Although the CDMs were the most frequently detected, they only accounted for ~17% of the total P-Pharms concentration in biosolids. In contrast, there were 17 antibiotics (primarily fluoroquinolones and macrolides) detected in biosolids that accounted for ~25% of total P-Pharm detections in biosolids yet they accounted for over half (~55%) of the total P-Pharms concentration. In livestock waste, antibiotics were the most frequently detected class of P-Pharms and were present in greatest concentrations. There were 16 antibiotics (primarily tetracyclines and sulfonamides) that accounted for ~66% of all detections in livestock waste and ~82% of the total P-Pharms concentration. Antidepressants accounted for ~18% of detections and ~28% of the total P-Pharms concentration in biosolids, whereas pain relievers and stimulants accounted for only ~9% of detections and only ~0.1% of the P-Pharms concentration in biosolids. Apart from frequent detection of the bronchodilator theophylline (82%) in livestock waste, overall detection of CDMs, pain relievers, and stimulants were sporadic and infrequent in livestock (<20% of samples) and drilling (<15% of samples) wastes (Fig. 4 and Table SI-9). The infrequent detection of trace amounts of P-Pharms in drilling waste sampled for our study was unexpected as drilling fluids are carefully designed with specific materials not expected to contain pharmaceuticals. Possible sources of P-Pharms in drilling wastes could be from offsite water used to make drilling fluid or from accidental mixing of employee waste in containers used to store spent drilling waste before disposal. No antidepressants were detected in livestock or drilling wastes.

Of the 53 individual P-Pharms detected in biosolids sampled for our study, 34 were frequently detected (>50% of samples) with 22 being pervasively detected (≥90% of samples; Fig. 4). In biosolids, the pervasively detected P-Pharms included six antidepressants, six antihypertensive CDMs, five additional CDMs (*e.g.* metformin), four antibiotics, and thiabendazole (antiparasitic agent used in the treatment of pinworms). Although no pain relievers or stimulants were pervasively detected, cocaine (stimulant schedule II drug), codeine (opioid pain reliever), and amphetamine (stimulant) were frequently detected in 80%, 60%, and 50%, respectively, of biosolid samples (Table SI-9). Of the 11 CDMs that were pervasively detected in biosolids, the six antihypertensive CDMs had median concentrations that ranged from 30 ng g^{-1} (propranolol) to 1.4 ng g^{-1} (diltiazem; Fig. 4). Other pervasively detected CDMs in biosolids had median concentrations that ranged from 17.1 ng g^{-1} (triamterene, diuretic) to 0.8 (benztropine, an anticholinergic used to treat Parkinson's). Excluding carbamazepine and three antihypertensives (propranolol, norverapamil, and verapamil) in biosolids, which had concentrations an order of magnitude lower in our study, concentrations of the pervasively detected CDMs were similar to concentrations reported in previous

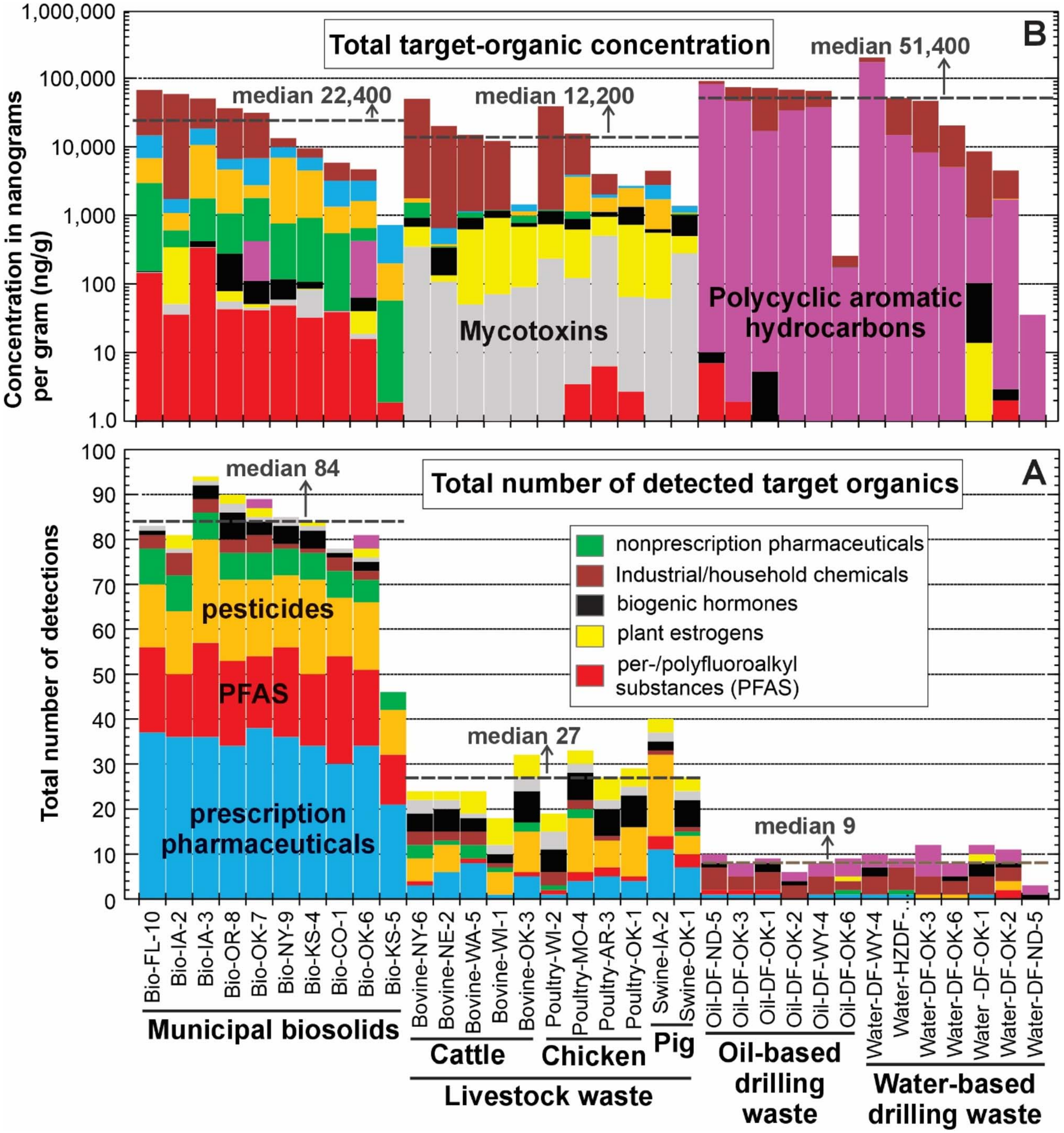

Fig. 3 Graph showing total number of target-organic chemical detections (A) and total concentrations (B) for municipal biosolid, livestock, and drilling wastes samples.

research.[94–96] Theophylline, a bronchodilator that is commonly used to treat asthma and other respiratory diseases, was detected in both biosolids (100% of samples) and livestock waste (82% of samples; Fig. 4). To our knowledge, our study is the first to document theophylline concentrations in biosolid and livestock wastes.

Of the 17 individual antibiotics detected in biosolids, 8 were frequently detected: three fluoroquinolone antibiotics (ciprofloxacin, 100% of samples; ofloxacin, 100%; and enrofloxacin, 70%), three macrolides (azithromycin, 100%; erythromycin-H_2O, 90%; and clarithromycin, 70%), and 2 tetracyclines (doxycycline, 70%; and tetracycline, 60%). Concentrations were greatest for ciprofloxacin, ofloxacin, doxycycline, and azithromycin (Fig. 4 and Table SI-9). Excluding ciprofloxacin and tetracycline in biosolids, which had concentrations an order of magnitude lower in our study, concentrations of antibiotic were similar to concentrations reported in previous biosolid research.[97] Ciprofloxacin in agricultural soils amended with

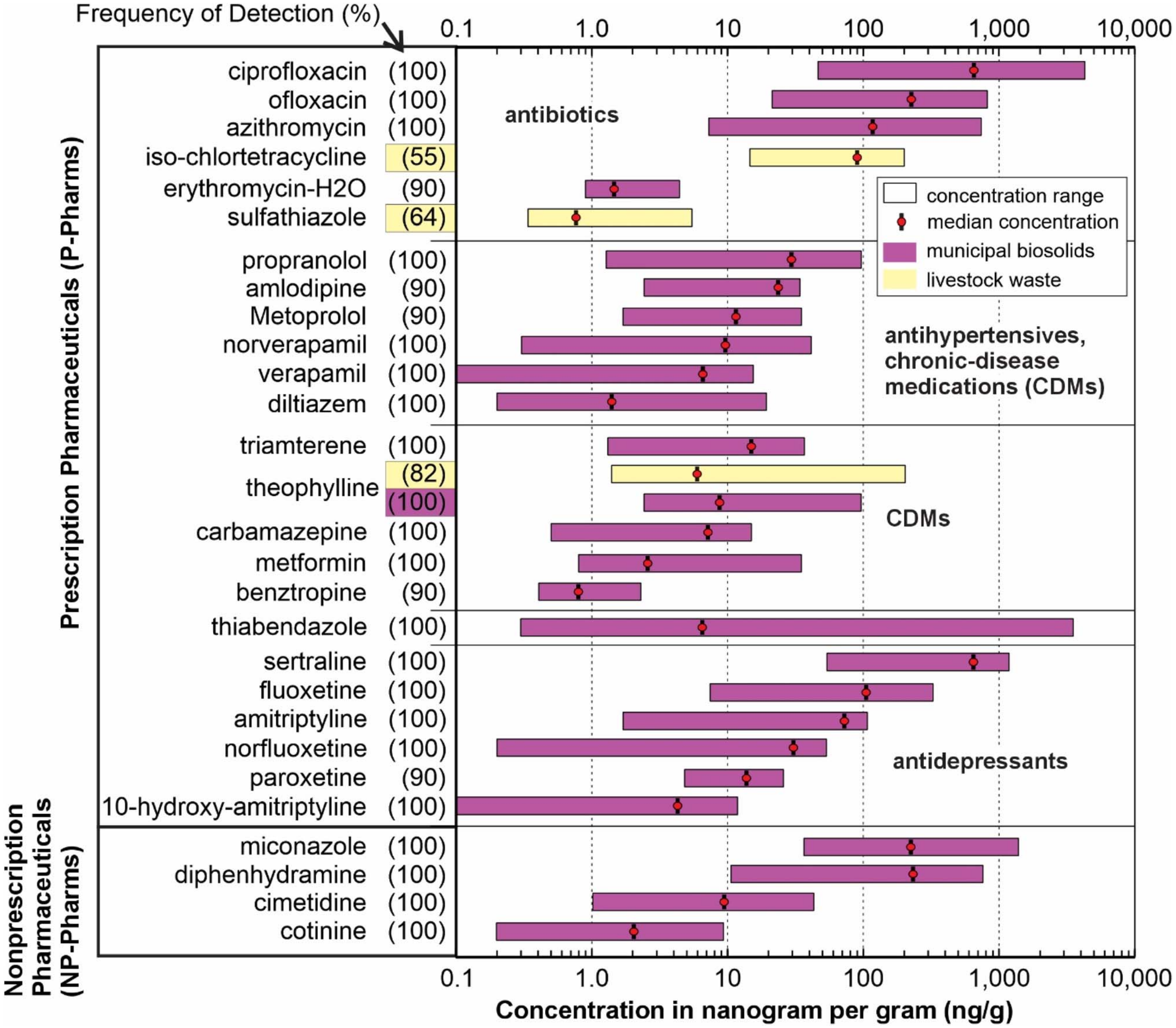

Fig. 4 Range of detected prescription pharmaceutical (P-Pharms) and nonprescription pharmaceutical (NP-Pharms) concentrations that were pervasively detected (≥90% of samples) in municipal biosolid samples and frequently detected (≥50% of samples) in livestock waste samples. Grouped by pharmaceutical class and sorted from top to bottom by decreasing median concentrations.

biosolids has been shown to be a critical compound (risk quotient > 1) for ecotoxicological risk at concentrations greater than 2.14 ng g^{-1} in soils[98] and decreased plant biomass.[99]

Although there were 16 individual antibiotics detected in livestock waste, most of the detected antibiotics were sporadic and infrequent across bovine, poultry, and swine samples (Table SI-9). There were only 3 antibiotics that were frequently detected across livestock samples and not detected in biosolids. Sulfathiazole, a veterinarian-use sulfonamide antibiotic, and two chlortetracycline metabolites (iso-chlortetracycline and *epi*-iso-chlortetracycline) were detected in 64%, 55%, and 45%, respectively, of livestock samples (Fig. 4 and Table SI-9). Upon availability of less toxic antibiotic alternatives, the U.S. Food and Drug Administration withdrew approval of sulfathiazole for human use except when used in combination with sulfabenzamide and sulfacetamide.[100] Sulfathiazole concentrations ranged from 0.33 to 5.5 ng g^{-1} in livestock samples, whereas concentrations of iso-chlortetracycline and *epi*-iso-chlortetracycline concentrations ranged from 13 to >200 ng g^{-1} and 5.3 to 34 ng g^{-1}, respectively. Two other tetracycline antibiotics, tetracycline and oxytetracycline were detected less frequently (18% and 36% of samples, respectively) but at concentrations >200 ng g^{-1}. With respect to livestock wastes, antibiotics were detected more frequently and at greater concentrations in swine waste than in bovine and poultry wastes, likely due to continuous antibiotics dosage in feed additives given to swine compared to bovine and poultry.[101] The median total detected antibiotic concentration (comprised primarily of tetracycline antibiotics) was 650 ng g^{-1} in swine waste compared to 46 ng g^{-1} in bovine waste and 45 ng g^{-1} in poultry waste. The large number of antibiotics present in land-applied biosolids and livestock wastes sampled in our study pose environmental concerns for adverse phytotoxicity effects,[102] uptake and accumulation in food crops,[99,103] and development of ARB/ARG through consumption of food crops grown in soils that receive repeated low-dose antibiotic exposure.[104]

There were six antidepressants (four selective serotonin-reuptake inhibitors [SSRIs] and two tricyclic antidepressants [TCAs]) that were pervasively detected in biosolid samples (Fig. 4). The newer (second-generation) SSRI class of antidepressants, sertraline and fluoxetine, are among the most prescribed antidepressants, accounting for 13% and 9%, respectively, of all antidepressants dispensed in the U.S.[105] Median concentrations of sertraline (670 ng g^{-1}) and fluoxetine (107 ng g^{-1}) were greater than median concentrations for the other SSRIs norfluoxetine (30 ng g^{-1}) and paroxetine (15 ng g^{-1}) in biosolids (Fig. 4). The older (first-generation) prescribed TCA antidepressant amitriptyline and its transformation product 10-hydroxy-amitriptyline had median concentrations of 72 ng g^{-1} and 4.2 ng g^{-1}, respectively. Excluding amitriptyline in biosolids, which had concentrations an order of magnitude lower in our study, concentrations of antidepressants were similar to those reported in previous research.[95,97] The lower concentrations of amitriptyline in our study compared to concentrations documented in previous research is likely due to increased use of the less toxic second-generation SSRIs class of antidepressants that are known to have fewer side effects than the first-generation TCAs.[106]

Additional P-Pharms that were detected in biosolid samples included thiabendazole (treatment of intestinal pinworms, 100%), cocaine (stimulant, 80%), codeine (stimulant/pain reliever, 60%), and amphetamine (stimulant, 50%) (Table SI-9). Concentrations of these P-Pharms in our study were similar to concentrations reported in previous research.[107,108]

There were nine individual non-prescription pharmaceuticals (NP-Pharms) detected in biosolids, six in livestock waste, and only two in drilling waste (Table SI-9). Of the nine individual NP-Pharms detected in biosolids, four were pervasively detected: cimetidine (acid reducer, 100%), cotinine (nicotine transformation product, 100%), diphenhydramine (antihistamine, 100%), miconazole (fungicide, 100%; Fig. 4) and two were frequently detected: caffeine (stimulant, 80%), and ibuprofen (pain reliever, 80%) (Table SI-9). In biosolids, median detected concentrations were greatest for diphenhydramine (269 ng g^{-1}), miconazole (220 ng g^{-1}), and ibuprofen (152 ng g^{-1}), followed by caffeine (15 ng g^{-1}), cimetidine (9.0 ng g^{-1}), and cotinine (2.0 ng g^{-1}). With the exclusion of the pain relievers acetaminophen and ibuprofen that were detected in 36% and 45%, respectively, of livestock waste samples, detection of NP-Pharms was sporadic and infrequent in livestock and drilling wastes.

3.1.2 Per-/polyfluoroalkyl substances.

PFAS were detected more frequently and at greater concentrations in biosolids compared to livestock and drilling wastes (Fig. 3). Of the total number of PFAS detections and concentrations across all samples, biosolids accounted for 90% of all detected PFAS and 97% of the total PFAS concentration (Fig. SI-1). In total, there were 28 individual PFAS (177 total detections) in biosolids, seven PFAS (15 detections) in livestock waste, and four PFAS (5 detections) in drilling waste. The number of individual PFAS detected in biosolid samples ranged from 11 to 24, in livestock wastes (0 to 3), and drilling waste (0 to 2). Maximum total PFAS concentrations in biosolid samples were as large as 338 ng g^{-1}, two orders of magnitude greater than the maximum total concentration in livestock waste (6.3 ng g^{-1}) and drilling waste (7.1 ng g^{-1}) samples (Fig. 3).

Overall, the long-chain (>8 carbon atoms) perfluorocarboxylate compounds were detected more frequently and accounted for ~47% of detected PFAS in biosolids, followed by the precursors (~37%) and perfluorosulfonates compounds (~16%). Of the 28 individual PFAS detected in biosolids, 18 were frequently detected (Fig. 5). Sixteen of these frequently detected PFAS were long-chain compounds (seven precursor, seven perfluorocarboxylates, and two perfluorosulfonates). Although long-chain and short-chain PFAS are both persistent and toxic chemicals, long-chain compounds have greater sorption and bioaccumulation potentials whereas short-chains have greater solubility.[109] Thus, it is not unexpected that the longer-chained PFAS were more frequently detected in biosolids due to their preference to sorb to organic solids. There were nine long-chain PFAS and one short-chain PFAS (perfluorohexanoate, PFHxA) that were pervasively detected (>90% of samples) across all biosolid samples, including *N*-ethylperfluorooctanesulfonamidoacetic acid (*N*-EtFOSAA, 100%), *N*-methylperfluorooctanesulfonamidoacetic acid (*N*-MeFOSAA, 100%), perfluorodecanoate (PFDA, 100%), perfluorododecanoate (PFDoA, 100%), perfluorooctanoate (PFOA, 100%), perfluorooctanesulfonate (PFOS, 100%), perfluorooctanesulfonamide (PFOSA, 100%), perfluorodecanesulfonate (PFDS, 90%), and perfluorononanoate (PFNA, 90%).

Although perfluorocarboxylate substances in biosolids were detected more frequently than precursor substances, the precursors were measured at greater concentrations (Fig. 5). Concentrations for 11 precursor substances accounted for 76% of the total PFAS concentration across biosolid samples, followed by the perfluorocarboxylates (14%) and perfluorosulfonates (10%). Maximum concentrations for seven frequently detected precursors in biosolids ranged from 176 ng g^{-1} for 7 : 3 perfluorodecanoic acid (7 : 3 FTCA) to 1.2 ng g^{-1} for PFOSA (Fig. 5 and Table SI-9). The precursor concentrations observed in our study indicate potential for in-field transformation to terminal PFAS (end members along PFAS degradation pathways) when biosolids are applied to agricultural fields. Long-term monitoring of agricultural soils has documented temporal fluctuations on PFAS production rates in soils due to transformation of precursor substances into final terminal compounds (*e.g.*, PFDA, PFDoA, PFOA and PFOS).[110] Maximum concentrations of frequently detected terminal PFAS in biosolids sampled in our study ranged from 26.1 ng g^{-1} for PFOS to 6.2 ng g^{-1} for PFOA (Fig. 5). Although PFAS compositions in our study were similar to those in older national biosolid surveys, the median total PFAS concentration (40 ng g^{-1}) in our study was substantially less than the median total PFAS concentrations from a 2013 survey in France (220 ng g^{-1})[111] and a 2001 survey in the U.S. (539 ng g^{-1}).[112] The lower PFAS burden in biosolids measured in our study might be due

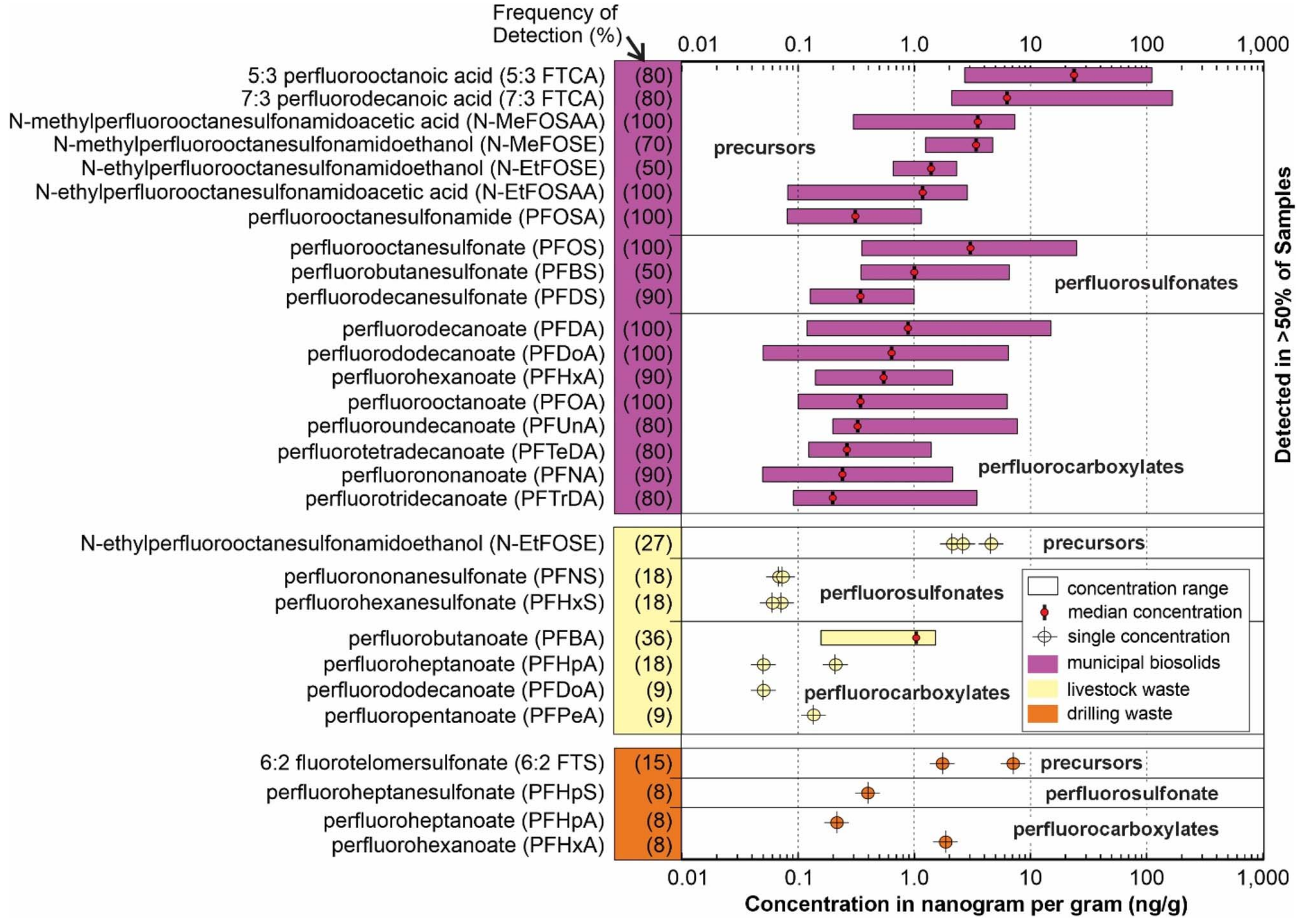

Fig. 5 Range of detected per-/polyfluoroalkyl substances (PFAS) concentrations that were frequently detected (≥50% of samples) in municipal biosolid samples and detected in livestock and drilling wastes samples. Grouped by PFAS class and sorted from top to bottom by decreasing median detected concentration.

to policies and regulations implemented in the early 2000s to reduce PFAS in manufacturing processes globally.[113]

PFOS and PFOA are two of the most commonly studied PFAS globally due to their mobility, toxicity, and bioaccumulation potential that can result in adverse effects on the environment and human health.[29] In our study, maximum concentrations of PFOS (26.1 ng g^{-1}) and PFOA (6.2 ng g^{-1}), as well as 13 other PFAS (Table SI-9), were detected in a sample of an unrestricted Class AA biosolid (Biosolid-FL-10). Of all 10 biosolid samples in our study, the Biosolid-FL-10 was the only sample with Class AA biosolid classification. All other biosolid samples were restricted Class B biosolids. Biosolid treatment at the Biosolid-FL-10 site was like other sites except for the additional time-and-temperature treatment regime that occurred as part of a biosolid-pelletizer system. The biosolid-pelletizer system used was based on high-temperature heating and drying to eliminate pathogens, thus creating a Class AA biosolid that can be released to the public and used for a wide range of unrestricted residential and agricultural purposes.[114] Previous research has documented greater PFAS production rates in activated-sludge systems operating at longer retention times and greater temperatures.[92,93] Further research can help elucidate PFAS concentrations in Class A and Class AA biosolids as well as the potential formation/production rates during treatment of biosolids to achieve Class A or AA status.

Our study documents that biosolids contain substantially greater concentrations of PFAS when compared to livestock and drilling wastes. The median total PFAS concentrations in bovine (0.07 ng g^{-1}) and swine (0.20 ng g^{-1}) waste were substantially lower than in poultry waste (3.1 ng g^{-1}). The primary contribution of PFAS in poultry waste was from concentrations of N-EtFOSE and perfluorobutanoate (PFBA) that were detected in 75% of poultry waste samples at concentrations as large as 4.6 ng g^{-1} and 1.7 ng g^{-1}, respectively (Table SI-9). There are significant data gaps on PFAS concentrations in various livestock waste types. A possible pathway of PFAS in poultry waste sampled in our study could be from the consumption of PFAS contaminated feed and/or water. Previous research also has documented greater PFAS concentrations in sewage sludge and municipal biosolids when compared to livestock waste.[111] At the time of our study, no research was found that reported on PFAS concentrations in drilling wastes. With the exclusion of two detections of 6 : 2 FTS at concentrations of 7.1 ng g^{-1} and 1.8 ng g^{-1}, overall PFAS detections in drilling waste samples were infrequent (<20% of samples), sporadic, and potentially due to contamination from specific materials or equipment used on site.

3.1.3 Pesticides. Overall, pesticides (insecticides, fungicides, and herbicides) were detected more frequently and were present at greater concentrations in biosolids than in livestock and drilling wastes (Fig. 3). Pesticide detections in biosolids (161 total detections) accounted for ~67% of the total detected pesticides across all biosolid, livestock waste (76 detections), and drilling waste (4 detections) samples (Fig. SI-1). In total, there were 36 individual pesticides detected in biosolid samples, 36 detected in livestock wastes (21 in swine, 17 in poultry, and 14 in bovine), and only two pesticides (the herbicide glyphosate and its transformation product amino phosphonic acid [AMPA]) detected in water-based drilling waste (no detections in oil-based) samples (Table SI-9). Insecticides and their transformation products were the most frequently detected class of pesticides in biosolids (87 total detections) and livestock waste (44 detections). The detected insecticides accounted for over half of the total detected pesticides in biosolid (~54%) and livestock wastes (~58%) samples. Pesticide concentrations in biosolids accounted for ~83% of the total pesticide concentration across all samples (Fig. SI-1), whereas concentrations in livestock and drilling wastes accounted for ~17% (poultry ~12%, swine ~3%, and bovine ~1.3%) and ~0.2%, respectively. The greatest total pesticide concentration in a single biosolid sample was 8880 ng g^{-1} (Bio-NY-9), followed by poultry waste (2497 ng g^{-1}, Poultry-MO-4), swine (1078 ng g^{-1}, Swine-IA-2), bovine (254 ng g^{-1}, Bovine-

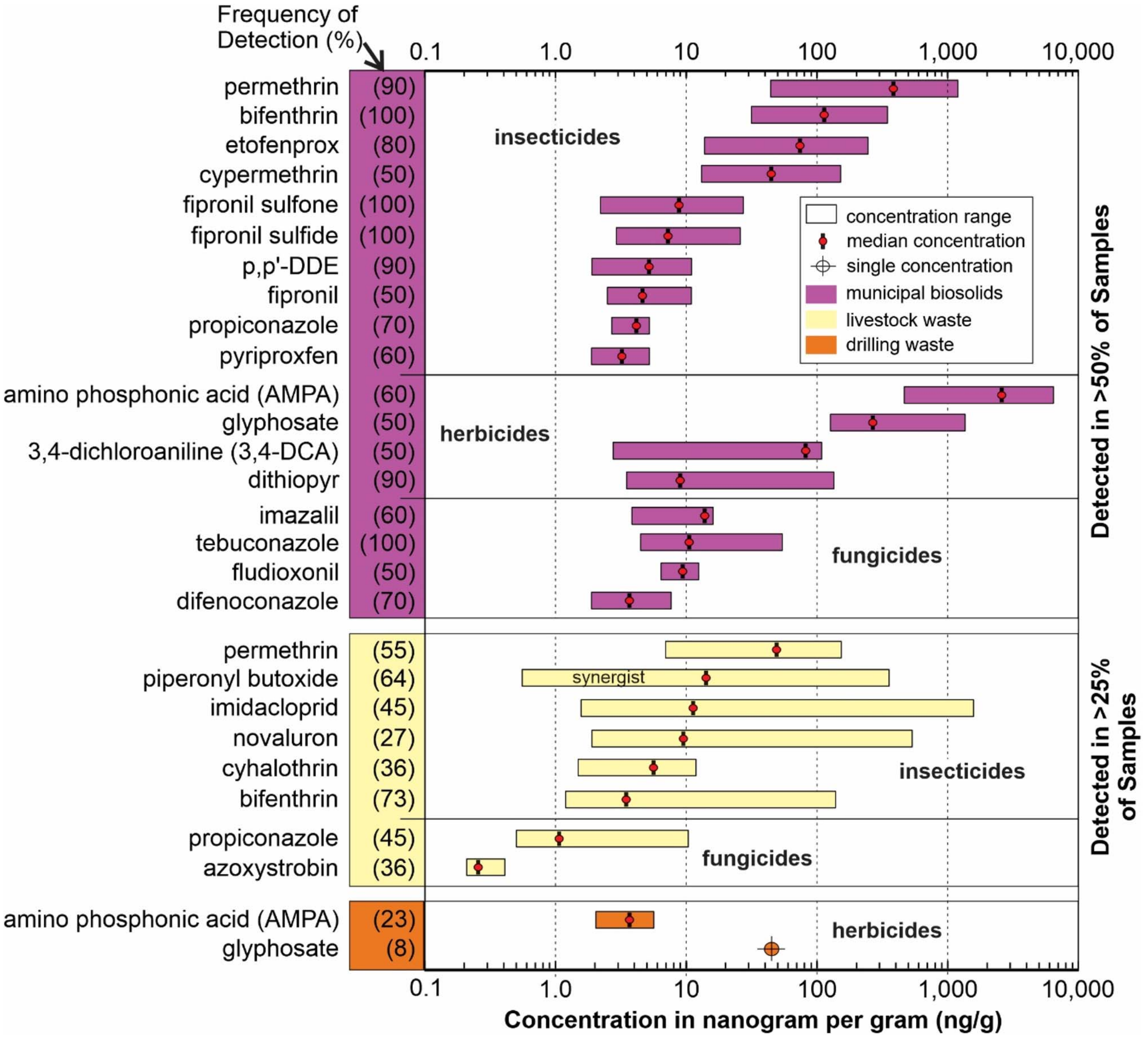

Fig. 6 Range of detected pesticide concentrations that were frequently detected (≥50% of samples) in municipal biosolid samples, detected in ≥25% of livestock waste samples, and detected in drilling waste samples. Grouped by pesticide class and sorted from top to bottom by decreasing median detected concentration.

NY-6), and drilling waste (47.0 ng g^{-1}, Water-DF-OK-2) (Fig. 3, Table SI-9).

Although insecticides were detected more frequently than herbicides in biosolids, concentrations of the herbicide glyphosate and its transformation product AMPA were up to two orders of magnitude greater than the maximum insecticide concentrations (Fig. 6). The total concentration of all detected herbicides in biosolids (20 300 ng g^{-1}) and insecticides in poultry waste (4340 ng g^{-1}) provided the greatest pesticide burden in biosolid and livestock waste samples. Concentrations for glyphosate, AMPA, and six other herbicides (Table SI-9) accounted for ∼70% of the total pesticide concentration in biosolids, whereas concentrations for 14 insecticides in poultry waste accounted for ∼73% of the total pesticide concentration across all livestock waste samples.

For the frequently detected pesticides, there were 18 pesticides (10 insecticides, 4 fungicides, and 4 herbicides) detected in biosolids and 3 pesticides (insecticides bifenthrin and permethrin and the synergist piperonyl butoxide) detected in livestock wastes (Fig. 6 and Table SI-9). The commonly used herbicide glyphosate and its transformation product, AMPA, were frequently detected in biosolid samples at concentrations that ranged from 116–1380 ng g^{-1} and 487–6230 ng g^{-1}, respectively. Glyphosate is a widely used broad-spectrum herbicide that is used in both urban and agricultural landscapes.[115] Exposure to glyphosate-based herbicides can alter the equilibrium of soil microorganisms[116] and can result in increased risks of neurotoxic effects in animals[117,118] and non-Hodgkin lymphoma in humans.[119,120] The two pyrethroid insecticides (bifenthrin and permethrin) were pervasively detected in biosolids (100% and 90% of samples, respectively) and frequently detected in livestock waste samples (73% and 55% of samples, respectively) (Fig. 6). Pyrethroid insecticides are commonly detected in almost all environmental media (solids, water, tissue) due to their widespread usage in both urban and agricultural landscapes to control mosquitoes, flies, and other insects.[121,122] Bifenthrin exposure to non-target organisms has been linked to lethal and sub-lethal effects to fish and other aquatic organisms.[123,124] Overall, there are limited data that include a broad suite of pesticide compositions and concentrations in biosolids. In our study, pyrethroid concentrations (at part-per-billion, ppb) in biosolids samples were two orders of magnitude greater than concentrations (low parts-per-trillion, ppt) in municipal wastewater effluent.[125] In addition to permethrin and bifenthrin, there were five additional pesticides that were pervasively detected (>90% detection) in biosolid samples: tebuconazole (fungicide, 100%), fipronil sulfide (fipronil insecticide transformation product, 100%), fipronil sulfone (fipronil insecticide transformation product, 100%), dithiopyr (herbicide, 90%), and *p*,*p*′-DDE (dichlorodiphenyltrichloroethane [DDT] insecticide transformation product, 90%). Concentrations of these pervasively detected pesticides in biosolids ranged from ∼1 to 100 s ng g^{-1} (Fig. 6). With the exclusion of cypermethrin (pyrethroid insecticide) and 3,4-DCA (diuron herbicide transformation product) which had concentrations in biosolids as large as 172 ng g^{-1} and 105 ng g^{-1}, respectively, the remaining frequently detected pesticides had concentrations that ranged from ∼1 to 10 s ng g^{-1} (Table SI-9).

Although more individual pesticides were detected in swine waste (21) than in poultry waste (17), overall pesticide concentrations were substantially greater in poultry waste (Table SI-9). Concentrations in poultry waste accounted for ∼73% of the total pesticide concentration across all livestock waste samples compared to swine (∼19%) and bovine (∼8%) wastes. There were 12 detections of neonicotinoid insecticides in livestock wastes and only 2 detections of neonicotinoids in biosolids. The more hydrophobic insecticides (*e.g.*, permethrin, bifenthrin, fipronil) are likely detected in biosolids due to their preference to adsorb to biosolids during wastewater treatment, whereas the more hydrophilic insecticides (*e.g.*, imidacloprid) are frequently detected in WWTP effluent.[40,126] Following this premise, the detection of the more hydrophilic insecticides like the neonicotinoid imidacloprid in poultry waste for our study indicates a direct exposure input likely from management operations of poultry. Neonicotinoids, a group of neurotoxic insecticides, are the most heavily used insecticides globally and are commonly applied in both urban and agricultural settings to protect crops and in the treatment of pets and livestock to control insects.[127–129] The neonicotinoid insecticides were dominant in poultry waste (10 total detections), with imidacloprid concentrations in one poultry sample (Poultry-MO-4) as large as 1760 ng g^{-1}, including transformation products imidacloprid-olefin (63 ng g^{-1}) and 5-hydroxy-imidacloprid (6.0 ng g^{-1}). Combined neonicotinoid concentrations in poultry waste (2550 ng g^{-1}) accounted for ∼99% of the total neonicotinoid concentrations across all biosolid and livestock waste samples. The USEPA reported that the use of neonicotinoid insecticides (*e.g.*, clothianidin, imidacloprid, and thiamethoxam) would likely result in adverse effects to >67% of endangered or threatened species and >56% of their critical habitats.[130] Clothianidin was detected at concentrations as large as 24 ng g^{-1} in poultry waste and 18.8 ng g^{-1} in swine waste. The largest agricultural use of clothianidin is for corn and canola seed treatments, but is also commonly applied in poultry and other AFOs for treatment against pests such as beetles and flies.[131]

3.1.4 Household and industrial chemicals. Overall, household and industrial chemicals were detected more frequently, and were present at greater concentrations, in drilling wastes than in biosolids and livestock wastes (Fig. 3). Household/industrial chemical detections in drilling wastes (44 total detections) accounted for over half (∼51%) of the total detected household and industrial chemicals across all drilling waste, biosolid (25 total detections), and livestock waste (17 detections) samples. The median total household and industrial chemicals concentration across drilling waste samples (28 000 ng g^{-1}) was two times greater than median total concentration in biosolids (14 100 ng g^{-1}) and livestock waste (11 000 ng g^{-1}). Of the 12 household and industrial chemicals that were detected in one or more biosolid, livestock, and drilling waste samples (Table SI-9), there were four chemicals in drilling waste, two in livestock waste, and one in biosolids that were frequently detected (>50% of samples, Fig. 7). The volatile organic BTEX (benzene, toluene, ethylbenzene, and xylene) compounds were frequently detected in drilling waste, whereas the aromatic cresols (*M*,*P*-cresol) and a carboxylic acid (benzoic acid) were frequently detected in livestock waste. The phthalate plasticizer (2-ethylhexyl phthalate, DEHP) was dominant in biosolid samples, detected in all but one biosolid sample.

Maximum concentrations of BTEX compounds in drilling waste ranged from 2300 ng g^{-1} (benzene) to 46 000 ng g^{-1} (total xylenes). Toluene and ethylbenzene were detected in drilling waste at concentrations as large as 9900 ng g^{-1} and 5800 ng g^{-1}, respectively. Individual median BTEX concentrations in drilling waste were greatest for total xylenes (21 000 ng g^{-1}), followed by ethylbenzene (2300 ng g^{-1}), toluene (2100 ng g^{-1}), and benzene (190 ng g^{-1}). Both the oil-based and water-based drilling waste samples had frequent detections of BTEX compounds and exhibited similar BTEX concentrations. Previous research has documented that drilling fluids are a source of volatilized organic air pollutants, including BTEX compounds, that pose adverse and carcinogenic health[132] risks to workers during onsite drilling operations[133] and offsite where drilling wastes are land applied.[134] The fate of BTEX compounds in spent drilling waste and the potential for environmental health effects after land application are not well studied. To our knowledge, our study is the first to document BTEX concentrations in spent drilling waste within 1–10 days before land application. No BTEX compounds were detected in livestock waste. Toluene was the only BTEX compound detected in biosolids but only at 20% frequency of detection and at concentrations that were 2 orders of magnitude less than concentrations in drilling waste (Table SI-9).

In livestock waste, *M*,*P*-cresol and benzoic acid were detected in 55% of samples at median concentrations 8950 ng g^{-1} and 6550 ng g^{-1}, respectively (Fig. 7 and Table SI-9). Although cresols and benzoic acid are widely used in the manufacturing of plastics and other household/industrial materials, they are also natural occurring compounds in soils and plants and are formed during the degradation of natural organic matter; thus, their frequent detection in livestock waste is not surprising. In biosolids, DEHP was frequently detected at concentrations that ranged from 1300–14 000 ng g^{-1} (median 3500 ng g^{-1}, Fig. 7). DEHP is classified as a probable human carcinogen[135] that is a widely used plasticizer in vinyl household and industrial materials. Previous research has documented that DEHP is a highly insoluble and recalcitrant compound that can exhibit toxicological effects to methanogens and could therefore limit biodegradation of other organic compounds in sewage treatment systems.[136] In addition to negative implications of DEHP in sewage treatment systems, microbial exposure to DEHP in soils could result in deleterious effects to methanogens and soil function effecting emissions of methane and other volatile organic compounds.[137] Land application of biosolids containing DEHP is of potential environmental concern as previous research has documented uptake of DEHP in plants[138] grown in soils amended with plastic mulch[139] and bisolids.[140]

3.1.5 Polycyclic aromatic hydrocarbons. PAHs were detected more frequently and at substantially greater concentrations in drilling waste compared to biosolids and livestock waste (Fig. 3). Of the total PAH detections and concentrations across all samples, drilling waste accounted for 88% of all PAHs

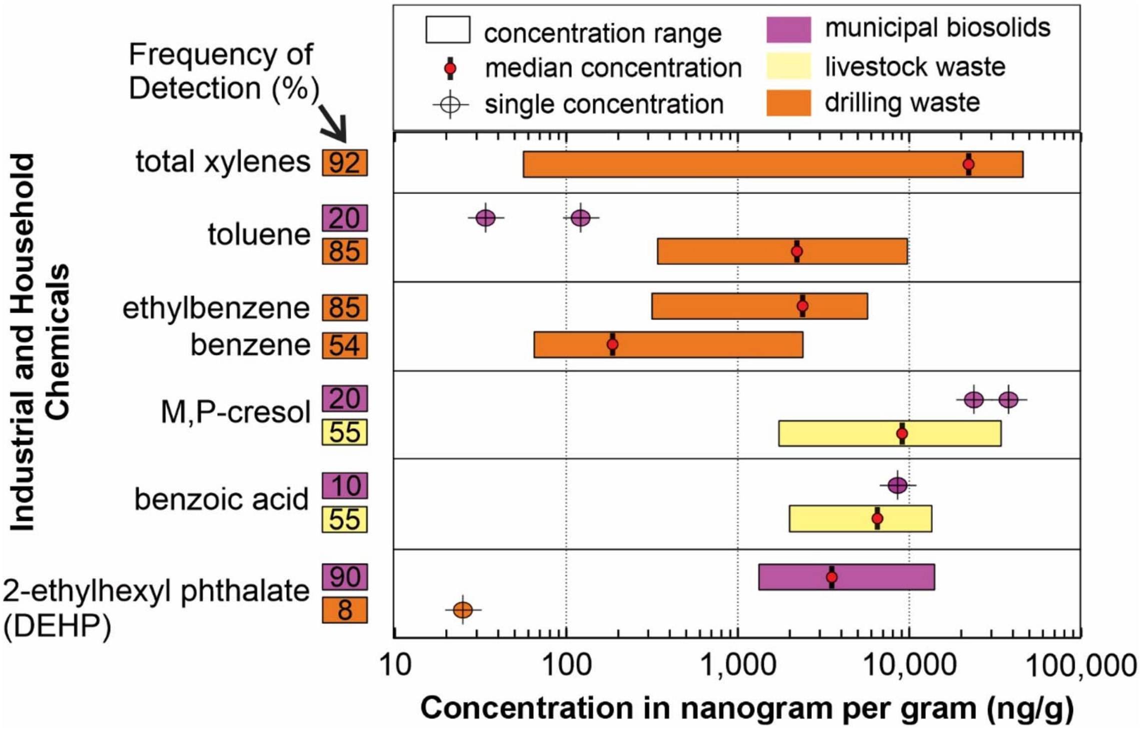

Fig. 7 Range of detected household and industrial chemical concentrations that were frequently detected (≥50% of samples) in municipal biosolid, livestock waste, and drilling waste samples. Grouped by chemical class and sorted from top to bottom by decreasing median detected concentration.

detected and ~99.8% of the total PAH concentration (Fig. SI-1). In total, there were eight individual PAHs (37 total detections) detected in drilling waste and three individual PAHs (5 total detections) in biosolid samples (Fig. 8 and Table SI-9). No PAHs were detected in livestock waste. The maximum total PAH concentration in a single drilling waste sample (171 000 ng g^{-1}) was more than 3 orders of magnitude greater than the maximum total PAH concentration in biosolids (360 ng g^{-1}). PAH detections in biosolids were infrequent (<22% of samples), with only two biosolid samples having low concentrations of pyrene, fluoranthene, and benzo(*b*)fluoranthene that ranged from <100–160 ng g^{-1}. Previous research on PAHs in biosolids have documented more frequent detection of PAHs also at overall low concentrations.[141] The reporting limits for the targeted PAHs in our study (Table SI-9) may have been too high to effectively characterize low concentrations of PAHs in biosolid samples.

Of the eight individual PAHs detected in drilling waste in our study, seven are classified as priority-pollutants based on potential for human exposure and toxicity and two (benzo(*a*) anthracene and chrysene) are designated as probable human carcinogens.[142] The maximum total PAH concentration of 171 000 ng g^{-1} in drilling waste samples from our study was similar to maximum total PAH concentrations in samples of oil-based drilling waste from Nigeria (223 520 ng g^{-1})[143] and China (140 883 ng g^{-1}).[59] The two most frequently detected PAHs in drilling waste in our study, 2-methylnaphthalene (92% of samples) and phenanthrene (62% of samples), also had the greatest detected concentrations of 110 000 ng g^{-1} and 32 000 ng g^{-1}, respectively (Fig. 8). Soil PAH concentrations above 20 000 to 100 000 ng g^{-1} have been shown to significantly inhibit plant growth.[144] Whereas phenanthrene concentrations in our study were similar to those reported in previous research, the median 2-methylnaphthalene concentration (7550 ng g^{-1}) documented in our study was substantially greater than the maximum concentration (1960 ng g^{-1}) reported previously.[59,143] Naphthalene and pyrene were detected in about half (46%) of drilling waste samples, with maximum concentrations of 29 000 ng g^{-1} and 3900 ng g^{-1}, respectively. Both the oil-based and water-based drilling wastes samples for our study had frequent detections of PAHs and exhibited similar PAH contaminant profiles. The fate of PAHs in spent drilling waste after land application and the potential for environmental health effects are not well studied. To our knowledge, our study is the first to document PAH concentrations in spent drilling waste from across the U.S. prior to land application.

Due to their low solubility and affinity for sorption to particulate matter, the PAH compounds will likely be largely retained in soils affected by land application of these wastes, with their transport into water, air and biota being ultimately controlled by a complex set of physical, chemical and biological factors. Previous research found that particle size greatly influenced the leaching into water of PAHs from oil-based drill cuttings.[59] Microbial biodegradation can control the fate of these compounds in soils but will vary depending on factors such as the chemical structure, temperature, pH, availability of nutrients and microbial populations.[145,146] Potential for uptake of PAHs by plants growing in affected soil has long been recognized,[147] however, there currently is a limited understanding of how PAHs persist and influence ecosystems temporally due to a lack of long-term studies.[148]

3.1.6 Estrogenicity, cytotoxicity, and target-hormonally active chemicals. The total concentration of estrogenic compounds in leachate generated from biosolid, livestock, and

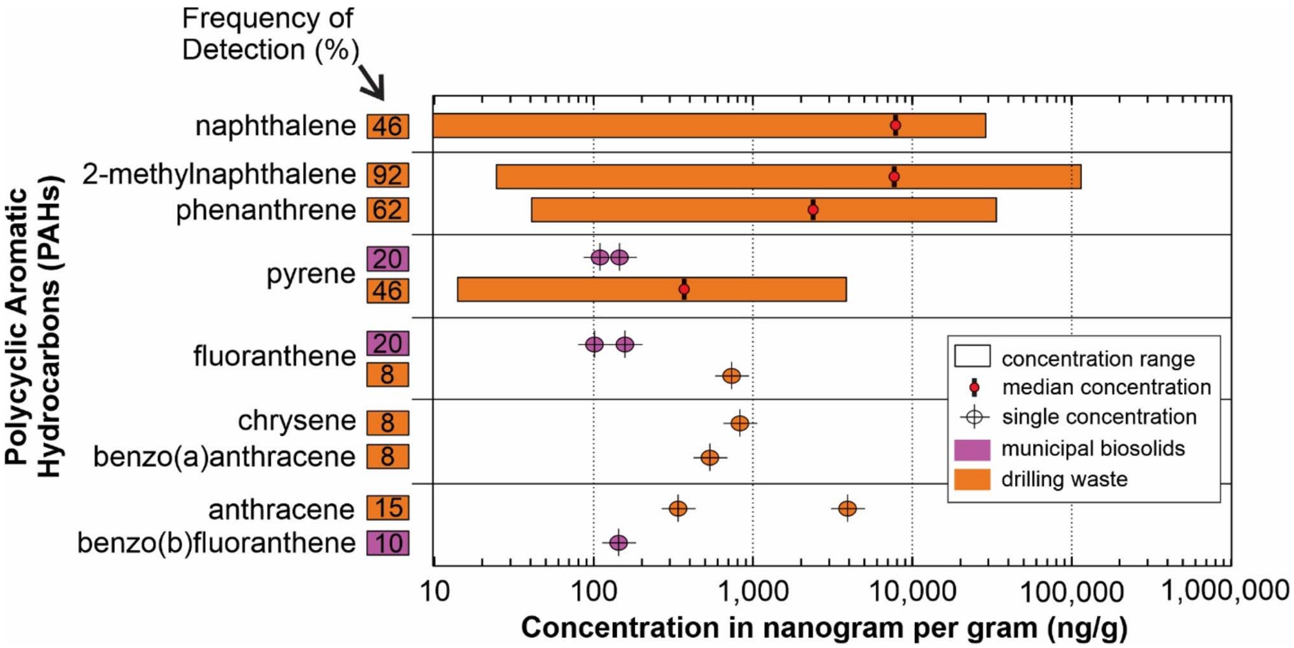

Fig. 8 Range of detected polycyclic aromatic hydrocarbons (PAHs) concentrations in municipal biosolid, livestock waste, and drilling waste samples. Sorted from top to bottom by decreasing median detected concentration.

drilling waste samples was estimated as 17β-estradiol equivalents (E2Eq) using a bioluminescent yeast estrogen screen (BLYES).[66] Estrogenic activity was detected more frequently and at greater concentrations in livestock wastes and biosolids when compared to drilling wastes. Estrogenic activity was measurable in 100% of biosolid and livestock waste samples, whereas estrogenic activity was only measurable in 3 of 13 (23%) of drilling waste samples (Table SI-13). Current effects-based trigger (EBT) values for estrogens are defined at 0.5 ng L^{-1} E2Eq.[149] BLYES concentrations were greatest in livestock waste in which concentrations ranged from 2.02 to 9.93 ng L^{-1} E2Eq; all observed concentrations in livestock waste were greater than the 0.5 ng L^{-1} E2Eq EBT as well as the USEPA estrogenicity trigger value of 1 ng L^{-1} E2Eq.[150,151] BLYES concentrations in biosolids ranged from 0.454 to 6.45 ng L^{-1} E2Eq. Only one of the 10 biosolid samples (Biosolid-KS-5) had a lower concentration than the EBT threshold. For drilling waste samples, 10 of 13 were less than the limit of detection (LOD) of the BLYES assay; the three samples with detections ranged from 0.290 to 0.520 ng L^{-1} E2Eq (Table SI-13). Detected values of water-based drilling waste (Water-DF-OK-1 and Water-DF-ND-5) were less than biologically relevant estrogenic concentration (>0.5 ng L^{-1}), whereas one detected value (0.52 ng L^{-1} E2Eq) obtained from oil-based drilling waste (Oil-DF-OK-1) was only marginally above the 0.5 ng L^{-1} E2Eq EBT threshold.

The bioluminescent cytotoxicity yeast reporter (BLYR; 490 BioTech) was used to discern if any observed photoinhibition was due to the presence of anti-estrogenic, cytotoxic, or assay inhibiting compounds in leachate generated from biosolid, livestock, and drilling waste samples. As both bioassay methods (BLYES and BLYR) can be influenced by the presence of light absorbing molecules in the sample matrix; cytotoxicity was only confirmed if a >20% reduction in bioluminescence was observed compared to the negative control[152,153] and optical density (OD) of the analyte (or subsequent dilutions) was less than 0.1 (OD600). Although, 10 of 11 screened livestock waste extracts, and 8 of 10 biosolid extracts demonstrated 20% or greater reduction in bioluminescence, they also failed to satisfy the OD criteria to exclude pigmentation-based inhibitor effects. For a single livestock waste sample (Swine-OK-1) and two biosolid samples (Biosolid-IA-2 and Biosolid-FL-10) the diluents reached an OD600 nanometer wavelength of <0.1, signifying the potential for both cytotoxic and mixed inhibition effects (Table SI-13). For the oil-based drilling wastes, 5 of 6 samples were found to be cytotoxic with dilutions meeting both cytotoxicity criteria.

Our study documents that biosolid and livestock wastes contain substantially greater concentrations of hormonally active compounds at concentrations that could cause estrogenic effects to aquatic organisms. Although drilling waste in our study was not a source of estrogenic compounds, drilling waste (predominately oil-based drilling waste) is a source of substances that could be expected to cause cell damage or cell death. The additional targeted analysis of biogenic hormones (*e.g.*, estrogenic, and endocrine-disrupting compounds) in our study largely confirmed the findings of the BLYES assay. Biogenic hormones (*e.g.*, estrone, 17β-estradiol, and estriol) and mycotoxins (*e.g.*, beauvericin, deoxynivalenol), potential endocrine disrupting chemicals,[154] were detected more frequently and at greater concentrations in livestock wastes and biosolids when compared to drilling wastes (Fig. 3 and Table SI-9). Previous research has documented that estrone, 17β-estradiol, and estriol are frequently observed in human and animal waste products,[28] with equilenen, 17α-estradiol, progestrone, *cis*-androsterone, androstenedione, ketotestosterone, dihydrotestosterone, epitestosterone, testosterone also observed in biosolid runoff.[26,27] Our study supports this previous research and indicates that land application of biosolid, livestock, and drilling wastes followed by subsequent precipitation-induced runoff events could provide a pathway for potential exposures of estrogenic compounds (as related to biosolids and livestock wastes) and harmful toxic substances (as related to drilling wastes) in aquatic environments. In addition, our study indicates that broad-target bioassays can provide context which may complement and support other analytical methods. Targeted hormone analysis largely confirmed the findings of the bioassays, but such analysis requires prior expectations of presumptive hormonally active compounds found within a sample matrix. Overall, our study can benefit from additional correction factors to enable more direct interpolation of widely varied data sets.[155]

3.1.7 Nutrients and metals. Among the nutrients, biosolids and livestock waste provided substantially greater concentrations of the primary macronutrients, total phosphorous (P) and total inorganic nitrogen (TIN), when compared to drilling waste (Fig. 9 and Table SI-14). The median P concentration in biosolids (26 900 μg g^{-1}) and livestock waste (13 800 μg g^{-1}) were two orders of magnitude greater than the median P concentration in drilling waste (481 μg g^{-1}). TIN concentrations were greatest in livestock waste (median 21 300 μg g^{-1}), followed by biosolids (median 5400 μg g^{-1}) and drilling waste (median 33 μg g^{-1}). Whereas biosolids and livestock waste sampled in our study provide substantial sources of P and TIN, land-application of drilling waste to increase P and TIN concentrations in soils to optimum levels required for most crops[156] would be insufficient (Fig. 9). Biosolids, livestock wastes, and drilling wastes were each a substantial source of calcium (Ca), sulfur (S), magnesium (Mg), and potassium (K), that if land applied, could provide beneficial reuse by increasing overall concentrations of these macronutrients in receiving soils. Overall, median Ca, S, and Mg concentrations in biosolids (27 400 μg g^{-1}, 12 900 μg g^{-1}, and 6000 μg g^{-1}, respectively) were similar to median Ca, S, and Mg concentrations in livestock waste (23 300 μg g^{-1}, 6990 μg g^{-1}, and 7720 μg g^{-1}, respectively) and drilling waste (26 800 μg g^{-1}, 12 300 μg g^{-1}, and 7500 μg g^{-1}, respectively). Livestock waste, however, was a greater source of K (median 26 400 μg g^{-1}) than drilling waste (median 14 500 μg g^{-1}) or biosolids (median 3930 μg g^{-1}).

The inorganic geochemical composition of biosolids, livestock waste, and drilling waste varied substantially between each of the waste types and among individual samples within waste types. The pH of the wastes was generally alkaline, with a median pH of 7.9 for biosolids, 8.6 for livestock wastes, and 9.9 for drilling wastes (Table SI-14). During the drilling of O&G

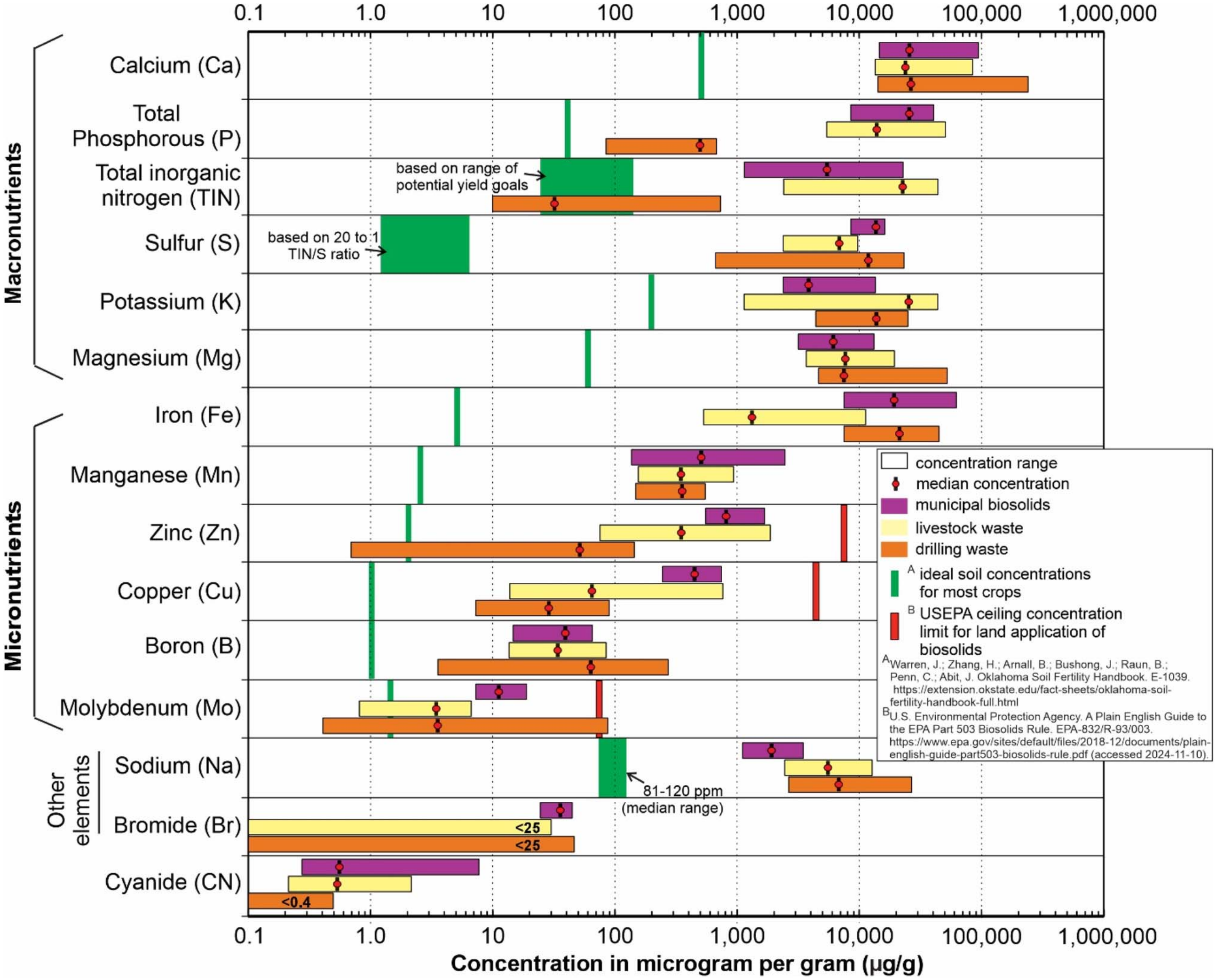

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Fig. 9 Range of nutrient concentrations in municipal biosolid, livestock waste, and drilling waste samples. Sorted from top to bottom by decreasing maximum biosolid concentration. Green bars indicate range of general soil target concentrations for most agricultural crops.

wells, drilling fluids are purposely engineered to have an alkaline pH level, generally pH > 10, to help protect workers from exposure to hydrogen sulfide, inhibit scaling and corrosion of drilling equipment and pipe, and enhance the characteristics and properties of drilling fluids.[157] The high pH of spent drilling waste sampled in our study in indicates amendments are likely needed to lower the pH of drilling waste prior to land application to inhibit negative effects to plant growth and soil function.[158] Sodium (Na), iron (Fe), aluminum (Al), titanium (Ti), Ca, Mg, and K were the dominant cations across the three waste types (>2000 μg g^{-1} median concentration). Previous research on the risks associated with metals leaching from soils amended with biosolids[159] or drilling waste[160] included environmental concern for potential exposures from 10 heavy metals: arsenic (As), barium (Ba), cadmium (Cd), copper (Cu), lead (Pb), mercury (Hg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se), and zinc (Zn).

Aside from one Mo concentration of 89 μg g^{-1} from a single drilling waste sample (Oil-DF-OK-1) that exceeded the USEPA pollutant limit concentration (75 μg g^{-1}), concentrations of all current biosolid regulated elements that were analyzed in our study were below the allowable ceiling concentrations for land application of biosolids (Fig. 9–11).[161]

Drilling waste had high concentrations of Ba and strontium (Sr), as large as 49 200 μg g^{-1} and 3640 μg g^{-1}, respectively (Fig. 11 and Table SI-14). Livestock waste and biosolids had relatively high concentrations of Zn as large as 1900 μg g^{-1} and 1840 μg g^{-1}, respectively (Fig. 9). In addition, the median Ba concentration in drilling waste (25 000 μg g^{-1}) was two and three orders of magnitude greater than median Ba concentrations in biosolids and livestock waste, respectively. Ba has been reported at concentrations up to 33 000 μg g^{-1} in drilling waste in previous research[162] which is substantially less than the maximum Ba concentration (49 200 μg g^{-1}) reported in our study. High concentrations of Ba in drilling waste are expected due to the use of the mineral barite in the production of drilling fluids. Barite is used as a weighting agent in drilling fluids to enhance their ability to withstand increased hydrostatic

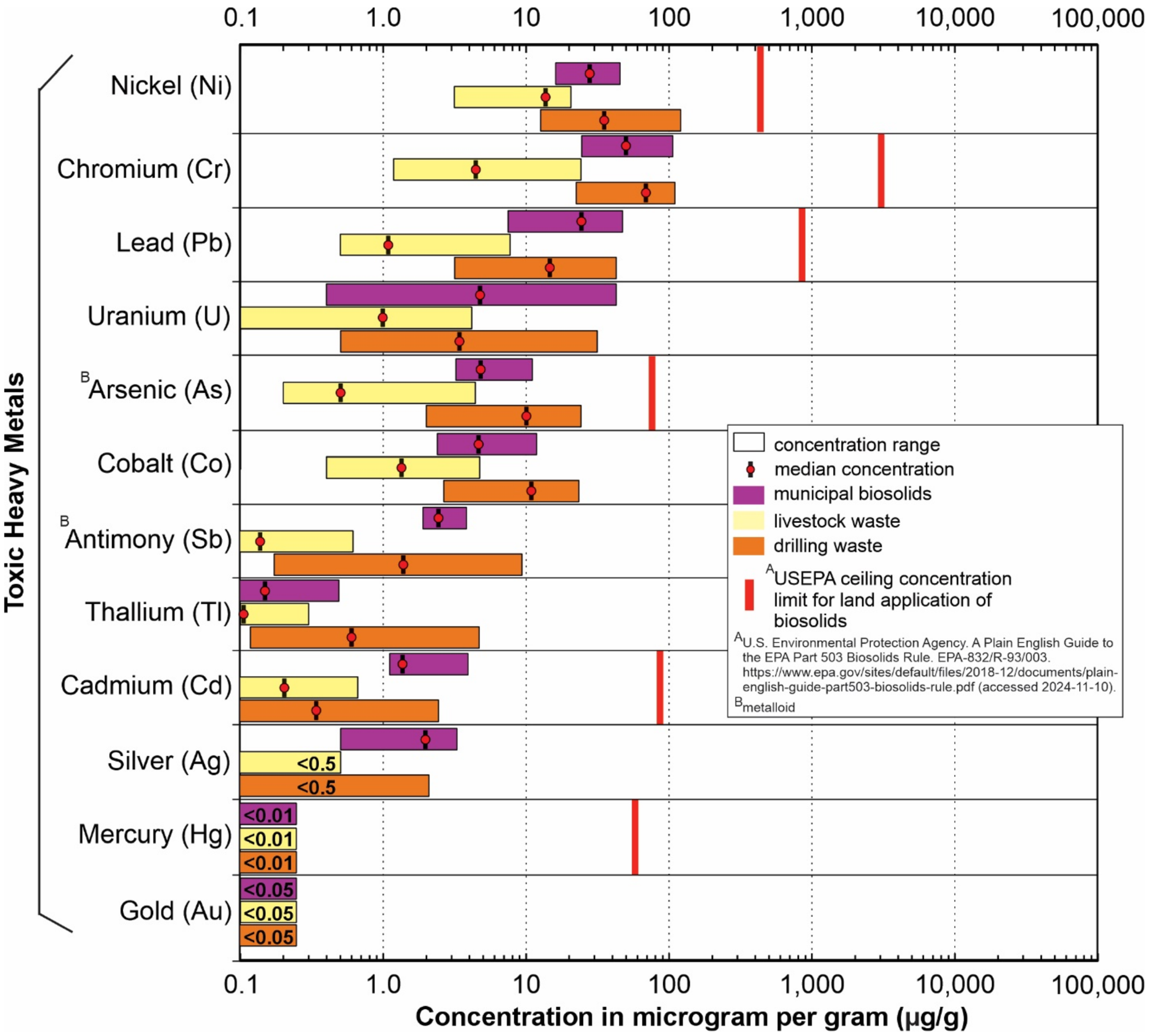

Fig. 10 Range of toxic heavy metal concentrations in municipal biosolid, livestock waste, and drilling waste samples. Sorted from top to bottom by decreasing maximum drilling waste concentration.

pressure and control formation pressure to maintain the integrity of the wellbore during drilling. Accidental release of drilling waste at two disposal sites documented that Ba and Sr were two of the greatest indicators of drilling waste pollution and migration, with soil concentrations of 798 μg g^{-1} Ba and 706 μg g^{-1} Sr.[163] Previous research has documented toxic effects in plants exposed to high concentrations of Ba[164] and significant reduction in uptake of essential nutrients upon exposure to Sr at elevated concentrations.[165] The elevated Ba and Sr concentrations in drilling waste sampled for our study raise potential concerns for plant health in fields that may have received drilling waste under current land-application management practices.

3.1.8 Rare-earth elements. The REEs: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu) are used to produce various technological devices.[64] The global production of REEs has substantially increased over the last 50 years, due to demand of REEs in agricultural, medical, and hi-tech sectors, to more than 80 kiloton annually.[166] This increased use of REEs has raised concerns about human health and potential for REE exposures in the environment.[167] REEs were detected at concentrations that were an order of magnitude greater in drilling waste when compared to concentrations in biosolids and livestock wastes (Fig. SI-2). Overall, the REE concentrations in drilling waste (Table SI-14) was similar to the REE abundance in the continental crust (∼40 μg g^{-1} of Ce to ∼0.3 μg of Lu).[166,168] There was greater variability in concentrations for individual REEs in biosolids and livestock waste when compared to drilling waste. Individual REE concentrations spanned two orders of

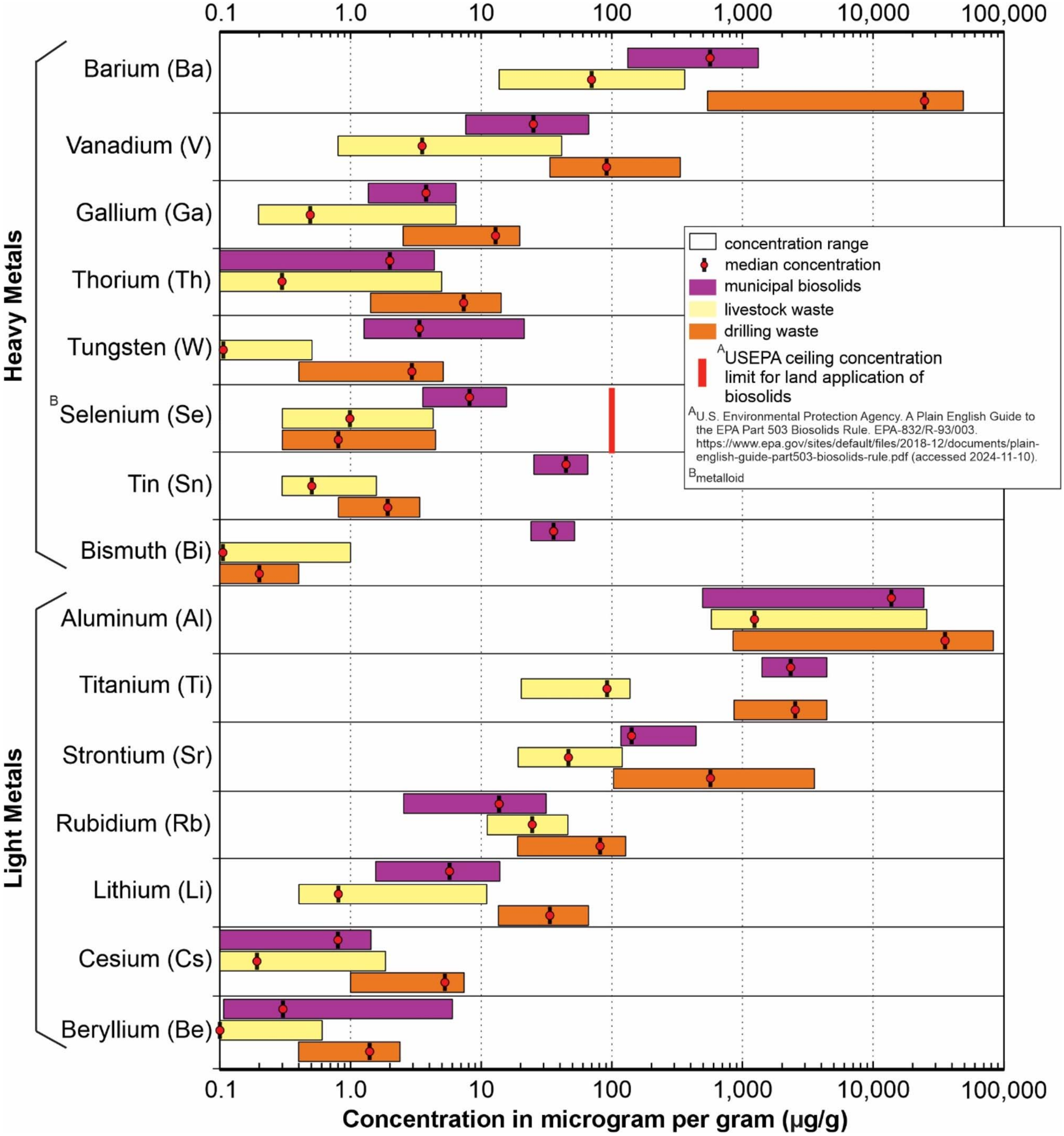

Fig. 11 Range of light and heavy metal concentrations in municipal biosolid, livestock waste, and drilling waste samples. Sorted from top to bottom by decreasing maximum drilling waste concentration.

magnitude in biosolids and livestock waste, whereas individual REEs concentrations in drilling waste generally spanned one order of magnitude (Fig. SI-2). Apart from yttrium (Y), the light REEs (*e.g.*, La, Ce, and Pr) were detected at greater concentrations than the heavy REEs (*e.g.*, Tm and Lu), in all three waste types. La and Ce have traditionally been considered low-value byproducts in rare earth mining processes, but their use in aluminum alloy products may increase, resulting in improved REE supply chain stability and increased demand for all REEs.[169] The total of the mean individual REE concentrations in biosolid (107 µg g^{-1}), livestock (14.9 µg g^{-1}), and drilling waste (139 µg g^{-1}) sampled in our study were less than 300 µg g^{-1} (ppm), the total REE interest level concentration for economically feasible REE recovery set by the U.S. Department of Energy.[170]

REE concentrations in biosolids, livestock waste, and drilling waste in our study were normalized against the North American Shale Composite (NASC) dissolved REE patterns[171,172]

Table 1 Summary of radionuclide data: minimum, median, and maximum activity of U–Th series, cosmogenic and primordial radionuclides in picocuries per gram (pCi g^{-1}) in municipal biosolids, livestock, and drilling wastes, including number of detects per number of analyses (frequency of detection)[a]

Radionuclide	Biosolids				Livestock waste				Oil-based drilling waste				Water-based drilling waste			
	Min.	Med.	Max.	No. of detects, analyses	Min.	Med.	Max.	No. of detects, analyses	Min.	Med.	Max.	No. of detects, analyses	Min.	Med.	Max.	No. of detects, analyses
U-238 series																
U-238 (indirect *via* Th-234)	<MDC	<MDC	15	2, 10	<MDC	<MDC	<MDC	0, 11	<MDC	<MDC	6.4	1, 5	<MDC	<MDC	<MDC	0, 7
Ra-226 (indirect *via* Pb-214)	<MDC	0.71	5.3	8, 10	<MDC	<MDC	0.63	1, 11	<MDC	1.4	8.6	5, 6	0.52	1.1	1.2	7, 7
Ra-226 (indirect *via* Bi-214)	<MDC	nd	5.1	5, 10	<MDC	<MDC	<MDC	0, 11	<MDC	1.1	7.8	5, 6	0.54	0.68	1.1	7, 7
Th-232 series																
Ra-228 (indirect *via* Ac-228)	<MDC	<MDC	1.7	3, 9	<MDC	<MDC	<MDC	0, 11	<MDC	<MDC	0.94	1, 4	<MDC	<MDC	2.1	1, 3
Pb-212	<MDC	nd	0.73	5, 10	<MDC	<MDC	0.49	1, 11	<MDC	0.58	1	5, 6	0.51	1.1	2.5	7, 7
Tl-208	<MDC	<MDC	0.19	2, 10	<MDC	<MDC	<MDC	0, 11	<MDC	nd	0.39	3, 6	<MDC	nd	0.63	5, 7
Cosmogenic and primordial																
Be-7	<MDC	<MDC	3.9	3, 10	<MDC	<MDC	<MDC	0, 11	<MDC	<MDC	<MDC	0, 6	<MDC	<MDC	<MDC	0, 7
K-40	<MDC	<MDC	11	4, 10	<MDC	22	46	10, 11	5.4	8.3	19	6, 6	2.4	16	23	7, 7

[a] Min., minimum; Med., median; Max., maximum; MDC, minimum detectable concentration. Medians include values <MDC but are not determined (nd) where frequency of detection is 50% to 80%, where results would not be statistically meaningful. Analyses showing spectral interference or resulting in tentative identifications were not included in this summary table. Some radionuclides are determined indirectly *via* listed decay products.

to assess anomalies. There were positive europium (Eu) anomalies present for most of the drilling waste samples (Fig. SI-3). The positive Eu anomalies in the drilling wastes may be plausible if the Eu^{2+} ion was the dominant reducing species in subsurface conditions. However, the Eu anomaly also may be an analytical artifact during ICP-MS analysis as the barium oxide (BaO) dimer can interfere with Eu analysis. This is likely the case due to the high concentrations of Ba in drilling waste in our study and the positive correlation between Eu and Ba (Fig. SI-4). The light REEs, La and Ce, from one biosolid sample in Colorado (Biosolid-CO-1) exhibited positive anomalies, but they were consistent with NASC-normalized REE values in other biosolid samples from municipal WWTPs in Colorado.[173] Apart from these localized exceptions, the REE concentrations in samples of biosolid, livestock, and drilling waste normalized to the NASC did not result in any clear and straightforward anomalies (Fig. SI-3).

3.1.9 Gamma emitting radionuclides.

Uranium–thorium (U–Th) series radionuclides associated with naturally occurring radioactive material (NORM) were less than the minimum detectable concentration (MDC) in livestock waste (Table 1). This includes uranium-238 (U-238) series radionuclides, such as thorium-234 and radium-226 (Ra-226), and thorium-232 (Th-232) series radionuclides, such as radium-228. In contrast, these U–Th series radioisotopes had low measurable radioactivity near the MDC in biosolids and drilling waste (Table 1), likely because of the entrainment of geologic material in these sample types. Thorium-232 series radionuclides were relatively greater in water-based drilling waste, whereas U-238 series radionuclides were relatively greater in oil-based drilling waste. Synthesized radionuclides are associated with medical use, such as iodine-131 and sodium-22, and industrial use including OG industry applications, such as scandium-46 in fluid tracking of drilling fluids, metastable silver-110 in hydraulic-fracturing sand tracing, and antimony-124 used as a tracer in pipelines.[174,175] However, these synthesized radionuclides were not detected in any samples for our study. This result indicates minimal radionuclide influence of medical, commercial, and OG industry-use additions to biosolid, livestock, and drilling wastes.

Potassium-40 (K-40), a naturally occurring radioisotope of potassium (K), was observed in all sample types and was relatively low in biosolids and relatively high in livestock waste (Table SI-15). This distribution of K-40 activity is directly related to K concentration in the samples. Given the low activity of U–Th series radionuclides in livestock waste samples, K-40 represents the primary source of gamma radiation in these samples. In drilling waste, U–Th series radionuclide gamma activity is the same order of magnitude as that from K-40, whereas in biosolids U–Th series radionuclides seem to be the predominant source of gamma radiation.

Cosmogenic beryllium-7 (Be-7) was observed in 3 of 10 biosolids samples, and its presence indicates that some part of the material was recently exposed to Be-7, likely from atmospheric deposition. The presence of Be-7 was not observed in any other sample types. In the Interagency Steering Committee on Radiation Standards (ISCORS) Study of Wastewater

Treatment Plant TENORM,[176] greater Be-7 activity was associated with surface water being the primary source of drinking water.[177] Our study further suggests that some contribution of atmospherically derived contaminants may be expected in some biosolids due to exposure to atmospheric conditions.

Across U.S. states, the existing or proposed limits for radium waste acceptance for land application range widely from about 3 to 50 pCi g^{-1} for solid waste, and up to 200 pCi g^{-1} for water treatment residues.[178] There were three samples (Biosolid-FL-10, Oil-DF-OK-1, and Oil-DF-OK-2) in this study that exceeded 5 pCi g^{-1} in Ra-226 (a typical acceptance value for OG industry waste).[178] Overall, our results for biosolids appear generally consistent with previous research that documented relatively low radionuclide concentrations in biosolids and that the associated radiation exposure to workers and the general public is low, however previous research has documented potential concern for indoor radon buildup in areas with history of long term (50–100 years) application of biosolids.[176,179]

3.2 Microbial cultivation and sequencing

Microbial communities were assessed in all three waste materials using cultivation and community sequencing approaches. Compared to drilling wastes, biosolid and livestock wastes had greater culturable heterotrophic bacteria, halophilic bacteria, *Escherichia coli* (*E. coli*), enterococci, and staphylococci concentrations (Fig. 12 and Table S-16). Drilling waste samples had no *E. coli* growth; however, three drilling waste samples had enterococci growth that ranged from 10 to 1.4×10^3 colony forming units per gram (CFU g^{-1}) by wet weight. All but one biosolid sample and all but one livestock waste sample had viable *E. coli* and enterococci growth. The Class AA biosolid sample (Biosolid-FL-10) was the only biosolid sample that did not produce *E. coli* or enterococci growth; however, viable bacteria growth, including staphylococci, were detected.

General bacteria load, heterotrophic bacteria count, halophilic bacteria, *E. coli*, enterococci, and staphylococci concentrations were significantly different ($p < 0.05$) between biosolids, livestock wastes, and drilling wastes (Fig. 12). Enumerated bacteria concentrations were similar between biosolid and livestock wastes. Biosolids and drilling wastes had significantly different ($p < 0.05$) general bacteria, *E. coli*, and enterococci concentrations.

Nine (90%) of the biosolid and nine (82%) of the livestock waste samples analyzed produced extended spectrum β-lactamase (ESBL)-producing Enterobacteriaceae (including *E. coli*) growth indicating resistance to extended-spectrum cephalosporins. Carbapenemase-producing Enterobacteriaceae growth (including *E. coli*) were detected from eight (80%) of the biosolids and eight (73%) of the livestock waste samples analyzed. Since the drilling wastes did not produce *E. coli* growth, these samples could not be screened for ESBL- or carbapenemase-producing Enterobacteriaceae growth.

Microbial community characterization using a Bacteria 16S rRNA gene sequencing-based approach revealed similar patterns between biosolids and livestock wastes. The number of observed species was lowest for drilling waste (78–238 operational taxonomic units [OTUs]) compared to 706–1167 OTUs for biosolids and 385–1104 OTUs for livestock waste (Fig. 12 and Table SI-17). The number of observed OTUs was not significantly different between biosolids and livestock wastes but was significantly different ($p < 0.05$) between drilling wastes and biosolids and biosolids and between drilling wastes and livestock wastes (Fig. 12). Significant differences ($p < 0.05$) in alpha diversity measures (*e.g.*, Shannon Diversity Index, non-parametric Shannon Diversity Index, and inverse Simpson's Index) were observed between drilling wastes and biosolids and between drilling wastes and livestock wastes; no significant differences were observed between biosolids and livestock wastes. Drilling waste samples had the lowest average diversity measures for all indices analyzed, while the biosolid samples and livestock waste samples had greater, and similar, average diversity measures (Table SI-17).

3.3 Comparison of national chemical loadings to agricultural fields from land application

The estimated national (U.S.) land-applied livestock waste load (1240 B kg) was two orders of magnitude greater than biosolid waste (12.1 B kg) and drilling waste (14.1 B kg) loads (SI). These national waste load estimates were used with median concentrations of total organic-chemical classes and other selected target chemicals from our study to calculate annual chemical loadings to agricultural fields from biosolid, livestock, and drilling wastes. Across all three waste types, median of total concentrations for household chemicals, nonprescription and prescription pharmaceuticals, pesticides, PFAS, Ca, and P were greatest in biosolids, whereas median of total concentrations of biogenic hormones, mycotoxins, plant estrogens, TIN, and K were greatest in livestock wastes (Table SI-18). Median of total concentrations for industrial BTEX compounds, PAHs, Ba, and Sr were greatest in drilling waste. Due to greater overall waste loads and concentrations of biogenic hormones, mycotoxins, plant estrogens, N, and K in livestock waste, chemical loadings were greatest from livestock waste. Even with a two orders of magnitude greater waste load of livestock waste compared to biosolids and drilling waste loads, chemical loadings for PFAS (~485 kg per year), herbicides (~12 840 kg per year), prescription antidepressants (~11 040 kg per year), and prescription pain relievers (~50.0 kg per year) were greatest from biosolids, whereas chemical loadings for the industrial BTEX compounds (~395 400 kg per year), PAHs (208 700 kg per year), and Ba (353 M kg per year) were greatest from drilling waste (Table SI-18). The large contributions of PAHs, BTEX compounds, and Ba from drilling waste are explained by the presence of these compounds both in drilling fluid additives such as diesel fuel (lubrication and base fluid)[180] and barite (for density control)[181] and in the petroleum reserves targeted. The fate of PAHs, BTEX, and Ba in spent drilling waste after land application and the potential for environmental health effects are not well studied. However, the high concentrations of PAHs and BTEX compounds documented in our study, as well as their designation as probable human carcinogens or classification as priority-pollutants for human exposure and toxicity, can be an environmental concern.

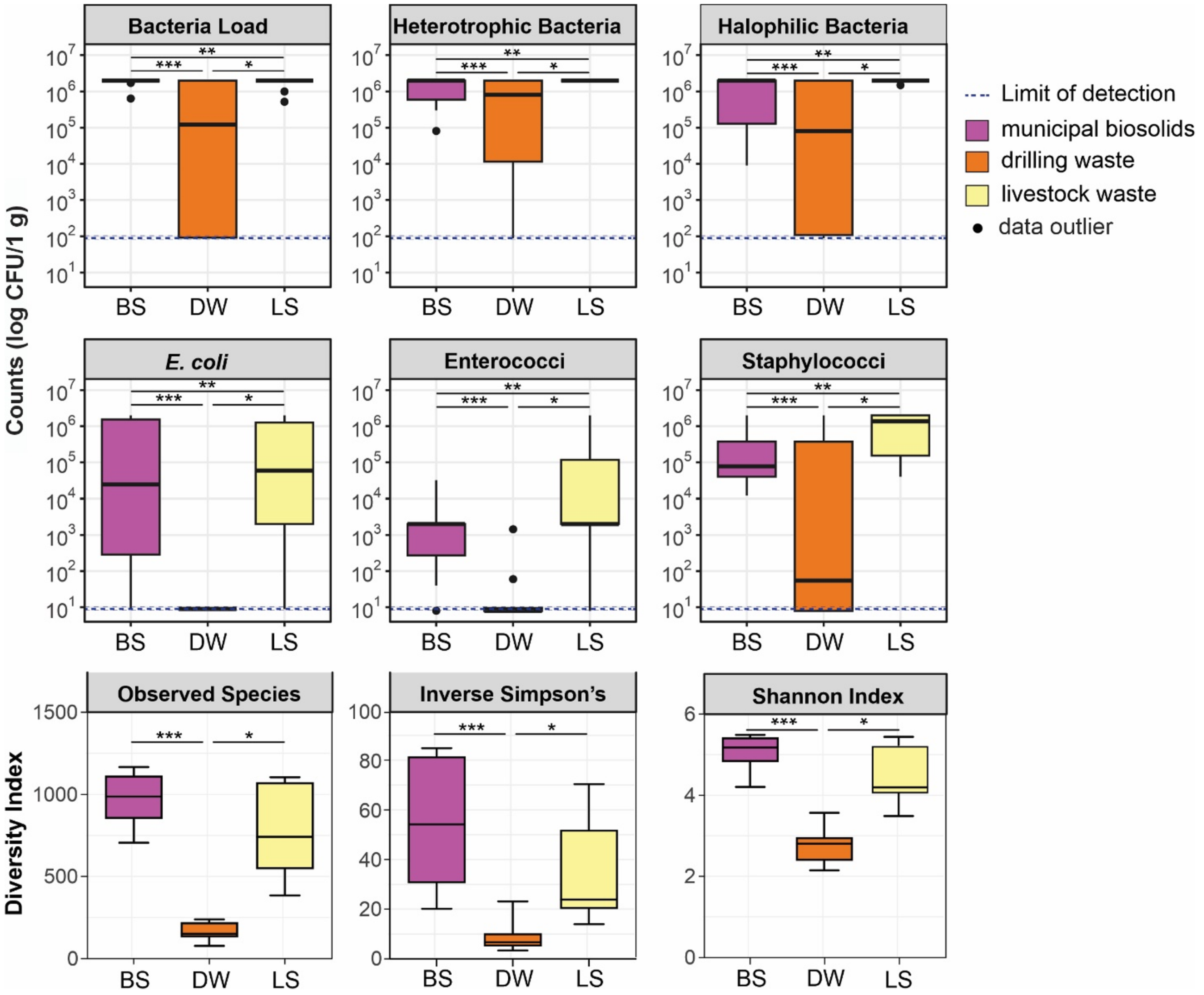

Fig. 12 Microbial community of biosolid (BS), livestock (LS), and drilling wastes (DW) determined *via* cultivation on selective media and Bacteria 16S rRNA gene sequencing. Upper and middle plots show bacterial load, heterotrophic bacteria counts (HPC) and halophilic bacteria, *Escherichia coli* (*E. coli*), enterococci, and staphylococci concentrations. Lower plots illustrate the calculated alpha diversity metrics of Observed Species, inverse Simpson's Index, and Shannon Diversity Index. Significant differences (p < 0.05) are indicated by asterisks.

The median total PFAS concentration of 40 ng g^{-1} and resulting national 485 kg per year loading estimate to agricultural lands calculated in our current study was substantially less than observed in a previous 2001 study that documented national land-applied biosolid PFAS loadings of 1375–2070 kg per year.[112] The lower PFAS loadings in biosolids compared to the previously published study could be attributed to policies and regulations that were implemented in the early 2000s to reduce PFAS use in manufacturing processes globally.[113] However, the PFAS load of ~485 kg per year in our study was comparable to the national PFAS load of ~600 kg per year from U.S. landfills that discharge untreated leachate to WWTPs.[182] Landfills are known as the final repository for heterogeneous mixtures of municipal solid and liquid waste composed of discarded materials from residential, commercial, and industrial sources known to contain substantial concentrations of PFAS.[182,183] Our study indicates that the total PFAS load from treated biosolids land-applied to U.S. farmland was comparable to PFAS loads from untreated leachate from U.S. landfills discharged to WWTPs.

3.4 Conclusions and environmental implications from land application

While the land application of biosolid, livestock, and drilling wastes to agricultural lands is commonplace, limited research has been conducted that resulted in a comprehensive understanding of the potential contaminant exposure profiles and effects on environmental, wildlife, and human health. Our study provides important insights into the chemical compositions and concentrations of land-applied wastes that can be used by stakeholders and resource managers to help develop best-management practices to maximize beneficial reuse/disposal and minimize risks to the environment and human health. Our results document that current reuse/disposal practices for biosolids, livestock wastes, and drilling wastes provide a potential pathway for the redistribution of unique and complex contaminant mixtures into the environment that have bioactive, endocrine disrupting, or carcinogenic characteristics. The number of target-organic chemicals detected per site (median of 84) in biosolids was over three times greater than those in livestock wastes (median 27), and over nine times greater than those in drilling wastes (median 9). Although there were substantially fewer target-organic chemicals in drilling waste, the median total target-organic concentration, comprised predominantly of BTEX and PAHs, in drilling waste was over 2 times greater when compared to the median total target-organic concentration in biosolids and 4 times greater when compared to livestock waste (Fig. 3B). Whereas exposure to BTEX compounds and PAHs are known to pose adverse and carcinogenic health risks,[132] their fate in spent drilling waste after land application and the potential for environmental health effects are not well studied. Biosolids provided the greatest source of PFAS and designed-bioactive chemicals (P-Pharms and pesticides), whereas livestock waste provided the greatest sources of endocrine-disrupting chemicals (mycotoxins, biogenic hormones, and plant estrogens). Previous research on plant-response effects from exposure to P-Pharms such as carbamazepine[102] and metformin[99] in soils has documented significant ($p < 0.05$) decreases in plant biomass. Negative physiological responses also have been documented in plants from exposure to a mixture of 17 pharmaceuticals in soils.[184]

The estimated PFAS load to U.S. agricultural fields (~485 kg per year) from land application of treated biosolids was comparable to the PFAS load from untreated leachate discharged from U.S. landfills to WWTPs (~600 kg per year).[182] The parts per billion (ppb) to low parts per million (ppm) individual concentrations of numerous bioactive PFAS, P-Pharms, and pesticides are of potential environmental concern as many of these chemicals are resistant to biotic transformation, exhibit bioaccumulation potential, and are known to cause negative biological effects and disruption to key cellular functions in animals, humans, and microorganisms at these environmental concentrations.[31–34,185] The land application of biosolids and livestock wastes to agricultural fields provides a potential route for the distribution of numerous pesticides, antibiotics, ARB, and ARG. Our study documented that biosolids and livestock wastes contained fluoroquinolone and tetracycline antibiotics at concentrations that can pose environmental and human health concerns[40,49,50] for the proliferation of ARB and ARG,[43,44] and other adverse effects to aquatic[45,46] and terrestrial ecosystems.[47] Biosolids and livestock waste contained high bacteria loads, including viable bacteria cells associated with pathogenic and ARB characteristics. Land application of these waste types has the potential to result in exposures of bacterial pathogens, ARB, and ARG to humans, wildlife, and plants on or near waste applied sites.[186–190] The growing and production of food crops requires healthy soils with adequate nutrients and diverse soil biota to perform soil functions. The large number of pesticides, antibiotics, and other bioactive contaminants in biosolids and livestock waste could have implications for exposures to soil biota and resulting synergistic effects that could reduce overall soil health and function processes.[185] The large number of individual hydrophobic pesticides present in biosolids increases the potential for these contaminants to be retained in soils that receive biosolids and raises concern for exposures to soil biota. The results of this study can be helpful to land and water resource managers when assessing the potential for the leaching and mobilization of these chemicals following such reuse/disposal practices and can be used to inform on the development of best-management practices to maximize beneficial reuse while minimizing risks to the environment and human health. Additional research may further clarify whether current land-applied reuse/disposal management practices might result in contaminant exposures at concentrations that could result in deleterious effects to ecosystem and human health.

Conflicts of interest

The authors acknowledge that there are no conflicts of interest to declare.

Data availability

All data are available for review in the supplementary information (SI) and upon journal publication will be accessible as a publicly available data release in a machine-readable format at USGS Science Base **https://doi.org/10.5066/P1G9CSQS** and **https://doi.org/10.5066/P1P74TUA**. Supplementary information: Method details, sampling information, and additional sample results. See DOI: **https://doi.org/10.1039/d5em00312a**.

Acknowledgements

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