ZIONTZ CHESTNUT
ATTORNEYS AT LAW

RICHARD M. BERLEY
MARC D. SLONIM
BRIAN W. CHESTNUT
BRIAN C. GRUBER
BETH A. BALDWIN
WYATT F. GOLDING
ANNA E. BRADY

FOURTH AND BLANCHARD BUILDING
2101 FOURTH AVENUE, SUITE 1230
SEATTLE, WASHINGTON 98121-2331
TELEPHONE: (206) 448-1230
FAX: (206) 448-0962
WWW.ZIONTZCHESTNUT.COM

July 12, 2021

Submitted via the Online Public Comment Form

Washington State Department of Ecology
Solid Waste Program
P.O. Box 47600
Olympia, WA 98504-7600

Re: Comments on the New Draft Statewide General Permit for Biosolids Management and Associated SEPA Checklist

Ms. Kijowski,

Thank you for accepting and reviewing comments on the draft general permit for biosolids and septage application. These comments and materials are submitted on behalf of Ed Kenney, a Washington resident with deep concern for water quality, human health, and fisheries in the State.

Please consider these comments to apply both to the draft permit and the associated State Environmental Policy Act (SEPA) checklist and proposed determination of non-significance (DNS). In general, the proposed permit and DNS are inadequate in that they focus solely on regulated metals, nitrogen, and bacteria, without accounting for modern pollutants with significant human health risks: microplastics, PBDEs, PFAS, pharmaceuticals, and other contaminants of emerging concern. This deficiency means that Ecology cannot meaningfully assess environmental impacts of issuance of the general permit for application of biosolids, and that the protections for surface waters and groundwater are insufficiently protective.[1]

In a June 24, 2021 public meeting, Ecology stated that 86,000 tons of biosolids were land applied in Washington in 2019. Even under a conservative and unrealistic assumption that the use of biosolids will remain unchanged, that amounts to a total of 430,000 tons (860 million pounds) over the five-year life of the general permit. This staggering quantity mandates caution in regulating biosolids.

At the same meeting, Ecology asserted that it lacks means to regulate pollutants other than the nine metals identified by the United States Environmental Protection Agency (EPA) in 40 CFR § 503.13, and nitrogen. As explained herein, this position is both inaccurate and fails to meet Ecology's statutory duties to protect waters of the State. Given inadequate information and

---

[1] The term "biosolids" in this letter refers to both biosolids and septage unless specified. *See* RCW 70A.226.010(1).

reasonable risk of harm to the environment and human health, Ecology must take a precautionary approach, make a determination of significance, and prepare an environmental significance. While Mr. Kenney acknowledges that Ecology faces legislative direction to make beneficial use of biosolids in a manner that minimizes risk to public health and the environment, preparation of an environmental impact statement will allow the agency the time and information needed to balance these dual mandates. Careful consideration of alternatives is essential before approving such an extensive, impactful, and risky program.

A. Biosolids Statutory and Regulatory Criteria

The Department of Ecology is affirmatively responsible for ensuring that permitted activities, including land application of biosolids, protects waters of the State. RCW 90.48.010 states in part that:

> It is declared to be the public policy of the state of Washington to maintain the highest possible standards to insure the purity of all waters of the state consistent with public health and public enjoyment thereof, the propagation and protection of wild life, birds, game, fish and other aquatic life, and the industrial development of the state, and to that end require the use of all known available and reasonable methods by industries and others to prevent and control the pollution of the waters of the state of Washington. Consistent with this policy, the state of Washington will exercise its powers, as fully and as effectively as possible, to retain and secure high quality for all waters of the state.

As part of effectuating that policy, RCW 90.48.080 mandates that:

> It shall be unlawful for any person to throw, drain, run, or otherwise discharge into any of the waters of this state, or to cause, permit or suffer to be thrown, run, drained, allowed to seep or otherwise discharged into such waters any organic or inorganic matter that shall cause or tend to cause pollution of such waters according to the determination of the department, as provided for in this chapter.

This provision is broad in scope, covering any mechanism by which “any organic or inorganic matter” pollutes groundwater or surface waters. These broad provisions are reinforced by the State Environmental Policy Act, RCW 43.21C.020, which recognizes that “each person has a fundamental and inalienable right to a healthful environment,” and commands that it is the “continuing responsibility of the state of Washington and all agencies of the state to use all practicable means” to protect a safe, healthful, and productive environment. SEPA further requires that “[t]he policies, regulations, and laws of the state of Washington shall be interpreted and administered in accordance with the policies set forth” in SEPA. RCW 43.21C.030.

With respect to biosolids specifically, RCW 70A.226.005(2) states:

> The legislature declares that a program shall be established to manage municipal sewage sludge and that the program shall, to the maximum extent possible, ensure

> that municipal sewage sludge is reused as a beneficial commodity and is managed in a manner that minimizes risk to public health and the environment.

This provision presents dual mandates that apply "to the maximum extent possible." While biosolids must be reused, Ecology may only authorize such reuse in a manner that minimizes environmental and health risk. If Ecology cannot ensure that environmental and health risks are minimized, the agency may not permit biosolids application.

Ecology implements RCW Chapter 70A.226 through the rules promulgated at WAC Chapter 173-308. The regulations detail testing requirements and concentration thresholds for certain pollutants, WAC 173-308-160, require pathogen and vector reduction, WAC 173-308-170 to -180, require screening of manufactured inerts, WAC 173-308-205, and set agronomic rate of application, WAC 173-308-190, among other requirements. Notably, WAC 173-308-190(6) provides that "[w]hen the potential for groundwater contamination due to biosolids application exists, the department may require groundwater monitoring or other conditions in accordance with the provisions of chapter 173-200 WAC. If it is determined that an enforcement criterion may be violated, an evaluation must be conducted to demonstrate compliance with the provisions of chapter 173-200 WAC." Finally, WAC 173-308-191 mandates that "[b]iosolids may not be applied to the land if they are likely to adversely affect a threatened or endangered species or its critical habitat."

While the biosolids regulations focus on specific pollutants, this does not mean that those are the only pollutants that are subject to regulation or that may cause contamination. WAC 173-380-030 confirms that "[b]iosolids facilities and sites where biosolids are applied to the land must comply with the requirements of chapter 90.48 RCW and chapters 173-200 and 173-201A WAC," which are the Water Pollution Control statute and regulations protecting groundwater and surface water. The regulations contain anti-degradation provisions which prohibiting contamination of waters of the State. WAC 173-200-030; WAC 173-201A-300. WAC 173-201A-240 prohibits introduction of toxic substances to surface waters beyond background levels.

The State law requirements are in addition to those imposed by the Federal Clean Water Act and implementing regulations. 40 CFR § 503.5 ("[n]othing in this part precludes a State or political subdivision thereof or interstate agency from imposing requirements for the use or disposal of sewage sludge more stringent than the requirements in this part or from imposing additional requirements for the use or disposal of sewage sludge."). Where there is land application within the confines of a wastewater treatment facility, a NPDES permit is required. 40 CFR § 122.26(b)(14)(ix).

B. SEPA Procedural Requirements

SEPA requires that Ecology prepare an environmental impact statement (EIS) for major actions having a probable significant, adverse environmental impact. RCW 43.21C.031. In order to determine whether an EIS is required, Ecology must prepare a threshold determination based on a rigorous review of direct, indirect, and cumulative effects of the proposal. WAC 197-11-330. Impacts likely to be significant include impacts "to environmentally sensitive or special areas, such as loss or destruction of historic, scientific, and cultural resources, parks, prime farmlands, wetlands, wild and scenic rivers, or wilderness," impacts that "[a]dversely affect endangered or threatened species or their habitat," actions that "[c]onflict with local, state, or federal laws or requirements for the protection of the environment" and those impacts that "involve unique and unknown risks to the environment, or may affect public health or safety." WAC 197-11-330(3)(e).

Ecology must make the threshold determination "based upon information reasonably sufficient to evaluate the environmental impact of a proposal," and may require the applicant to submit more information or conduct independent further analysis if such reasonably sufficient information is not provided by the project proponent. WAC 197-11-335. The reasonably sufficient information requirement is ongoing. The lead agency "shall withdraw" the determination of nonsignificance if "[t]here is significant new information indicating, or on, a proposal's probable significant adverse environmental impacts" or "[t]he DNS was procured by misrepresentation or lack of material disclosure." WAC 197-11-340(3).

While SEPA review may reference thresholds and requirements set forth in other statutes and regulations, SEPA compliance is an independent legal duty, and SEPA supplements existing authority. *Polygon Corp. v. Seattle*, 90 Wash. 2d 59, 65, 578 P.2d 1309, 1313 (1978); *Columbia Riverkeeper v. Port of Vancouver USA*, 188 Wash. 2d 80, 95, 392 P.3d 1025, 1032 (2017).

C. The General Permit Fails to Protect Against Dangerous Chemicals

The fundamental failing of the general permit is that, even though Ecology knows and recognizes that biosolids contain dangerous contaminants of emerging concern and microplastics, Ecology requires no testing or control for these substances whatsoever. This is a very significant concern given the capacity of these substances to penetrate to groundwater and enter drinking water and surface waters. There is also concern that biosolids directly applied or in compost will expose farmworkers. Lack of adequate regulation of contaminants is a systemic concern which poses cumulative effects. The issues referenced in this letter should be dealt with at the programmatic general permit level and not deferred until site specific review.

Because the areas that produce the most biosolids tend to be the most populated and affluent urban areas in Washington, and the areas that receive biosolids tend to be less affluent, rural areas, the general permit raises serious environmental justice issues that Ecology has not evaluated.

1. *Public health and environmental risk*

The proposed general permit poses grave risk of contaminating both surface and groundwaters. Because biosolids derive from our collective waste stream, they contain concentrations of untreated chemicals from household and business use—everything we eat, drink, use for cleaning, and launder. This means that biosolids inherently contains myriad harmful substances, including: dozens of different chemicals derived from detergents, fragrances, and pharmaceuticals, that are collectively referred to as "contaminants of emerging concern," including PFAS;[2] polybrominated diphenyl ethers (PBDEs) and other dioxins;[3] phthalates; and biological contaminants such as norovirus and the novel coronavirus.[4] Many of these substances can cause significant short and long-term ecological and human health impacts at relatively low concentrations, raising significant public health and environmental risks.

Contaminants of emerging concern and dioxins found in biosolids evade treatment in municipal wastewater treatment plants. As such, they tend not to break down in soil, and can be transported by and to water. According to at least one peer-reviewed study of runoff following biosolids application, contaminants in biosolids are transported by runoff and can enter surface waters in dangerous concentrations.[5] Another peer-reviewed study states that "[r]ecent studies have demonstrated that the application of PFC contaminated biosolids can have important effects on local environments, ultimately leading to demonstrable human exposures," notes that "relatively high transport from soils to surface and well water is possible," and describes a case study in Alabama.[6]

Contamination would contribute to an already dangerous level of pollution in many areas. For example, the Nisqually River, Nisqually Reach, and McCallister Creek exceed water quality standards for fecal coliform, and water and sediments contain contaminants of emerging concern. According to a recent Seattle Times article summarizing an EPA study,

> The Nisqually estuary was more contaminated than expected with drugs, including cocaine, Cipro and Zantac. The source of the drugs there was unknown, the researchers reported. However, the Nisqually River, Nisqually Reach and McAllister Creek do not meet water-quality standards for fecal coliform. That makes leaking septic systems a possible source of the drugs.[7]

---

[2] These chemicals include perfluorinated chemicals (PFOS, PFOA); polychlorinated alkanes (PCAs), polychlorinated naphthalenes (PCNs); organotins (OTs), polybrominated diphenyl ethers (PBDEs), triclosan (TCS), triclocarban (TCC); benzothiazoles; antibiotics and pharmaceuticals; synthetic musks; bisphenol A, quaternary ammonium compounds (QACs), steroids; phthalate acid esters (PAEs) and polydimethylsiloxanes (PDMSs). *See* Bradley O. Clarke, Stephen R. Smith, Review of 'emerging' organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids, Environment International, Volume 37, Issue 1, 2011, Pages 226-247, ISSN 0160-4120, https://doi.org/10.1016/j.envint.2010.06.004; *see also* Kinney et al., 2006, Survey of organic wastewater contaminants in biosolids destined for land application. Environmental Science and Technology, Vol. 40, No. 23, pp. 7207-7215.

[3] Kim et al., 2017, Review of contamination of sewage sludge and amended soils by polybrominated diphenyl ethers based on meta-analysis. Environmental Pollution, Vol. 220 Part B, pp. 763-765 (finding consistent presence of PBDEs in biosolids in varying concentrations across 288 samples).

[4] Viau et al., 2011, Toward a Consensus View on the Infectious Risks Associated with Land Application of Sewage Sludge. Environmental Science and Technology, Vol. 45, Issue 13, pp. 5459–5469.

[5] Yang et al., 2012, Steroid hormone runoff from agricultural test plots applied with municipal biosolids. Environmental Science and Technology, Vol. 46, No. 5, pp. 2746-2754, doi:10.1021/es203896t.

[6] Lindstrom AB, Strynar MJ, Delinsky AD, Nakayama SF, McMillan L, Libelo EL, Neill M, Thomas L. Application of WWTP biosolids and resulting perfluorinated compound contamination of surface and well water in Decatur, Alabama, USA. Environ Sci Technol. 2011 Oct 1;45(19):8015-21. doi: 10.1021/es1039425. Epub 2011 Apr 22. PMID: 21513287.

[7] Seattle Times, Drugs found in Puget Sound salmon from tainted wastewater (Feb. 23, 2016). Available at: https://www.seattletimes.com/seattle-news/environment/drugs-flooding-into-puget-sound-and-its-salmon/

If these chemicals are present in leaking septic effluent they are certainly also present in septage and biosolids. When present in water and sediments, the chemicals make their way into salmon and cause adverse health effects and death.[8]

Similarly, testing of sediment in outfall areas near the King County Elliott West CSO treatment plant has exceeded screening levels, including total PCBs, benzo(a)anthracene, benzo(a)pyrene, benzo(g,h,i)perylene, benzyl butyl phthalate, bis(2-ethylhexyl) phthalate, chrysene, dibenzo(a,h)anthracene, fluroanthene, indeno(1,2,3-c,d)pyrene, and mercury.[9] Like leaking septic, overflow sewage likely presents many of the same threats as biosolids.

One contaminant of particular concern is PFAS. According to the Department of Health, Per- and polyfluoroalkyl substances (PFAS) are a family of chemicals used since the 1950s to manufacture stain-resistant, water-resistant, and non-stick products. PFAS are widely used as coatings in common consumer products such as food packaging, outdoor clothing, carpets, leather goods, ski and snowboard waxes, and more. Ecology has recognized the risks posed by these chemicals, and has prioritized regulating them through a chemical action plan (CAP).

Federal and State agencies increasingly recognize PFAS as widespread and a serious health risk. On February 22, 2021, the United Stated Environmental Protection Agency (EPA) made final determinations to regulate PFOS and PFOA in drinking water. On April 27, 2021, Administrator Regan called for the creation of a new “EPA Council on PFAS” that is charged with building on the agency’s ongoing work to better understand and ultimately reduce the potential risks caused by these chemicals. EPA has recognized that PFAS pose serious health risks that can no longer simply be ignored.

Likewise, the State has acknowledged that PFAS are chemicals of serious public health concern that is likely present in biosolids and wastewater, highly mobile in water and soil, do not degrade, bioaccumulate in humans and other animals, and cause likely human health effects.

Ecology’s website provides a fact sheet for PFAS, reading in part that:

> **PFAS have become a serious public health concern across our country and state. Over time, some PFAS released from manufacturing sites, landfills, firefighting foam, and other products seep into surface soils. From there, PFAS leaches into groundwater and can contaminate drinking water.** PFAS have also been found in rivers, lakes, fish, and wildlife.
> …
> PFAS do not break down easily and stay in the environment for a long time. As a result, PFAS are widely detected in air, soil, water, and food. Exposure can occur when someone uses certain products that contain PFAS, eats PFAS-contaminated food, or drinks PFAS-contaminated water. When ingested, some PFAS can build

---

[8] Seattle Times, Puget Sound salmon do drugs, which may hurt their survival (April 16, 2018). Available at: https://www.seattletimes.com/seattle-news/puget-sound-salmon-do-drugs-which-may-hurt-their-survival/

[9] Fact Sheet for NPDES Permit WA0029181 West Point Wastewater Treatment Plant (WWTP) and Combined Sewer Overflow (CSO) System December 19, 2014.

> up in the body and, over time, these PFAS may increase to a level where health effects could occur.
>
> Studies in animals show that exposure to some PFAS can affect liver function, reproductive hormones, development of offspring, and mortality.
>
> Although nearly all of us are exposed to PFAS, their toxicity in humans is not completely understood. Experts investigating the effects on people have found probable links to immune system toxicity, high cholesterol, reproductive and developmental issues, endocrine system disruption, ulcerative colitis, thyroid issues, certain cancers, and pregnancy-induced hypertension. [10]

Media accounts and increasing science support these conclusions.[11] The Ecology fact sheet for PFAS similarly acknowledges that Ecology is "concerned" because

> Certain PFAS are highly mobile in the environment, meaning they can contaminate groundwater. Some PFAS transform into highly persistent perfluorinated chemicals—no natural processes can break these substances down. Once in the environment, PFAS can contaminate water and bioaccumulate in wildlife. The drinking water supplies in several parts of Washington are contaminated with PFAS above Environmental Protection Agency's health advisory level. They are costly to filter out.

Accordingly, the draft chemical action plan recognizes biosolids as potential sources of PFAS contamination to waters of the State, and calls for Ecology to, *inter alia*, "[e]stablish biosolids and soil sample collection and handling methods for PFAS analysis," "[a]ccredit Washington labs for EPA-validated analysis methods," "[i]nvestigate land application sites where procedures mimic rates and practices under current state rule (Chapter 173-308 WAC15)," "[e]valuate realistic exposure pathways," and "[e]valuate risk modeling using realistic input values."

For wastewater, the draft CAP recommends that "Ecology should evaluate PFAS in WWTP influent and effluent to better understand PFAS discharges in Washington state," "Ecology should develop a study design to sample PFAS in three different types of plants," "Ecology should consider additional monitoring requirements for WWTP dischargers…Based on this evaluation Ecology should require possible PFAS monitoring for some or all domestic and industrial WWTPs."

According to the draft CAP, the Legislature provided Ecology "$235,000 to conduct a WWTP sampling study by June 30, 2021. This includes costs for sample analysis, which can range from $1,000 to $1,500 per sample as well as project staff salaries."

---

[10] https://ecology.wa.gov/Waste-Toxics/Reducing-toxic-chemicals/Addressing-priority-toxic-chemicals/PFAS

[11] *See, e.g.*, https://www.nytimes.com/2020/09/23/parenting/pregnancy/pfas-toxins-chemicals.html?searchResultPosition=1 "These Everyday Toxins May Be Hurting Pregnant Women and Their Babies"

Despite a long record of Ecology recognizing the risks of PFAS, including those risks specific to wastewater treatment and biosolids land application, the draft general permit has no protections in place for PFAS which Ecology recognizes as a priority-toxic chemical. The same is true for pharmaceuticals and other contaminants of emerging concern. Lastly, pathogens deemed dead may actually be dormant. When applied to land in sewage wastes, dormant pathogens can regenerate when spread on the soil, especially wet soil.

There is also no meaningful discussion of contaminants beyond those specified in regulation in the draft general permit or associated documents, no disclosure of risk, and no indication that Ecology has seriously considered how to address PFAS, PBDE, and other contaminants.

2. *Proposed changes to the general permit and SEPA review*

Mr. Kenney acknowledges that Ecology has incomplete information and cannot fully know the contents of all biosolids. However, these challenges are not a valid reason to ignore the presence of harmful contaminants. Ecology has a duty to the public to protect waters of the State, and a duty under SEPA to obtain and consider all reasonable available information: "If information on significant adverse impacts essential to a reasoned choice among alternatives is not known, and the costs of obtaining it are not exorbitant, agencies shall obtain and include the information in their environmental documents." WAC 197-11-080(1).

Ecology's SEPA obligation requires the agency to consider environmental impacts of all contaminants likely present in biosolids, even if they are not specified under biosolids regulations. *Columbia Riverkeeper*, 188 Wash. 2d at 95.

Accordingly, Mr. Kenney requests that Ecology make the following changes to the general permit documentation and SEPA review to better protect the environment and public health:

- Coordinate internally with Ecology staff working on the PFAS CAP, and coordinate and consult with the Washington Department of Health, the Washington Department of Fish and Wildlife, and Washington tribal governments.

- Given the risk to groundwater and surface waters and limited testing conducted of biosolids available for a variety of contaminants, ban biosolids application on hydric soils and periodically inundated areas, impose greater buffers from surface waters, and require more distance to groundwater for all biosolids application.

- In the SEPA analysis, identify information gaps and obtain information to fill those gaps to the maximum extent feasible. To the extent information truly cannot be obtained, "indicate in the appropriate environmental documents its worst case analysis and the likelihood of occurrence." WAC 197-11-080(3)(b).

- Disclose and discuss the progress on the WWTP sampling study referenced in the draft PFAS CAP, including the methodology and any initial results.

- Identify and discuss all other States (such as Maine) that monitor, test, and/or regulate PBDEs or PFAS and other chemicals in biosolids. Explain the implications for this information on the Washington regulatory program.

- Prior to making a threshold determination, specifically identify a list of contaminants of priority concern (including PBDEs and PFAS) and: 1) assess their likely prevalence in biosolids, 2) assess their probable human health and environmental impacts given the scale of application in Washington, 3) test biosolids from various WWTPs, 3) test groundwater and runoff at application sites.

- Require as a condition of the general permit that WWTP operators test biosolids for PFAS and other contaminants of emerging concern and report to Ecology. Ecology indicates that these tests are available for $1,000-$1,500, which is a reasonable cost to impose on the regulated entity given the risk to public health. If entities profit from land application of biosolids, it is entirely appropriate and reasonable to pass through costs of testing to those companies to gather data. Requiring testing would provide Ecology with a broad data set to effectively regulate PFAS and other chemicals.

- Evaluate and disclose the extent to which biosolids application sites risk becoming contaminated over time in a manner that requires cleanup under State or Federal law (including the Model Toxics Cleanup Act, RCW 70A.305.010, *et. seq.*, and the Resource Conservation and Recovery Act, 42 U.S.C. § 6901 *et. seq.*).

In public meetings and comments on prior applications, the public has rightfully raised concerns regarding lack of testing and monitoring for PBDEs, PFAS and other chemicals in biosolids. In general, Ecology has responded that it is not financially or technically feasible to test for PFAS because there is not a validated testing methodology, and that the more efficient method of regulating PFAS is "upstream" in consumer products.

As an initial matter, many chemicals, such as PBDEs, phthalates, illegal drugs, and pharmaceuticals, are readily tested. To fulfill its statutory mandates and duties to protect the public and environment, Ecology must sample biosolids for these contaminants. Furthermore, as noted, Ecology has received funding to complete testing for PFAS associated with wastewater. This testing effort should be incorporated into permit review. Ecology should also draw from ongoing testing and information gathering from drinking water regulation to inform environmental review of the biosolids program, in consultation with the Department of Health.[12]

Mr. Kenney notes that other states require that WWTPs use an isotope dilution method like Method 537.1, ASTMD7979-19M, or CWA Method 1600 for PFAS analysis of biosolids in the interim and until EPA completes its work. Such methods are reliable for biosolids because they use an isotope-dilution method to measure sample extraction recoveries and correct for matrix

---

[12] https://www.doh.wa.gov/CommunityandEnvironment/DrinkingWater/RegulationandCompliance/RuleMaking

suppression effects in the LCMSMS. Ecology should allow the use of these methods as do other states.

Mr. Kenney also notes that PFAS is a nationally recognized concern on and around lands used for training by the Department of Defense. In these locations, the DOD regularly tests water using EPA-approved methods for PFAS. For example, testing has been underway for PFAS on Whidbey Island associated with the Naval training area since 2016.[13] Water sampling at Joint Base Lewis McChord revealed elevated levels of PFAS in 2018, which required cessation of drinking water use to protect public safety.[14] As such it is entirely possible for Ecology to test groundwater and surface water associated with biosolids applications sites.

With respect to consumer product regulation, Mr. Kenney welcomes those efforts. However, even if implemented immediately the benefits would be limited and long-term, given the prevalence of PFAS in widespread consumer products and the global nature of commerce.

D. The General Permit Fails to Protect Against Microplastics

WAC 173-308-205(1) requires that "all biosolids…must be treated by a process such as physical screening or another method to significantly remove manufactured inerts prior to final disposition." Additionally, "biosolids (including septage) that are land applied…must contain less than one percent by volume recognizable manufactured inerts." WAC 173-308-205(4).

Biosolids generally contain large volumes of small plastics, referred to as microplastics and nanoplastics. A recent synthesis of literature focused on microplastics in biosolids, titled "An overview of microplastic and nanoplastic pollution in agroecosystems" (Ng et al. 2018),[15] states that "polyethylene, plastic fibres, and polystyrene foam occupied up to 5% w/w in compost from mixed municipal solid waste for all size fractions between 420 μm and 25 mm; with around 0.5 to 0.6% having sizes b2 mm." Prevailing agronomic rates in the United States suggest maximum potential rate of microplastic inputs from biosolid in the order of 0.5 to 3.2 t·ha−1·yr−1. This unit measurement equates to 0.2 to 1.3 metric tons per acre per year of plastics present in biosolids (one hectare equals 2.471 acres). Plastics are "manufactured inerts." Extensive study, widespread publicity dedicated to microplastic contamination in soils and waters, and the ability to eliminate microplastics if desired indicates that microplastics are "recognizable." WAC 173-308-205(4).

The general permit would authorize approximately 430,000 tons of biosolids land application over a five-year period. Even a conservative estimate under which microplastics compose 2.5% of those biosolids would mean that 10,7050 tons of microplastics will be land applied under the

---

[13] https://www.navfac.navy.mil/navfac_worldwide/pacific/fecs/northwest/about_us/northwest_documents/environmental-restoration/pfas-groundwater-and-drinking-water-investigation/nswi_pfas.html; see also https://www.navfac.navy.mil/niris/SOUTHWEST/FALLON_NAS/N60495_000011.PDF (Naval Air Station Fallon);

[14] https://home.army.mil/lewis-mcchord/application/files/2015/6106/2504/CCR_2018_Lewis_DIGI_FINAL.pdf

[15] Ng et al., 2018, An overview of microplastic and nanoplastic pollution in agroecosystems. Science of the Total Environment, Vol. 627, pp. 1377-88.

general permit. Plastics take hundreds of years to break down: "projections indicate that the lifetime of polyolefins on land is in the vicinity of hundreds of years."[16] This means that microplastics not dispersed into surface or groundwaters (with resulting harm to aquatic species), or ingested and adsorbed by grazing cattle, will bioaccumulate on site and quickly add up. The plastics are harmful in their own right, and also can transport and degrade into a variety of contaminants. The health effects of microplastics are believed to be detrimental but are still poorly understood. According to Ng et al.:

> Classical soil ecotoxicological approaches use isolated organisms and standard substrates, with measures taken for survival, growth, reproduction and avoidance behaviour over a period of days and weeks. Such approaches may not capture the full impact of chemical additives in plastics that act as endocrine disruptors in addition to those which bioaccumulate, where long-term exposure at low doses may alter cell functions or cause DNA damage. Such damage manifests later in life or across generations as the damage accumulates.[17]

The most recent studies of microplastics suggest that they are highly mobile in water. Crossman et al. (2020) measured microplastics biosolids at various application sites, found high levels of contamination, and determined that 99 percent of the microplastics appeared to be transported by water over time.[18]

In short, the proposed application would put cumulatively significant amounts of plastic onto application sites, that would likely enter surrounding waters and organisms and cause uncertain long-term impacts to the native ecosystem and human health.

Despite these risks, the general permit does not specify any means by which to comply with the requirement to remove manufactured inerts. As a result the general permit is deficient and must be conditioned to require rigorous screening for microplastics and nanoplastics.

Accordingly, Mr. Kenney requests that Ecology make the following changes to the general permit documentation and SEPA review to better protect the environment and public health:

- Identify and discuss all other jurisdictions that monitor, test, and/or regulate microplastics in biosolids. Explain the implications for this information on the Washington regulatory program.

---

[16] Ng et al., 2018, An overview of microplastic and nanoplastic pollution in agroecosystems. Science of the Total Environment, Vol. 627, p. 1380.

[17] *Id.* at 1385.

[18] Crossman, Rachel R. Hurley, Martyn Futter, Luca Nizzetto,
Transfer and transport of microplastics from biosolids to agricultural soils and the wider environment,
Science of The Total Environment, Volume 724, 2020, 138334, ISSN 0048-9697,
https://doi.org/10.1016/j.scitotenv.2020.138334
(https://www.sciencedirect.com/science/article/pii/S0048969720318477)

- Identify mechanisms to remove microplastics from biosolids, and the viability of these methods.
- In the SEPA analysis, identify information gaps and obtain information to fill those gaps to the maximum extent feasible. To the extent information truly cannot be obtained, "indicate in the appropriate environmental documents its worst-case analysis and the likelihood of occurrence." WAC 197-11-080(3)(b).
- Require as a condition of the general permit that WWTP operators remove microplastics from biosolids in accordance with WAC 173-308-205.
- Ecology should test runoff and groundwater associated with select recent biosolids application sites after rain and report the results.

As with PFAS, PBDEs, and contaminants of emerging concern, Ecology cannot fulfill its public statutory obligations by simply ignoring microplastics. Mr. Kenney requests that Ecology take reasonable, affirmative steps to address this serious issue and comply with its statutory mandate to protect waters of the state.

E. The General Permit Fails to Protect Threatened and Endangered Species

Biosolids application is not allowed where the application is likely to adversely affect a threatened or endangered species or its critical habitat as listed under Title 232 WAC or section 4 of the Endangered Species Act. WAC 173-308-191. Notably, the regulation prohibits any likely harm to threatened or endangered species or their critical habitat and does not allow for *de minimus* exceptions or mitigation measures. This is a particularly significant issue for southern resident killer whales, which are top tier predators of salmon and marine life and thus bioaccumulate toxins.

Issuance of the general permit without protections for protected species would not only potentially violate State law, it would also likely violate the Federal Endangered Species Act (ESA). The ESA prohibits the "take" of species listed as threatened or endangered on the federal endangered species list. 16 U.S.C. § 1538(a)(1)(B). The ESA defines "take" as "to harass, harm, pursue, hunt, shoot, wound, kill, trap, capture, or collect, or to attempt to engage in any such conduct." *Id.* § 1532(19). By regulation, the National Marine Fisheries Service has defined "harm" to include "significant habitat modification or degradation which actually kills or injures fish or wildlife by significantly impairing essential behavioral patterns, including, breeding, spawning, rearing, migrating, feeding or sheltering." 50 C.F.R. § 222.102; *Babbitt v. Sweet Home Chapter, Communities for Great Ore.*, 515 U.S. 687 (1995).

Under what is known as the "*Strahan* theory," a governmental entity may be liable under the ESA for authorizing harm carried out by private third parties. *See Strahan v. Coxe*, 127 F.3d 155, 158, 163 (1st Cir. 1997) (state agency caused takings of the endangered right whale because it "licensed commercial fishing operations to use gillnets and lobster pots in specifically the manner that is likely to result in violation of [the ESA]"), cert. denied, 1998 U.S. LEXIS 7103 (Nov. 2, 1998) (No. 97-1485); *Defenders of Wildlife v. Administrator, Envtl. Protection Agency*, 882 F.2d 1294, 1300-01 (8th Cir. 1989) (federal agency caused takes of the endangered black-footed ferret through its "decision to register pesticides" even though other persons actually distributed or used the pesticides); *Loggerhead Turtle v. Cty. Council of Volusia Cty.*, 148 F.3d 1231, 1251 (11th Cir. 1998) (finding plaintiffs had standing where they alleged harm from county's failure to regulate artificial beach lighting, which harmed turtles).

An agency may receive authorization from the U.S. Fish and Wildlife Service and/or National Marine Fisheries Service to issue permits that cause harm to listed species, under ESA Section 10. *See* 16 U.S.C. § 1539(a)(2)(B). For example, Washington State Department of Natural Resources has an incidental take permit for authorization of forest practices that cause likely harm to listed species. Ecology lacks such authorization for the biosolids program.

The ESA authorizes citizen suits "to enjoin any person, including the United States and any other governmental instrumentality or agency (to the extent permitted by the eleventh amendment to the Constitution), who is alleged to be in violation of any provision" of the Act. 16 U.S.C. § 1540(g)(1)(A). Agency officials acting in their official capacity are not protected by the eleventh amendment, and so state agencies are functionally subject to suit. Such suits may result in injunctive relief, civil penalties, and an award of costs and attorneys' fees.

In order to fully protect listed species and protect the State from liability, Mr. Kenney suggests that Ecology consult with the National Marine Fisheries Service and U.S. Fish and Wildlife Service to determine whether an incidental take permit and associated habitat conservation plan is required.

F. SEPA Checklist Specific Comments

The SEPA Checklist and associated threshold determination must fully disclose sufficient information to determine whether a proposal has probable significant adverse environmental impacts. WAC 197-11-335. The determination includes consideration of cumulative effects, WAC 197-11-330(3)(c), and may not weigh purported benefits of the proposal against the adverse impacts, WAC 197-11-330(5). "Significant" means "a reasonable likelihood of more than a moderate adverse impact on environmental quality."

The general permit authorizes millions of pounds of land application of biosolids over a period of five years, which, as documented above, contain unknown amounts of dangerous chemicals and microplastics. While Mr. Kenney recognizes that there would be phased SEPA review for individual projects, in order to be meaningful SEPA review must be carried out "at the earliest possible time to ensure that planning and decisions reflect environmental values, to avoid delays later in the process, and to seek to resolve potential problems." WAC 197-11-055(1). Early review is particularly necessary here, where there are significant cumulative effects of biosolids application across the State, and the identified issues are common to all biosolids. PFAS, contaminants of emerging concern, and microplastics exist in all biosolids, and are not site-specific issues well suited for later phased review. The programmatic phase is also the only meaningful opportunity to conduct environmental review of Class A "exceptional quality" biosolids, application of which is not subject to later SEPA review.

The general permit clearly creates "a reasonable likelihood of more than a moderate adverse impact on environmental quality," and thus is significant and requires preparation of an environmental impact statement. Because application of biosolids can reasonably be anticipated to contaminate both groundwater and surface waters across the State with chemicals already recognized by Ecology to pose a serious threat to human health, the proposal presents cumulative effects to wildlife, "unique and unknown risks to the environment," and "may affect public health or safety." WAC 197-11-330(3).

Ecology mainly points to data gaps as the explanation for why it cannot regulate acknowledged risks. Under SEPA regulations, significance depends on context and intensity. "The context may vary with the physical setting. Intensity depends on the magnitude and duration of an impact." WAC 197-11-794. Here, PFAS are "forever chemicals," so the duration of the impact is perpetuity. Furthermore, "[t]he severity of an impact should be weighed along with the likelihood of its occurrence. An impact may be significant if its chance of occurrence is not great, but the resulting environmental impact would be severe if it occurred." The impacts of widespread biosolids application are undoubtedly severe, given the reasonable threat of harm to human health of PFAS, including, according to Ecology, "probable links to immune system toxicity, high cholesterol, reproductive and developmental issues, endocrine system disruption, ulcerative colitis, thyroid issues, certain cancers, and pregnancy-induced hypertension."

Preparation of a programmatic EIS is the statutorily mandated mechanism by which to address these data gaps and assess associated risks and impacts. Rather than forge ahead in the face of admitted incomplete information, Ecology must carefully assess the likelihood and severity of impacts, reasonable alternatives, and the mechanism to mitigate them.

In addition to the general request for a determination of significance and preparation of an EIS, Mr. Kenney raises the following specific concerns with the SEPA checklist:

- ¶ 1. The checklist improperly excludes consideration of population growth, when Washington is a quickly growing State. The checklist should consider more recent population trends, including during the COVID pandemic.

- ¶ 1. The description of pollutants should distinguish between pollutants that are regulated, and pollutants more broadly, as this section appears to use the terms interchangeably. The SEPA analysis must consider impacts of all pollutants reasonably likely to be contained in biosolids irrespective of their regulation. The general statement that "Generally, pollutants in biosolids occur in very low concentrations, below the level where an adverse effect is expected" is inadequate. This cursory analysis lumps all pollutants together and contains no useful information.

  As detailed above, high priority pollutants (including PBDEs and PFAS) should be identified, along with a discussion of their likely presence of the pollutants and risks to the environment and human health. The one summary sentence dedicated to a serious and complex systemic issue is clearly inadequate.

- ¶ 1. The citation to WAC 173-308-90003 should acknowledge that this is the minimum content of a land application plan, but not necessarily sufficient to protect groundwater or adequate to fulfill Ecology's duties to protect groundwater.

- ¶1. The checklist states that "If the regulation of other pollutants becomes necessary during the course of the permit cycle, that is sufficient cause for Ecology to open the permit for modification." This statement lacks basis or thresholds, and is circular in that it states that if regulation is necessary then it is necessary. In order to be meaningful, mitigation must include specific triggers, criteria, and regulatory responses as part of a robust adaptive management system with public involvement.

- ¶ 2. The general statements regarding "decades of science" are inadequate. Citation must be provided. Emphasis should be placed on recent science, rather than decades-old science, given the concerns regarding PFAS, microplastics and other more recently understood issues.

- ¶ 2. The purported benefits of biosolids are immaterial to the threshold determination.

- ¶ 4. The statement that "Parks, wilderness areas, and wild and scenic rivers are likely too remote to be desirable for the land application of non-EQ biosolids" is inaccurate.

- ¶ 4. Application of biosolids to hydric soils raises high probability of groundwater contamination, which must be analyzed. As a mitigation measure, Mr. Kenney recommends barring biosolids applications from hydric soils and areas that are periodically inundated.

- ¶ 6. The analysis states that "[t]he permit itself will not increase demands on transportation or public services and utilities." This is the incorrect legal standard for SEPA review, which requires consideration of both direct and indirect effects. Ecology must consider the full impacts of biosolids application over time, including emissions and traffic associated with application.

Thank you for your consideration of these comments. Please contact me at wgolding@ziontzchestnut.com with any response to comments or follow up questions or concerns.

Sincerely,

ZIONTZ CHESTNUT

Wyatt Golding
Attorney for Ed Kenney

Science of the Total Environment 627 (2018) 1377–1388

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Review

An overview of microplastic and nanoplastic pollution in agroecosystems

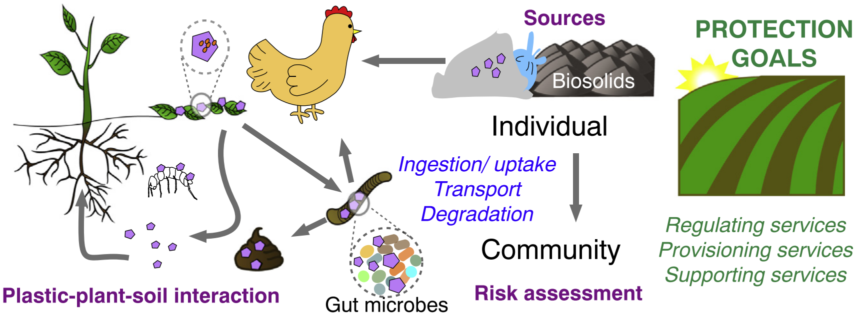
Ee-Ling Ng [a,*], Esperanza Huerta Lwanga [b,c], Simon M. Eldridge [a], Priscilla Johnston [d], Hang-Wei Hu [a], Violette Geissen [b], Deli Chen [a]

[a] School of Agriculture and Food, Faculty of Veterinary and Agricultural Sciences, The University of Melbourne, Victoria 3010, Australia
[b] Soil Physics and Land Management Group, Wageningen University & Research, Droevendaalsesteeg 4, 6708PB Wageningen, The Netherlands
[c] Agroecologia, El Colegio de la Frontera Sur, Unidad Campeche Av Polígono s/n, Cd. Industrial, Lerma, Campeche, Mexico
[d] CSIRO Manufacturing, Bayview Avenue, Clayton 3168, Victoria, Australia

HIGHLIGHTS

- We estimate maximum loadings in agroecosystem using existing regulations.
- Lifetime loading of 2.8–63 $t \cdot ha^{-1}$ of microplastics from biosolids use alone.
- Biotic response is mediated by the organism, soil and plastic properties.
- We deduce ecosystem impact by linking organismal response to ecological role.
- Estimated loadings can be used to set up ecotoxicology experiments.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 November 2017
Received in revised form 31 January 2018
Accepted 31 January 2018
Available online 20 February 2018

Editor: Jay Gan

Keywords:
Soils
Plant response
Ecotoxicology
Soil food web
Plastic degradation

ABSTRACT

Microplastics and nanoplastics are emerging pollutants of global importance. They are small enough to be ingested by a wide range of organisms and at nano-scale, they may cross some biological barriers. However, our understanding of their ecological impact on the terrestrial environment is limited. Plastic particle loading in agroecosystems could be high due to inputs of some recycled organic waste and plastic film mulching, so it is vital that we develop a greater understanding of any potentially harmful or adverse impacts of these pollutants to agroecosystems. In this article, we discuss the sources of plastic particles in agroecosystems, the mechanisms, constraints and dynamic behaviour of plastic during aging on land, and explore the responses of soil organisms and plants at different levels of biological organisation to plastic particles of micro and nano-scale. Based on limited evidence at this point and understanding that the lack of evidence of ecological impact from microplastic and nanoplastic in agroecosystems does not equate to the evidence of absence, we propose considerations for addressing the gaps in knowledge so that we can adequately safeguard world food supply.

Contents

---

[*] Corresponding author.
E-mail address: eeling.ng@unimelb.edu.au (E.-L. Ng).

https://doi.org/10.1016/j.scitotenv.2018.01.341
0048-9697/

1. Introduction: microplastics and nanoplastics as emerging environmental pollutants

Small plastic particles are ubiquitous throughout the environment, and cause considerable concern because micro (defined here as 100 nm to 5 mm in size) and nano (<100 nm in one dimension) sized particles are small enough to be taken up by many organisms (EFSA Panel on Contaminants in the Food Chain, 2016) and raises questions of potential bioaccumulation and biomagnification (see glossary in Box 1). There is growing evidence that microplastics are ingested by marine organisms, some evidence of translocation beyond the gut and fewer still evidence of transfer from one trophic level to the next (Galloway et al., 2017; GESAMP, 2015; Rochman et al., 2016). Nanoplastics are potentially more hazardous than microplastics because they can permeate biological membranes (Bouwmeester et al., 2015; EFSA Panel on Contaminants in the Food Chain, 2016; Nel et al., 2009). Terrestrial studies on microplastics ingestion are emerging for soil organisms (Huerta Lwanga et al., 2016; Rodriguez-Seijo et al., 2017). Recently, Horton et al. (2017) and Duis and Coors (2016) reviewed sources and fate of microplastics in terrestrial environment, and we build upon their work by exploring the extent to which plant and soil organisms in agroecosystems could be impacted, from individual level up to ecosystem level.

Leo Baekeland developed the world's first useful synthetic plastic in 1907 using formaldehyde and phenol (American Society of Chemistry National Historic Chemical Landmarks, 1993), but little was produced until around 1950s, when mass production of plastics begun and plastics found use in increasing range of applications; between 1950 and 2015, global plastic waste is estimated to be 6300 million tonnes, 79% of which has accumulated in landfills and other environmental compartments (Geyer et al., 2017). Based on the sources of microplastic pollution, agroecosystems are likely to be the most plastic-contaminated terrestrial system outside of landfills, urban spaces (Nizzetto et al., 2016) and beaches (Duis and Coors, 2016), and therefore they are excellent systems to study the implications of exposure to microplastic and nanoplastic. We will also include some findings from research on macro-plastics that we believe are relevant to understanding the overall effects of plastic pollution in agroecosystems.

In this synthesis, we present an overview of the multidisciplinary research on microplastics and nanoplastics in agroecosystems. While the relevant literature is vast, some aspects have fortunately been covered by recent reviews, which we will briefly summarise. Here, we emphasise on the following. Firstly, we identify the sources and estimate microplastics loading in agroecosystems, using reported estimates and our own calculations. Secondly, we examine the likely mechanisms and constraints underlying plastic degradation in soils and their dynamic behaviour. Thirdly, we report on the impact of these plastic

Box 1
Glossary.

Bioaccumulation	The process by which the amount of a substance, in this case, plastic particles, in an organism increases progressively because the rate of intake exceeds the rate of removal from the body.
Bioavailable	Amount of a substance that an organism absorbs (across a physiological membrane) as a result of physical, chemical and biological processes.
Biomagnification	Accumulation of a substance through a food chain by transfer of residues from diet to body tissue. The tissue concentration increases at each trophic level in the food web when uptake exceeds removal.
Cometabolism	The degradation of a substance catalyzed by an enzyme whose primary function is to react with another substrate. The other substrate is used as the primary carbon and energy source. For example, the breakdown of organopollutants, such as DDT, by white rot fungus *Phanerochaete chrysosporium* is catalyzed by enzymes responsible for breaking down lignin in plant material under normal conditions.
Home garden	Traditional, small scale agroforestry systems practiced in urban and rural areas, consisting of multipurpose trees and shrubs where livestock are often raised.
Nanoplastic	Plastic particles with one dimension between 1 and 100 nm.
Microplastic	Plastic particles in the size range between 100 nm and 5 mm.
Annual microplastic loading rate	The quantity of microplastic added per unit area per year.
Maximum or lifetime loading	This is the maximum amount of a substance per unit area given regulatory limits, e.g. contaminant limited biosolids application rate. In the case of biosolids, the limit is usually reached by a persistent contaminant such as heavy metals, thereby preventing further addition of biosolids to the land once this limit is reached.

particles on soil organisms and plants. This present work will serve as a synthesis of existing evidence as well as propose hypothetical implication at higher biological level of organisation built upon knowledge about plastic debris of all sizes and the ecological role of model organisms, such as earthworms. Finally, we propose approaches and considerations to determine the effects of microplastic and nanoplastic pollution.

2. Major sources of microplastics and nanoplastics in agroecosytems

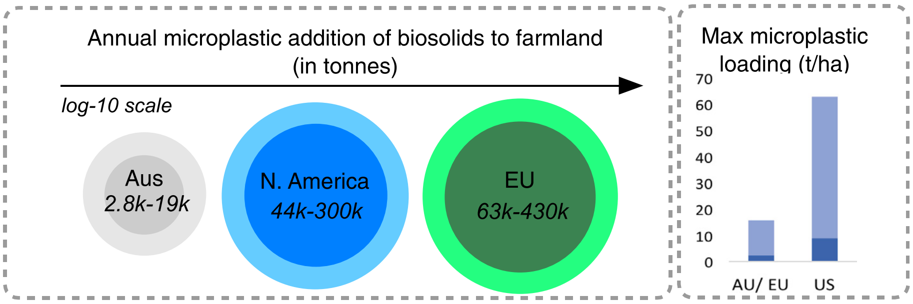
Microplastics and nanoplastics enter agroecosystems either as primary (manufactured) micro and nano materials (e.g. in waterborne paints, medical applications, electronics, coatings, adhesives), or indirectly as secondary microplastics and nanoplastics generated by the breakdown of larger plastic debris (Duis and Coors, 2016; Koelmans et al., 2015; Rillig, 2012). It was recently demonstrated that photodegradation of recovered marine microplastic debris (Gigault et al., 2016) and 1-cm^2-pieces of disposable polystyrene coffee cup lid (Lambert and Wagner, 2016) generated nanoplastics. Direct sources in agriculture include plastic mulch films and greenhouse materials and soil conditioners (e.g. polyurethane foam and polystyrene flakes). Indirect sources include general littering and the use of treated wastewater and biosolids (Duis and Coors, 2016; Horton et al., 2017). Microplastic and nanoplastic emissions per capita vary greatly between regions due to population size, affluence, presence and efficacy of waste management practices (Nizzetto et al., 2016; Ziajahromi et al., 2016). Here, we focus on plastics that end up in agroecosystems. Using existing data and estimates, we have derived potential annual and maximum plastic loadings in agroecosystems for Europe, USA and Australia, to illustrate the potential scale of the plastic problem.

Globally, between 0.8 and 2.5 million tonnes of microplastics – two-thirds of which are due to synthetic fibres released during washing and erosion of tyres while driving – are estimated to end up in oceans every year (Boucher and Friot, 2017). Of the microplastics that pass through wastewater treatment plants, some 95% of the microplastics are estimated to be retained in biosolids (Ziajahromi et al., 2016). As both treated wastewater and biosolids are used in agriculture for irrigation and as fertiliser (Mohapatra et al., 2016; Nizzetto et al., 2016), the microplastic loading on agricultural land is likely to be high. In Europe, Nizzetto et al. (2016) estimated that some 63,000 to 430,000 tonnes of microplastic enter agroecosystems annually through biosolids alone, while estimates for North America ranged from 44,000 to 300,000 tonnes of microplastics annually. We use Australia as a case study to further evaluate plastic particle loading rates per unit area per year and maximum (lifetime) loading given our in-depth knowledge of Australia's regulations on biosolids use. We estimate that between 2800 and 19,000 tonnes of microplastics are applied to Australian agroecosystems each year through biosolids (Box 2 and supplementary information, SI).

Besides biosolids, composts derived from non-source-separated residential waste or mixed municipal solid waste, and source-separated garden organic waste (to a lesser extent) are also sources of plastic pollution in agroecosystems. The physical degradation of plastics from these sources, abrasion and fragmentation due to mixing and transport,

Box 2

An estimation of loading rates and total loadings for microplastic from biosolids in agricultural soils in Australia, EU and USA.



In Australia, 1.5 million tonnes of wet biosolids were produced in 2015 (Australian and New Zealand Biosolids Partnership, 2016), with 64% of the biosolids used in agriculture and predicted to further increase in the future (Australian and New Zealand Biosolids Partnership, 2016). Using 125 to 850 tonnes of microplastics per million inhabitant (Nizzetto et al., 2016) as a basis, we estimate that between 2800 and 19,000 tonnes of microplastic could be applied to Australian agroecosystems each year through biosolids alone; Nizzetto et al. (2016) estimated 44,000–300,000 and 63,000–430,000 tonnes of microplastics could be applied to North American and European agroecosystems respectively. This estimate of between 2800 and 19,000 tonnes of microplastics in the 1.5 million wet tonnes of biosolids in Australia, equates to a likely presence of between 9 and 63 kg of microplastics per tonne of dry biosolids, assuming a total solids content of 20% (Eldridge et al., 2008) for the biosolids.

The application of biosolids in Australia is tightly regulated by state regulations which are largely derived from the New South Wales guidelines (EPA-NSW, 1997). Loading rates are limited by plant available N supply and contaminant loading to ensure that biosolids applications do not raise the level of contaminants in the soil above the accepted maximum allowable contaminant level for agricultural soils. There are also limits on the time interval between applications. Combined, these results in the theoretical maximum ceiling (lifetime loading) for biosolid application rate to agricultural land in Australia to be around 250 dry $\mathrm{t \cdot ha^{-1}}$. At 250 dry $\mathrm{t \cdot ha^{-1}}$, this would represent a maximum (lifetime) microplastic loading of between 2.3 and 15.8 $\mathrm{t \cdot ha^{-1}}$ incorporated into the top 75 to 100 mm of soil.

A comparison of estimates of microplastic loadings through biosolid application

The US regulations pertaining to biosolid application to agricultural land (i.e. USEPA 40 CFR 503, 1993) are less stringent than EU regulations (EU Directive 86/278/EEC, 1986). These limits on biosolid application rates would suggest maximum potential rate of microplastic inputs from biosolid in the order of 0.5 to 3.2 $\mathrm{t \cdot ha^{-1} \cdot yr^{-1}}$ in the US and from 0.045 to 0.63 $\mathrm{t \cdot ha^{-1} \cdot yr^{-1}}$ in Europe. Based on copper and zinc contaminants limited biosolid application rate for the respective regions, we would expect similar maximum microplastic loadings for agricultural land between Australia and Europe, while maximum (lifetime) microplastic loadings for US farmland may be as high as 9 to 63 $\mathrm{t \cdot ha^{-1}}$. Details for the regulations, calculations and uncertainties of the estimates for Box 2 are elaborated in SI.

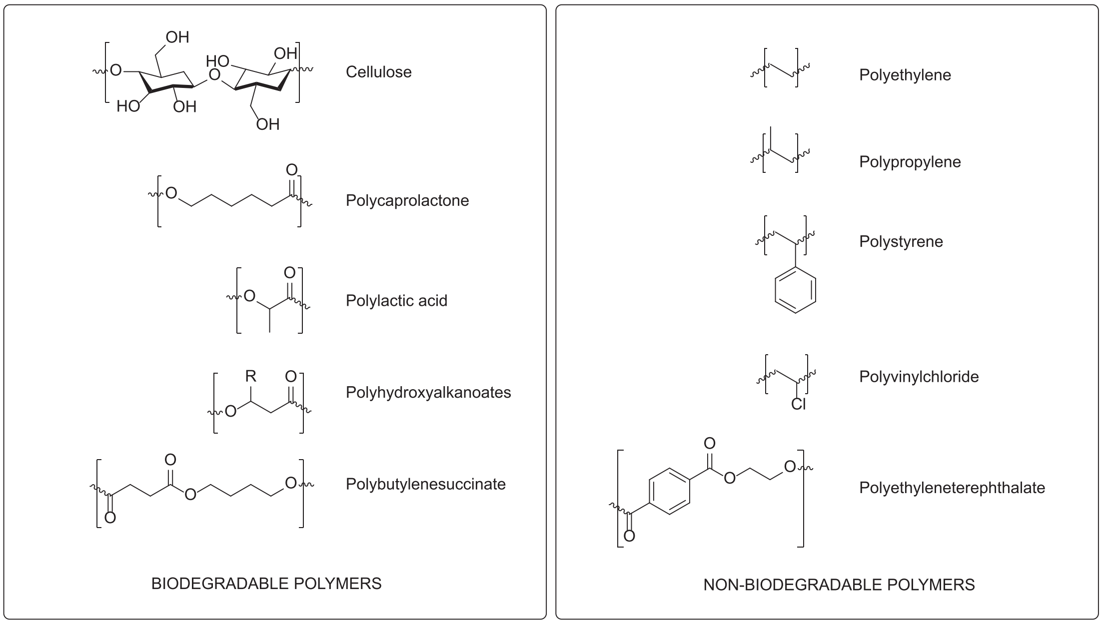


Fig. 1. Chemical structures of some important biodegradable polymers and examples of non-biodegradable polymers commonly contaminating soil.

is also likely to produce secondary microplastics. Brinton (2005) found that polyethylene, plastic fibres, and polystyrene foam occupied up to 5% w/w in compost from mixed municipal solid waste for all size fractions between 420 μm and 25 mm; with around 0.5 to 0.6% having sizes <2 mm. The quality and use of composts are regulated to varying degrees across the globe. For example, Australian standard (AS4454, 2012) for compost, soil conditioners and mulches retailed to backyard gardeners and farmers in Australia allows up to 0.5% dry matter w/w rigid plastic and 0.05% dry matter w/w of light, flexible or film plastics. This is equivalent to having up to 5 $t \cdot ha^{-1}$ of rigid plastic and 0.5 $t \cdot ha^{-1}$ of light plastic to a depth of 10 cm for a lifetime compost loading of 1000 $t \cdot ha^{-1}$. Hence, the potential contamination of agroecosystems by secondary microplastics and nanoplastics, could be significant.

In the early 2000s, 0.7 million tonnes of mulch film was used annually worldwide in agriculture, with China being the largest user (~80%; Espí et al., 2006). Plastic mulch film covers some 20 million hectares of farmland in China (Liu et al., 2014). Plastic mulch films with thicknesses between 6 μm and 20 μm are widely used in intensive production systems because of four perceived benefits: modification to soil temperatures, reduced evapotranspiration, better weed control, and reduced soil blemish of the product. As plastic mulch is applied with each crop cycle, soils become enriched with plastic residues that have been intentionally or unintentionally left behind on the field by farmers (Steinmetz et al., 2016). In the Xinjiang region of China, where plastic mulch is extensively used, the film residue content in soils ranged from 0 to 502 $kg \cdot ha^{-1}$ (mean 121.5 $kg \cdot ha^{-1}$), with the quantity being positively correlated with the number of years under mulching (Zhang et al., 2016).

3. Polymer degradation and dynamic behaviour of plastic particles on land

Polymer degradation refers to a chemical change in the molecular structure of the polymer that alters its properties. There exists an enormous number of polymers that, depending on their chemical structure, are rendered more or less susceptible to different types of degradation processes.

The biodegradable polymers possess heteroatoms (O, N, S) distributed along the polymer backbone that act as sites for hydrolytic or enzymatic reactions, leading to significant decreases in the molecular weight of the polymer in a relatively short timeframe (days to several years). These processes cause the structure of the polymer to break down into lower molecular weight molecular fragments that microbial cells can assimilate and subsequently mineralise to produce CO_2, H_2O and biomass in aerobic environments (or CO_2 and CH_4 in anaerobic environments). Examples of biodegradable polymers include aliphatic polyesters such as polylactic acid, polycaprolactone and polybutylenesuccinate, and natural biopolymers such as cellulose and polyhydroxyalkanoates (Fig. 1).

Many of the commonly used polymers contaminating our environment, such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC), possess a carbon backbone that is resistant to hydrolytic and enzymatic degradation (Fig. 1). As such, microbes are generally unable to assimilate and mineralise the polymers, resulting in the environmental accumulation of these materials. Some projections indicate that the lifetime of polyolefins on land is in the vicinity of hundreds of years (Kyrikou and Briassoulis, 2007). The ultimate degradation of these types of polymers in soil will involve several mechanisms including (i) photo- and thermo-oxidative degradation and (ii) some degree of biodegradation by microorganisms after a prolonged period of environmental exposure and oxidation. Nguyen (2008), and Singh and Sharma (2008) have authored thorough reviews on the general topic of plastic degradation. The present article will therefore provide an overview of the degradation processes on land.

3.1. Photo- and thermally-initiated oxidative degradation

Common polymer contaminants in or on soil are susceptible to some degree of photo- or thermo-oxidative degradation. The general mechanism for abiotic oxidative degradation of polymers with a carbon backbone is given in Box 3. Oxidative degradation is triggered by free radicals generated when the materials are exposed to ultraviolet or thermal energy under aerobic condition. As these degradation processes rely on the combination of radicals with oxygen, they will only occur when plastic is at, or very near to, the soil surface. In the field, radicals are most likely to form by (i) direct photolysis of C—C and C—H bonds in the polymer, (ii) residual catalyst or chromophoric chain defects present from synthesis, or (iii) as a result of other additives such as photosensitisers (e.g. TiO_2), pro-oxidants (usually salts of transition metals including iron, nickel, cobalt and manganese), fillers, dyes and pigments (Carlsson and Wiles, 1976; Gardette et al., 2013), which in

Box 3
General mechanisms for oxidative degradation of carbon-based polymers.

Initiation	$PH + X\bullet \rightarrow P\bullet + XH$	[1]
Propagation	$P\bullet + O_2 \rightarrow PO_2\bullet$	[2]
	$PO_2\bullet + PH \rightarrow POOH + P\bullet$	[3]
Chain branching (autocatalytic)	$POOH \rightarrow PO\bullet + \bullet OH$	[4]
	$PO\bullet + PH \rightarrow POH + P\bullet$	[5]
	$HO\bullet + PH \rightarrow HOH + P\bullet$	[6]
	$PO\bullet \rightarrow$ various chain scission reactions	[7]
Termination	$P\bullet + P\bullet \rightarrow P{-}P$ or $P{-}H + P({-}H)$	[8]
	$PO_2\bullet + PO_2\bullet \rightarrow$ inactive products	[9]

PH designates the polymer, P• is a macroradical and X• is an unspecified radical (Hawkins, 1964; Nguyen, 2008). This is the general mechanism for the oxidative degradation of polyolefins such as PE and PP and it is also applicable to other types of polymers with a carbon backbone.
The first step of the oxidation pathway begins by abstraction of hydrogen from the polymer to produce the macroradical species, P•, regardless of how the radical is generated (Eq. (1); Hawkins, 1964). A chain reaction ensues in the propagation stage, involving combination of the macro-radical with oxygen (Eq. (2)) to produce a peroxy polymer radical. The peroxy radical then abstracts hydrogen from another polymer molecule to produce a molecule of hydroperoxide and a new macroradical (which subsequently undergoes reactions [2] and [3], and so on). Eqs. (4–7) show the autocatalytic chain branching phase which increases the oxidation rate further. Here, the hydroperoxides formed in the previous step decompose into radicals, which in turn abstract hydrogen from polymer molecules to generate more macroradicals.
Termination eventually occurs when radicals couple together or undergo disproportionation. The interested reader is referred to the following articles for more specific details on the mechanisms of photo- and thermally-triggered oxidative degradation in PE (David et al., 1992; Gardette et al., 2013), PP (Carlsson and Wiles, 1976), PS (Grassie and Weir, 1965), PVC (Palma and Carenza, 1970) and PET (Jabarin and Lofgren, 1984).

some cases may involve the production of singlet oxygen as a reactive intermediate (Rabek and Rånby, 1975). The degree to which these oxidative processes can occur is highly dependent on the environmental conditions (e.g. UV exposure, temperature, soil composition, moisture, oxygen); as well as the chemical structure and crystallinity of the plastic (with oxygen diffusion and degradation occurring more readily in amorphous regions of the materials) (Nguyen, 2008).

At the macroscale, photo and thermally triggered oxidative degradation leads to the embrittlement, cracking and weakening of plastics with time. Thus the materials become more susceptible to fragmentation when they are exposed to abrasive or mechanical forces, e.g. from farm equipment, generating micro and nanoplastics. At the molecular level, the polymer chemical structure changes due to a combination of events including chain scission (decrease in polymer molecular weight), crosslinking (increase in molecular weight), branching (increase in molecular weight) and incorporation of oxygen containing functional groups at the surface of the plastic particle, e.g. esters, ketones and alcohols, which also reduces the surface hydrophobicity of the plastic (Singh and Sharma, 2008).

As plastic particles age in the environment, their movement through the soil profile is expected. Earthworms (Huerta Lwanga et al., 2017; Rillig et al., 2017) and collembola (Maaß et al., 2017) have been observed to transport microplastics, and agricultural practices such as ploughing, would also contribute to their vertical transport. This new subsurface location would negate photo and thermal degradation, which are crucial for reducing the size of polymers with carbon backbones like PE, PP, PS and PVC (as described above) before any substantial biodegradation can occur. Furthermore, anaerobic conditions may develop in deeper layers of the soil and inhibit oxidative degradation processes (Thomas et al., 2012).

3.2. Biodegradation

After extensive initial photo- or thermo-oxidative degradation, biodegradation plays an important role in the ultimate fate of plastics in soil. Biodegradation is the process of mineralisation of an organic material by microorganisms to generate CO_2 and H_2O under aerobic conditions, or CO_2 and CH_4 under anaerobic conditions (Mohan, 2011). The molecular weight, chemical structure and morphology, hydrophobicity, water absorption, and surface roughness of plastic materials all have an impact on their susceptibility to biodegradation (Table 1). Even low molecular weight components of PE subjected to extensive pre-oxidation in accelerated conditions (i.e. artificial weathering where UV light and/or heat between 50 and 70 °C is applied) not reflected in the field, can only be partly biodegraded (Thomas et al., 2012). The accelerated weathering conditions certainly decrease the molecular weight of the PE, a critical step towards achieving microbial degradation; however the majority of the oxidised sample is still too high in molecular weight to be mineralised (Table 1).

Although numerous organisms are recognised to biodegrade or partially biodegrade even some of the most persistant types of plastics – e.g.

Table 1
General rules of thumb indicating the likely impact of certain polymer properties on susceptibility to biodegradation.

Property	Impact on biodegradation	Sample format
Molecular weight	Only low molecular weight compounds can be assimilated by microbial cells and enzymatically degraded. Carbon-chain backbones do not biodegrade until the molecular weight is <1000 g/mol (Potts et al., 1973)	Molecular
Chemical structure and morphology	Certain functional groups provide sites for enzymatic cleavage (ester, ether, amide, urethane) (Kawai, 2010)	Molecular
	Branched structures are more difficult for microbes to assimilate (Potts et al., 1973)	Molecular
	Amorphous materials biodegrade faster than crystalline ones (Reed and Gilding, 1981; Yoo and Im, 1999)	Macro
Surface hydrophobicity	Hydrophobic surfaces inhibit biofilm formation, hydrophilic surfaces (water contact angle 40–70°) promote it (Lee et al., 1998)	Surfaces of thin films
Water absorption	Bulk hydrophilicity and water absorption give microbes access throughout the bulk material (Göpferich, 1997)	Macro
	Water absorption softens polymers, and softer materials biodegrade faster than harder ones (Foruzanmehr et al., 2015)	Macro
Surface roughness	Microbes adhere to rougher surfaces more easily than smooth ones (Wan et al., 2005)	Surfaces of thin films

certain bacteria (Huerta Lwanga et al., 2018; Yang et al., 2014; Yoshida et al., 2016) and insect larvae (Bombelli et al., 2017), these specific organisms (such as the bacteria *Ideonella sakaiensis* isolated from recycling site) and/or their hosts (such as the caterpillar of the moth *Galleria mellonella* or larvae of Indian mealmoth *Plodia interpunctella*) may not be naturally present in agroecosystems. Even if plastic-degrading organisms are present in soils, such as the plastic-degrading bacteria (*Microbacterium awajiense*, *Rhodococcus jostii*, *Mycobacterium vanbaalenii*, *Streptomyces fulvissimus*, *Bacillus simplex* and *Bacillus* sp.) identified from earthworm's gut (Huerta Lwanga et al., 2018), less energetically expensive carbon resources would be present in soils, therefore biodegradation of such plastic particles would be less likely to become a relevant process, with cometabolism being a more likely scenario. Cometabolism, which is the degradation of a compound in the presence of another compound that is used as carbon source, has been extensively studied for bioremediation of organic pollutant such polyaromatic hydrocarbon, but its effectiveness in field is thus far limited and requires extensive and costly intervention (Ghosal et al., 2016).

3.3. Particle changes through biophysicochemical interactions at particle-soil interface

During oxidative degradation, anionic or polar surface groups are likely to be introduced on plastic particles, providing surfaces for further interaction with soil components. The interaction between plastic particles and soil components is a dynamic process involving a series of interconnected physical-biological-chemical changes. As a result, the physicochemical state of plastics in soils is likely to be highly dynamic. Moreover, plastics are typically a complex mixture of polymers, residual monomers, catalysts and additives (Teuten et al., 2009), which affect the plastic particle characteristics and behaviour, and therefore the interactions of different plastics with soil organic and inorganic matter.

Consider the apparently simple two-way relationship between plastic and an agrochemical (e.g. pesticide) present in the soil. Studies so far indicate that there is a subtle interplay between environmental factors and plastic composition that can affect the stability of both agrochemicals and plastics commonly used in agriculture. Various pesticides' accumulate and/or become stabilised on the surface of plastic mulch film (Ramos et al., 2015), while other plastics treated with agrochemicals actually become more susceptible to photodegradation and embrittlement than the corresponding clean plastics (Schettini et al., 2014).

Additionally, as degradation proceeds, smaller sized plastic particles are generated. Studies on nanomaterials indicate that the smaller the particle, the larger its surface-to-volume ratio and its reactivity, thus, the more dynamic the behaviour of nanoparticles (P. Wang et al., 2016; Wiesner et al., 2011). The fragmented microplastics released in the casts of *L. terrestris* (Huerta Lwanga et al., 2016) are surrounded by ecocoronas or biofilms comprising soil biota, and soil-derived organic and inorganic macromolecules. These ecocoronas change the density, surface charge, size and shape of micro or nanoplastic particles, and may therefore also alter the mobility, degradation, bioavailability and toxicity of the encapsulated plastic particles (Artham et al., 2009; Galloway et al., 2017; Nel et al., 2009).

When considering nano-sized particles in soils, it is argued that the prevalence of black carbon and natural carbonaceous nanoparticles in soils would exceed that of manufactured nanomaterials (Koelmans

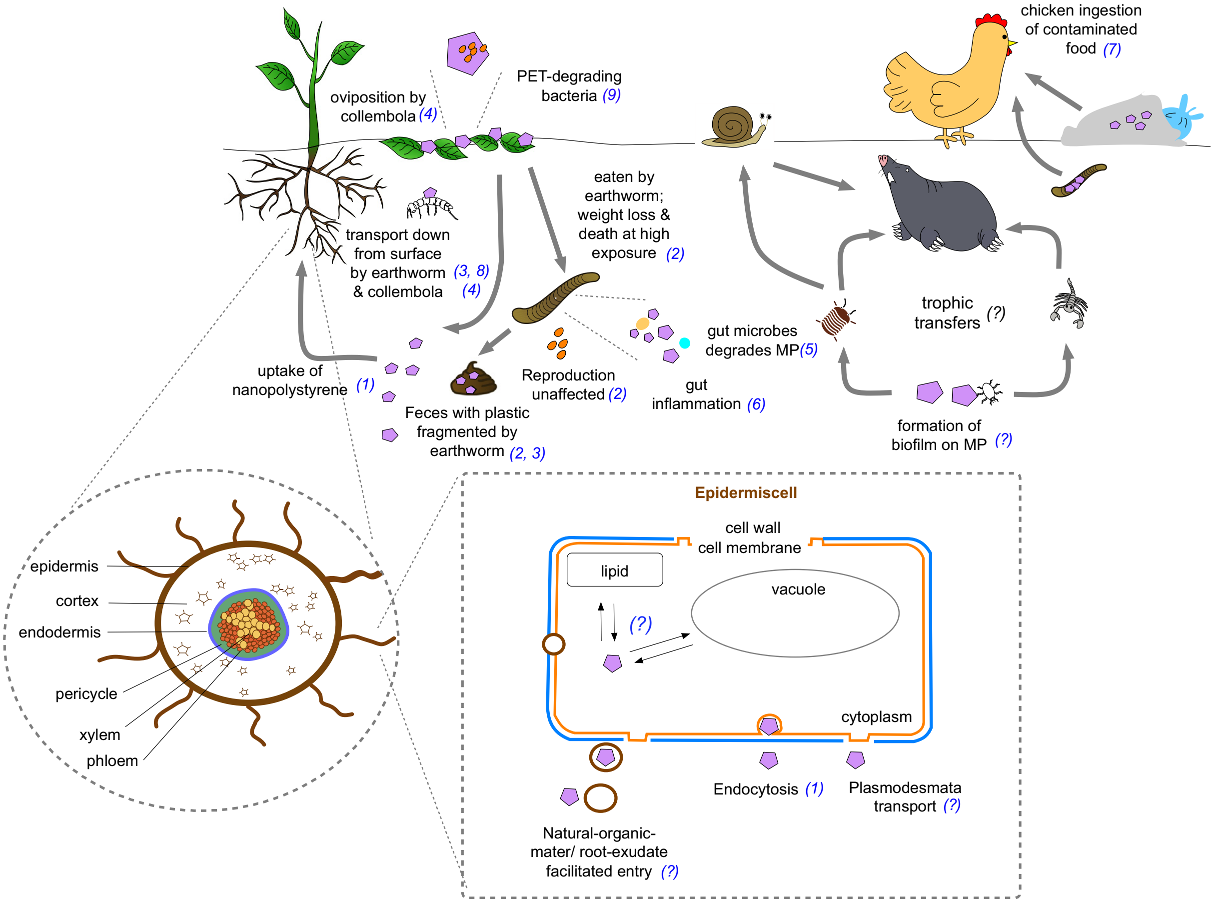


Fig. 2. Microplastic and nanoplastic uptake and interaction with soil biota and plants. (1) Bandmann et al. (2012); (2) Huerta Lwanga et al. (2016); (3) Huerta Lwanga et al. (2017); (4) Maaß et al. (2017); (5) Huerta Lwanga et al. (2018); (6) Rodriguez-Seijo et al. (2017); (7) Huerta Lwanga et al. (2017); (8) Rillig et al. (2017); (9) Yoshida et al. (2016); (?) refers to unknowns. MP refers to microplastic or nanoplastic.

et al., 2009). Using examples from Simpson and Hatcher (2004), there would be between 520 and 2010 $t \cdot ha^{-1}$ of black carbon to 7.5 cm depth for a Canadian Chernozem (5.2% total C) and German Mollisol (1.9% total C) respectively. In comparison, our estimates of maximum microplastic loading from biosolid use in agroecosystems in Box 2, assuming eventual 100% conversion into nano-sized particles, would correspond to between 2.3 and 63 $t \cdot ha^{-1}$ of nanoplastics in soils. This finding raises three questions: (1) what is the relative importance of plastic as a host or carrier of organic and inorganic matter relative to other carriers in the soil, such as mineral particles and natural soil carbonaceous polymers, (2) how will plastic interact with these soil carbonaceous materials, and (3) if soil biota and plants have historically evolved within this environment, do these materials pose no threat or has the biota developed mechanisms to live amidst these materials? These also highlight the crucial task to quantify actual plastic loading and their sizes in agroecosystems.

4. Response of soil biota to microplastic and nanoplastic pollution

4.1. Organismal-level response

It is reported by studies in marine environment that microplastic ingestion is rarely lethal at environmentally relevant concentrations (Galloway et al., 2017; Rochman et al., 2016). In earthworms, two outcomes have been observed so far in controlled experiments: i) the organism survives, the microplastics may be fragmented further internally, and plastic particles are transported in soil via defecation and when the organism moves or, ii) the organism suffers weight loss, and then dies at high exposure concentration (Fig. 2). In one study, earthworms *Lumbricus terrestris* exposed to concentration of 28% PE microplastics (w/w in dry plant litter) and above, experienced growth inhibition (<1.4 mg weight gain compared to 10.3 mg weight gain in control with no exposure to microplastic) and subsequently died (8–25% compared to 0% in control with no exposure to microplastic) even though their reproduction was unaffected (Huerta Lwanga et al., 2016). These are high exposure concentrations that could occur under contaminated land scenario. Another study using *Eisenia fetida* exposed to 0.25 and 0.5% of PS microplastic (w/w in dry soil) showed no growth inhibition, with growth inhibition only occurring at exposure concentrations >1% (Cao et al., 2017). In another study using *Eisenia fetida*, inflammation in the guts was observed when the earthworm is exposed to concentration of 0.0125% PE microplastic (w/w in dry soil) and above but this does not translate to any significant effects on survival, reproduction and biomass at concentration up to 0.1% of PE microplastic (w/w in dry soil) (Rodriguez-Seijo et al., 2017).

Studies on algae in the aquatic environment showed that nanoplastics are adsorbed onto the cell wall of microalgae such as *Scenedesmus*, *Chlorella* and *Pseudokirchneriella subcapitata* (Bhattacharya et al., 2010; Nolte et al., 2017a), with binding mediated by cell morphology (Bhattacharya et al., 2010), the particle's charge and ionic strength of the medium (Nolte et al., 2017a; Nolte et al., 2017b). These experiments, lasting for hours to a few days, indicated these nanopolystyrenes were not lethal to the algae at concentrations up to 100 $mg \cdot L^{-1}$. However, they did reveal that these nanoplastics can lead to the physical inhibition of algal photosynthesis due to increased water turbidity and light scattering, coverage of the algal cell surface with microplastics, or immobilisation of algae at concentration of around 1.5 $mg \cdot L^{-1}$ and above (Bhattacharya et al., 2010; Nolte et al., 2017a). It remains to be explored if interferences from nanoplastics in photosynthesis and induction of physiological stress responses can occur in soil-dwelling algae.

Despite their ecological importance, the exposure of soil filter feeders such as some nematodes, rotifers and ciliates to microplastics and nanoplastics have not yet been determined to our knowledge. Filter feeders in marine ecosystems have been shown to ingest microparticles (Van Cauwenberghe and Janssen, 2014; Wright et al., 2013) while filter feeders in freshwater ecosystems, *Daphnia magma* and *Thamnocephalus platyurus*, have been shown to be sensitive to nanoplastics (Besseling et al., 2014; Casado et al., 2013). Uptake by such organisms is determined by their ability to discriminate food and non-food, which depends on a mixture of chemical (taste and olfaction) and physical (size) mechanisms (Kiyama et al., 2012). Kiyama et al. (2012) demonstrated that the nematode *Caenorhabditis elegans* on buffer solution and agar plates take up PS microspheres of 0.5 and 1 μm, particularly in the absence of food bacteria. Organisms with other feeding modes are also susceptible to microplastic ingestion. Recently, Taylor et al. (Taylor et al., 2016) found synthetic microfibers on and inside six out of nine deep sea organisms from the phyla Cnidaria, Echinodermata and Arthropoda with predatory and detritivorous feeding mechanisms. As such, woodlice, snails, caecilians and other soil organisms with similar feeding mechanisms would be subjects of interest in agroecosystems.

Information about the bioavailability and bioaccumulation of microplastics in soil organisms is generally lacking. Early investigations indicate that mussels take up particles <10 μm and these particles were translocated from gut to the circulatory system and retained there for the duration of the testing period (48 days) (Browne et al., 2008). We know that nanoplastics can enter cells, as fluorescent nanoplastic polymers have been used as molecular probes for a wide range of biological studies with mammalian cells, for example to measure blood flow in tissue and as tracers for phagocytic processes (see e.g. carboxylate-modified microsphere F8888 by Invitrogen; Katz and Iarovici, 1990; Rembaum and Dreyer, 1980). The translocation of a range of microparticles by mammalian gut into the lymphatic system have been demonstrated in human (particle sizes 160 nm – 150 μm), rabbits (100 nm – 10 μm), dogs (3–100 μm) and rodents (10 nm – 40 μm) (see details in review by Hussain et al., 2001). There is no experimental evidence of nanoplastics being transferred from invertebrates to vertebrates in soils; there is evidence of the transfer of microplastics from contaminated land to vertebrates, and potentially from earthworm to chicken. In one study developed for homegardens, it was observed that chickens' digestive tract became polluted with plastic particles (62.6 ± 49.5 particles per gizzard, 16.45% of which were <5 mm and 83.55% were >5 mm; 11 ± 15.3 particles per crop, all of them macroplastics, no microplastics were found in crops; Huerta Lwanga et al., 2017).

Understanding organismal-level response is the basis for toxicological studies and risk assessments, and translating this response to population and ecosystem-level consequences upon which policy and decisions are often based, is a challenge. For the purpose of decision-making, complementing the above individual endpoint measurements with models could allow prediction of the pollutant burden over time and translate the individual-level response to a population model (Jager, 2016). For example, toxicokinetic and toxicodynamic models examine internal concentrations of a contaminant as function of uptake, transformation, distribution and elimination, and the subsequent response of the test organism (Rohr et al., 2016) could be applied to well-studied earthworm, where there is a strong understanding of the organism's biology.

4.2. Response of soil microbiome

The time and space scale for microbes, given their relatively short life history and small size, give us a chance to study processes that would be difficult at field scale (Jessup et al., 2004) and allow us to capture the emergent properties of a system which would be impossible with individual-level trait studies. While no studies have specifically examined micro- and nano-sized plastic particle effects on soil microbiome, an experimental study on plastic mulch residues provides some preliminary indication of potentially useful measures. In a pot trial experiment with 67.5 and 337.5 $kg \cdot ha^{-1}$ plastic mulch residues (20 mm × 20 mm) maintained at constant moisture content, soil microbial biomass, enzyme activities (dehydrogenase and fluorescein diacetate hydrolysis) and functional diversity (community level physiological profile) tended to decrease with increasing concentrations of plastic mulch residue (J. Wang et al., 2016). The concentration (67.5 kg·ha^{-1}) used in this experiment is environmentally relevant for soils with over 5 years of plastic mulch film use (Zhang et al., 2016). Given the long-term use and misuse of plastic mulch in some agroecosystems, studying their soil microbiome may provide insights into the long-term implications of plastic pollution on land.

5. Response of plants to microplastic and nanoplastic pollution

5.1. Uptake of nanoplastic by plants

Uptake of microplastics by plants is not expected. The high molecular weight or large size of the plastic particles (Teuten et al., 2009) prevents their penetration through the cellulose-rich plant cell wall. In contrast to microplastics, nanoplastics indeed have been shown to enter plant cells (Fig. 2). Bandmann et al. (2012) have demonstrated uptake of 20 and 40 nm nanopolystyrene beads by tobacco BY-2 cells in cell culture via endocytosis, while 100 nm beads were excluded. However, no studies have investigated whole plant, instead of plant cell culture, uptake of nanoplastics to the best of our knowledge.

Plant species vary in their uptake, translocation and accumulation of contaminants due to a range of anatomical and physiological differences. Plant properties that are known to affect the uptake of organic compounds include root properties (volume, density, surface area), xylem properties (volume, surface area), transpiration, growth rate, water and lipid fractions, plasma membrane potential, tonoplast potential, cytoplasm pH and pH of vacuoles (Trapp, 2000). Characteristics and permeability of the plant cell wall varies, but as a rule-of-thumb, particles <6 nm in one dimension may be able to permeate the cell wall (Carpita et al., 1979).

Studies on plant uptake of engineered carbonaceous nanoparticles – structurally dissimilar to plastics but they can be produced with similar particle size, shape, surface functional groups to microplastics – may shed light on the possible modes of nanoplastic interaction with plants and bioavailability (see reviews by Ma et al., 2010; Rico et al., 2011; J. Wang et al., 2016). In plants, such engineered carbon-based nanoparticles are being targeted as molecular transporters to study plant cell biology, or deliver agrochemicals and biomolecules (Morales-Díaz et al., 2017; J. Wang et al., 2016). Uptake of these carbon-based nanoparticles has been documented in whole plants such as rice (*Oryza sativa*), maize (*Zea mays*), soybean (*Glycine* max) and arabidopsis (*Arabidopsis thaliana*) (Lin et al., 2009; Zhao et al., 2017). Based on the above studies, the proposed pathways for entry of carbonaceous nanoparticles into plants, depending on plant species and nanoparticle properties, include endocytosis through the plasmodesmata; passage via ion transport channels, carrier proteins or aquaporins; and also soil carbon or root exudate mediated entry (Fig. 2).

There are no studies on translocation and storage of nanoplastics in plants. However, the translocation of engineered carbon nanoparticles in the size range of 40 to 70 nm to stem and/or leaf have been demonstrated in rice using fullerene C_{70} (Lin et al., 2009) and soybean, maize, rice and Arabidopsis using carbon nanotubes (Zhao et al., 2017). There have not been any studies evaluating the transgenerational transmission of nanoplastics. Transmission, has been reported in rice using fullerene C_{70} mixed with natural organic matter obtained from natural waters, which contains a mixture of hydrophobic and hydrophilic acids and other soluble organic compounds (Lin et al., 2009). The transport and fate of the engineered carbon nanoparticle is strongly influenced by interaction with natural organic matter (Hyung and Kim, 2008), and therefore, the effect of soil organic matter adsorption to nanoplastics should be explored if we are to understand its effects on the fate of nanoplastics in soil and plant.

5.2. Toxicity, stress and response of plants to nanoplastic

Similarly, there is no data on the toxicity of nanoplastics on plants. Since the first studies reported plant cell uptake of engineered carbon-based nanotubes and fullerenes (Lin et al., 2009; Liu et al., 2009), studies on nanotubes and fullerenes indicate a range of positive, neutral and negative effects in a range of edible crops (see reviews by Husen and Siddiqi, 2014; Ma et al., 2010; Rico et al., 2011; J. Wang et al., 2016). All four reviews presented a sum of six studies (with numerous overlaps) on nanotubes and two studies on fullerene C_{60}, with all crops being grown under hydroponic and broth culture, except the studies by Kole et al. (2013) who used sphagnum moss and Torre-Roche et al. (2013) who used a mixed vermiculite-soil medium.

General observations on toxicity of carbon nanoparticles that may have relevance to future studies using nanoplastics, are: (1) phytotoxicity tests such as germination, root elongation and growth measures across studies indicate that sensitivity depends on plant species and the physicochemical properties of the engineered carbon nanoparticle; (2) cell damage occurs through genotoxicity and cytotoxicity (Shen et al., 2010; Tan et al., 2009); and (3) interactions between different types of engineered carbon nanoparticle with pesticides can increase or decrease the uptake of pesticides by different crops (Torre-Roche et al., 2013).

Plant can metabolize a range of pollutants, including polychlorinated and polycyclic hydrocarbons (Sandermann Jr., 1992). During pollutant metabolism, oxidative stress can result from a combination of (1) reactive oxygen species generated during cytochrome P450 mediated oxidation, and (2) glutathione depletion through gluthatione-S-transferases catalyzed conjugation with pollutant (Scandalios, 2001). Zhao et al. (2017) measured the uptake of ^{14}C-labelled carbon nanotubes (2.25 ppm) in rice, maize, soybean and arabidopsis; and found that biochemical parameters, such as antioxidant enzyme activities, were more sensitive than physiological measures, such as pigment and total protein contents. Biochemical parameters, therefore, may be a good indicator of plant response to nanoplastics. Pollutants are often stored as soluble and insoluble conjugates in various parts of the plants rather than degraded (Sandermann Jr., 1992). As such, it is also necessary to determine whether detoxification processes produce harmless metabolites, or whether new toxins might be introduced into the food chain. Estimates made using plant uptake models and quantities of micropollutants in irrigation water, indicate that human exposure to 27 emerging micropollutants (including pharmaceuticals, fragrances, flame retardants and plasticizers) range from <1 to >461 ng per person per day through vegetable and fruit consumption (Calderón-Preciado et al., 2011). Several of these chemicals are additives in plastic production. We have, to maintain brevity in this overview, refrained from discussing the residual monomers, catalysts and additives that are part of plastic and need to be considered in future studies. Readers interested in this matter are referred to reviews on biological effects of plastic additives (Meeker et al., 2009; Oehlmann et al., 2009), or phthalate esters occurrence and degradation in the environment (Gao and Wen, 2016; Staples et al., 1997).

6. From organismal to ecosystem-level responses

So far, studies on the ecological impact of plastic in soils are mostly at organismal level, or on the soil microbiome. This approach is not unique to soils, since a majority of impact studies in marine ecosystems have demonstrated impacts only at suborganismal and organismal levels (Browne et al., 2015). Clearly, more work needs to be done at higher biological organisation levels (Browne et al., 2015; Galloway et al., 2017; Rochman et al., 2016). But impact studies at higher biological organisation are difficult. Browne et al. (2015) suggests that existing knowledge of ecological linkages, where known, and population models, where the linkages are unknown, can be used to deduce such impact.

There is evidence that water infiltration is correlated to earthworm biomass and burrow length (Blouin et al., 2013), that is soil porosity is linked to earthworm presence. Using the approach suggested by Browne et al. (2015), one can then hypothesise that when earthworm mortality is high as a result of high microplastic contamination, as per reported by Huerta Lwanga et al. (2016) and discussed in Section 4.1, soil porosity would be impacted. Currently, only one laboratory study explored such ecological linkage. The study showed that *L. terrestris* had lower biomass under the exposure of microplastics at 7% microplastics (w/w in dry plant litter) while the burrows occurred in significantly higher numbers and the burrow walls were denser compared to the control without exposure to microplastics, however the burrow length was similar across all treatments during the 14 day experiment (Huerta Lwanga et al., 2017). These results indicate soil porosity may increase as a result of earthworm-microplastic interaction but further work is still necessary to validate their longer-term implications for soil porosity. Additionally, microplastics may also have direct effect on soil porosity, as both synthetic water-soluble and gel-forming polymers are used as soil conditioners to improve water infiltration, water retention and soil stabilisation (Bouranis et al., 1995).

In aquatic systems, microplastics have become a floating mobile habitat for algae, bryozoans, dinoflagellates, isopods, marine worms and microbes (Reisser et al., 2014). There is evidence that the ingestion of plastic debris by seabirds is linked to dimethyl sulfide, a chemical cue released by phytoplankton in response to foraging activity (Savoca et al., 2016). Savoca and colleagues demonstrated experimentally that PE and PP microplastics exposed in the ocean for three weeks produce dimethyl sulfide. The migration facilitated by microplastics can affect population and ecosystem dynamics. In soils, there is no lack of substrate compared to open water but plastic particles could serve similar habitat functions. Collembola has been observed to use microplastics as a site for oviposition (Maaß et al., 2017). Earthworm casts are naturally rich ecosystems of microbes (Gómez-Brandón et al., 2011; Toyota and Kimura, 2000) and casts enriched with plastic particles (Huerta Lwanga et al., 2016) would be hosting microbiomes. These findings suggest that biofilms on plastic in soils could promote uptake by other organisms higher up in the food chain.

7. Considerations for assessing risks of microplastics and nanoplastics in agroecosystems

7.1. Challenges and lessons from studies on plastic particles, engineered nanoparticles and other persistent contaminants

Current methodologies used to extract, quantify and characterise microplastics from water or sediment samples, would require adjustment to enable equivalent information from soil samples; not to mention the entire lack of nanoplastic isolation methods (Duis and Coors, 2016; EFSA Panel on Contaminants in the Food Chain, 2016; Syberg et al., 2015). Soil is a heterogeneous medium which makes the isolation or enrichment of plastic particles from it extremely challenging. The presence of soil organic matter, sometimes stabilised by interaction with soil minerals, complicates the removal of soil organic matter that distort spectroscopic techniques for identification of plastic particles. Recently, a method for extracting and quantifying the number, size and mass of micro-sized low-density polyethylene and polypropylene from soil using flotation and heating was published by Zhang et al. (2018). Some similarities can be drawn from sediment studies, and adaptation of recent procedures for the isolation of microplastics from fine sediments could potentially be used in the future to quantify micro and nanoplastic loads in agricultural soils (Coppock et al., 2017). These allows the identification of microplastics in soils, but more efficient and faster techniques are required. In addition, standardisation of the units of measurement in terms of weight, number and/or volume should be prioritised to allow comparison of results from different experiments.

The representativeness of synthetic plastic particles used in many experiments is questioned, since the aging of plastics in the environment alters their surface chemistry and behaviour. Rapid aging could be simulated by subjecting plastics containing pro-oxidant additives to artificial, accelerated weathering and abrasion, but we would still need to relate the structure and chemical properties of the artificially generated microplastic or nanoplastics with those isolated from field samples. An alternative approach is the preparation of a range of standard testing materials aged in a set of selected soils with different characteristics.

The adoption of high doses is often used in assessing effects of a pollutant in laboratory studies to elicit toxicological endpoint and determine dose-response curves. However, studies on pesticides and other endocrine-disrupting chemicals have shown that nonlinear or non-sigmoidal dose-response relationships are common, such as the U-shape or inverted U-shaped responses, (Clotfelter et al., 2004; Imfeld and Vuilleumier, 2012), and studies on nanoparticles indicated that particle surface area or particle number concentration may be more relevant than mass-based dose metric for determining biological effects for nanoparticles (Petersen et al., 2015). The range of doses could be narrowed down through spatiotemporal data detailing the occurrence of microplastic and nanoplastic debris in agroecosystems. This can be achieved by prioritising data collection in agroecosystems that receive recycled organic inputs or use plastic mulch.

Choosing the right subjects, variables and controls in the studies is also challenging (Horton et al., 2017; Syberg et al., 2015). If the test organisms are already exposed to high background levels of the pollutant, its lack of response compared to the treatment can be merely an artifact of the organism's prior exposure. Certain organisms are also more sensitive; such as root crops (Eggen et al., 2013), or juvenile organisms in early developmental stages (Clotfelter et al., 2004; Talsness et al., 2009), and these should be prioritised in initial screenings. Interspecific variation in susceptibility within a taxonomic group, intraspecific variations between age class, sexes and populations and ability to recover must all be carefully considered. Beyond individual species, choosing the right measures at the population and ecosystem level is also necessary as other abiotic or biotic stressors may enhance the sensitivity of the test organism or system to plastic pollution (Rohr et al., 2016).

Classical soil ecotoxicological approaches use isolated organisms and standard substrates, with measures taken for survival, growth, reproduction and avoidance behaviour over a period of days and weeks. Such approaches may not capture the full impact of chemical additives in plastics that act as endocrine disruptors in addition to those which bioaccumulate, where long-term exposure at low doses may alter cell functions or cause DNA damage. Such damage manifests later in life or across generations as the damage accumulates (Clotfelter et al., 2004). The use of short-lived organisms is the norm and provides an opportunity to study multigenerational effects of plastic pollution. However, great care must be taken in any attempt to extrapolate laboratory studies to spatially and temporally relevant scales for processes, ecological interactions and ecosystems.

7.2. Knowledge gaps and key research questions

This review highlights several major gaps in our understanding of what happens to microplastics and nanoplastics in soils and their ecological consequences. Some broad issues and key questions are briefly summarised below.

1. Shortcomings in defining and standardising parameters for determining magnitude of microplastic and nanoplastic contamination on land; e.g.

- What cost-efficient techniques can we use to detect, isolate, measure, and identify microplastics and nanoplastics in soils, and in organisms?
- Can artificially generated micro and nanoplastics be used as suitable models to gain an understanding of their potential ecotoxicity?

2. Improve understanding of the dynamics and fate of microplastics and nanoplastics in soils; e.g.

- What is the concentration of microplastics and nanoplastics in soils from each major pollution source?
- How do the products of fragmented plastic particles behave in the soil profile?
- How does the interaction of plastic particles with agrochemicals affect their behaviour?

3. Determine the bioavailability of plastic particles to plants and soil organisms; e.g.

- What are the features of plants and soil organisms that determine uptake, the capacity to exclude, or the capacity to isolate or sequester plastic particles internally?

4. Insufficient understanding of the consequences on plants and soil biota; e.g.

- What are the physical, physiological, and biochemical impacts of plastic residues – polymer, additives and their degradation products – within plants or soil organisms?
- How do nanoplastics affect the microbiome in phyllosphere, endosphere, spermosphere and rhizosphere of the plant?
- Do plastic pollution alter plant and soil biota response to other existing agrochemical or environmental stressors?
- What is the impacts of plastic pollution on the capacity of the agroecosystem to produce biomass?

8. Concluding remarks

Currently, considerable uncertainty exists because of the limited number of studies that have been published regarding the impact of microplastic and nanoplastic on most trophic levels in agroecosystems – demonstrated evidence of effects and demonstrated evidence of no-effects are equally few at this point in time. The existing regulations based on heavy metal contaminants and available nitrogen for land application of biosolids provide us with the possibility to estimate plastic loading in some agroecosystems. We could then use these loading rates to set up ecotoxicology experiments to determine if these loadings would pose acceptable ecological risk and if not, at what loading concentration would there be a problem.

Based on the mechanisms and constraints described above, the degradation of plastics applied to land is expected to be limited within the timescale of a human lifetime. As such, precautionary measures, even if the cause and effect relationships are not established for agroecosystems, may be warranted. Ultimately, many actions to mitigate microplastic and nanoplastic emissions on land will also benefit the wider environment. They are also likely to be less costly in the long-term and allow us to reap the benefits of plastics with much lower plastic pollution on land and in water.

Acknowledgements

This work was supported by funding from the Australia-China Joint Research Centre – Healthy Soils for Sustainable Food Production and Environmental Quality (ACSRF48165) and its industry partners including BASF, Incitec Pivot and Xinyangfeng. Special thanks to Pablo Galaviz for help with the diagrams; David Ugalde and seven other anonymous reviewers for their detailed comments that has immensely benefitted the ideas expressed in this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.01.341.

References

American Society of Chemistry National Historic Chemical Landmarks, 1993. Bakelite: The World's First Synthetic Plastic [WWW Document]. URL. https://www.acs.org/content/acs/en/education/whatischemistry/landmarks/bakelite.html, Accessed date: 19 February 2017.

Artham, T., Sudhakar, M., Venkatesan, R., Madhavan Nair, C.s, Murty, K.V.G.K., Doble, M., 2009. Biofouling and stability of synthetic polymers in sea water. Int. Biodeterior. Biodegrad. 63:884–890. https://doi.org/10.1016/j.ibiod.2009.03.003.

AS4454, 2012. Australian Standard Composts, Soil Conditioners and Mulches. SAI Global Ltd. under licence from Standards Australia (80 p).

Australian and New Zealand Biosolids Partnership, 2016. Australian Biosolids Statistics [WWW Document]. URL. https://www.biosolids.com.au/guidelines/australian-biosolids-statistics/, Accessed date: 15 February 2017.

Bandmann, V., Müller, J.D., Köhler, T., Homann, U., 2012. Uptake of fluorescent nano beads into BY2-cells involves clathrin-dependent and clathrin-independent endocytosis. FEBS Lett. 586:3626–3632. https://doi.org/10.1016/j.febslet.2012.08.008.

Besseling, E., Wang, B., Lürling, M., Koelmans, A.A., 2014. Nanoplastic affects growth of S. obliquus and reproduction of D. magna. Environ. Sci. Technol. 48:12336–12343. https://doi.org/10.1021/es503001d.

Bhattacharya, P., Lin, S., Turner, J.P., Ke, P.C., 2010. Physical adsorption of charged plastic nanoparticles affects algal photosynthesis. J. Phys. Chem. C 114:16556–16561. https://doi.org/10.1021/jp1054759.

Blouin, M., Hodson, M.E., Delgado, E.A., Baker, G., Brussaard, L., Butt, K.R., Dai, J., Dendooven, L., Peres, G., Tondoh, J.E., Cluzeau, D., Brun, J.-J., 2013. A review of earthworm impact on soil function and ecosystem services. Eur. J. Soil Sci. 64:161–182. https://doi.org/10.1111/ejss.12025.

Bombelli, P., Howe, C.J., Bertocchini, F., 2017. Polyethylene bio-degradation by caterpillars of the wax moth Galleria mellonella. Curr. Biol. 27:R292–R293. https://doi.org/10.1016/j.cub.2017.02.060.

Boucher, J., Friot, D., 2017. Primary Microplastics in the Ocean: A Global Evaluation of Sources (Gland, Switzerland).

Bouranis, D.L., Theodoropoulos, A.G., Drossopoulos, J.B., 1995. Designing synthetic polymers as soil conditioners. Commun. Soil Sci. Plant Anal. 26:1455–1480. https://doi.org/10.1080/00103629509369384.

Bouwmeester, H., Hollman, P.C.H., Peters, R.J.B., 2015. Potential health impact of environmentally released micro- and nanoplastics in the human food production chain: experiences from nanotoxicology. Environ. Sci. Technol. 49:8932–8947. https://doi.org/10.1021/acs.est.5b01090.

Brinton, W.F., 2005. Characterization of man-made foreign matter and its presence in multiple size fractions from mixed waste composting. Compost Sci. Util. 13: 274–280. https://doi.org/10.1080/1065657X.2005.10702251.

Browne, M.A., Dissanayake, A., Galloway, T.S., Lowe, D.M., Thompson, R.C., 2008. Ingested microscopic plastic translocates to the circulatory system of the mussel, Mytilus edulis (L.). Environ. Sci. Technol. 42:5026–5031. https://doi.org/10.1021/es800249a.

Browne, M.A., Underwood, A.J., Chapman, M.G., Williams, R., Thompson, R.C., van Franeker, J.A., 2015. Linking effects of anthropogenic debris to ecological impacts. Proc. R. Soc. B Biol. Sci. 282.

Calderón-Preciado, D., Matamoros, V., Bayona, J.M., 2011. Occurrence and potential crop uptake of emerging contaminants and related compounds in an agricultural irrigation network. Sci. Total Environ. 412–413:14–19. https://doi.org/10.1016/j.scitotenv.2011.09.057.

Cao, D., Xiao, W., Luo, X., Liu, G., Zheng, H., 2017. Effects of polystyrene microplastics on the fitness of earthworms in an agricultural soil. IOP Conf. Ser. Earth Environ. Sci. 61, 12148.

Carlsson, D.J., Wiles, D.M., 1976. The photooxidative degradation of polypropylene. Part I. Photooxidation and photoinitiation processes. J. Macromol. Sci. Part C 14:65–106. https://doi.org/10.1080/15321797608076113.

Carpita, N., Sabularse, D., Montezinos, D., Delmer, D.P., 1979. Determination of the pore size of cell walls of living plant cells. Science 80 (205), 1144–1147.

Casado, M.P., Macken, A., Byrne, H.J., 2013. Ecotoxicological assessment of silica and polystyrene nanoparticles assessed by a multitrophic test battery. Environ. Int. 51: 97–105. https://doi.org/10.1016/j.envint.2012.11.001.

Clotfelter, E.D., Bell, A.M., Levering, K.R., 2004. The role of animal behaviour in the study of endocrine-disrupting chemicals. Anim. Behav. 68:665–676. https://doi.org/10.1016/j.anbehav.2004.05.004.

Coppock, R.L., Cole, M., Lindeque, P.K., Queirós, A.M., Galloway, T.S., 2017. A small-scale, portable method for extracting microplastics from marine sediments. Environ. Pollut. 230:829–837. https://doi.org/10.1016/j.envpol.2017.07.017.

David, C., Trojan, M., Daro, A., Demarteau, W., 1992. Photodegradation of polyethylene: comparison of various photoinitiators in natural weathering conditions. Polym. Degrad. Stab. 37:233–245. https://doi.org/10.1016/0141-3910(92)90165-2.

Duis, K., Coors, A., 2016. Microplastics in the aquatic and terrestrial environment: sources (with a specific focus on personal care products), fate and effects. Environ. Sci. Eur. 28:1–25. https://doi.org/10.1186/s12302-015-0069-y.

EFSA Panel on Contaminants in the Food Chain, 2016. Presence of microplastics and nanoplastics in food, with particular focus on seafood. EFSA J. 14, e04501. https://doi.org/10.2903/j.efsa.2016.4501.

Eggen, T., Heimstad, E.S., Stuanes, A.O., Norli, H.R., 2013. Uptake and translocation of organophosphates and other emerging contaminants in food and forage crops. Environ. Sci. Pollut. Res. 20:4520–4531. https://doi.org/10.1007/s11356-012-1363-5.

Eldridge, S.M., Chan, K.Y., Xu, Z.H., Chen, C.R., Barchia, I., 2008. Plant-available nitrogen supply from granulated biosolids: implications for land application guidelines. Soil Res. 46, 423–436.

EPA-NSW, 1997. Environmental Guidelines: Use and Disposal of Biosolid Products (Chatswood, NSW, Australia).

Espí, E., Salmerón, A., Fontecha, A., García, Y., Real, A.I., 2006. PLastic films for agricultural applications. J. Plast. Film Sheeting 22:85–102. https://doi.org/10.1177/8756087906064220.

EU Directive 86/278/EEC, 1986. Council Directive on the Protection of the Environment, and in Particular of the Soil, When Sewage Sludge is Used in Agriculture.

Foruzanmehr, M., Elkoun, S., Fam, A., Robert, M., 2015. Degradation characteristics of new bio-resin based-fiber-reinforced polymers for external rehabilitation of structures. J. Compos. Mater. 50:1227–1239. https://doi.org/10.1177/0021998315590262.

Galloway, T.S., Cole, M., Lewis, C., 2017. Interactions of microplastic debris throughout the marine ecosystem. Nat. Ecol. Evol. 1, 116.

Gao, D.-W., Wen, Z.-D., 2016. Phthalate esters in the environment: a critical review of their occurrence, biodegradation, and removal during wastewater treatment processes. Sci. Total Environ. 541:986–1001. https://doi.org/10.1016/j.scitotenv.2015.09.148.

Gardette, M., Perthue, A., Gardette, J.-L., Janecska, T., Földes, E., Pukánszky, B., Therias, S., 2013. Photo- and thermal-oxidation of polyethylene: comparison of mechanisms and influence of unsaturation content. Polym. Degrad. Stab. 98:2383–2390. https://doi.org/10.1016/j.polymdegradstab.2013.07.017.

GESAMP, 2015. Sources, Fate and Effects of Microplastics in the Marine Environment: A Global Assessment.

Geyer, R., Jambeck, J.R., Law, K.L., 2017. Production, use, and fate of all plastics ever made. Sci. Adv. 3, e1700782.

Ghosal, D., Ghosh, S., Dutta, T.K., Ahn, Y., 2016. Current state of knowledge in microbial degradation of polycyclic aromatic hydrocarbons (PAHs): a review. Front. Microbiol. 7:1369. https://doi.org/10.3389/fmicb.2016.01369.

Gigault, J., Pedrono, B., Maxit, B., Ter Halle, A., 2016. Marine plastic litter: the unanalyzed nano-fraction. Environ. Sci. Nano 3:346–350. https://doi.org/10.1039/c6en00008h.

Gómez-Brandón, M., Aira, M., Lores, M., Domínguez, J., 2011. Epigeic earthworms exert a bottleneck effect on microbial communities through gut associated processes. PLoS One 6, e24786. https://doi.org/10.1371/journal.pone.0024786.

Göpferich, A., 1997. Polymer bulk erosion. Macromolecules 30:2598–2604. https://doi.org/10.1021/ma961627y.

Grassie, N., Weir, N.A., 1965. The photooxidation of polymers. III. Photooxidation of polystyrene. J. Appl. Polym. Sci. 9:987–998. https://doi.org/10.1002/app.1965.070090316.

Hawkins, W.L., 1964. Thermal and oxidative degradation of polymers. Polym. Eng. Sci. 4: 187–192. https://doi.org/10.1002/pen.760040309.

Horton, A.A., Walton, A., Spurgeon, D.J., Lahive, E., Svendsen, C., 2017. Microplastics in freshwater and terrestrial environments: evaluating the current understanding to identify the knowledge gaps and future research priorities. Sci. Total Environ. 586: 127–141. https://doi.org/10.1016/j.scitotenv.2017.01.190.

Huerta Lwanga, E., Gertsen, H., Gooren, H., Peters, P., Salánki, T., Van Der Ploeg, M., Besseling, E., Koelmans, A.A., Geissen, V., 2016. Microplastics in the terrestrial ecosystem: implications for Lumbricus terrestris (Oligochaeta, Lumbricidae). Environ. Sci. Technol. 50:2685–2691. https://doi.org/10.1021/acs.est.5b05478.

Huerta Lwanga, E., Gertsen, H., Gooren, H., Peters, P., Salánki, T., van der Ploeg, M., Besseling, E., Koelmans, A.A., Geissen, V., 2017. Incorporation of microplastics from litter into burrows of Lumbricus terrestris. Environ. Pollut. 220:523–531. https://doi.org/10.1016/j.envpol.2016.09.096.

Huerta L, E., Mendoza Vega, J., Ku Quej, V., de los A. Chi, J., Sanchez del Cid, L., Chi, C., Escalona Segura, G., Gertsen, H., Salánki, T., van der Ploeg, M., Koelmans, A.A., Geissen, V., 2017. Field evidence for transfer of plastic debris along a terrestrial food chain. Sci. Rep. 7:14071. https://doi.org/10.1038/s41598-017-14588-2.

Huerta Lwanga, E., Thapa, B., Yang, X., Gertsen, H., Salánki, T., Geissen, V., Garbeva, P., 2018. Decay of low-density polyethylene by bacteria extracted from earthworm's guts: a potential for soil restoration. Sci. Total Environ. 624:753–757. https://doi.org/10.1016/j.scitotenv.2017.12.144.

Husen, A., Siddiqi, K.S., 2014. Carbon and fullerene nanomaterials in plant system. J. Nanobiotechnol. 12:16. https://doi.org/10.1186/1477-3155-12-16.

Hussain, N., Jaitley, V., Florence, A.T., 2001. Recent advances in the understanding of uptake of microparticulates across the gastrointestinal lymphatics. Adv. Drug Deliv. Rev. 50:107–142. https://doi.org/10.1016/S0169-409X(01)00152-1.

Hyung, H., Kim, J.-H., 2008. Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: effect of NOM characteristics and water quality parameters. Environ. Sci. Technol. 42:4416–4421. https://doi.org/10.1021/es702916h.

Imfeld, G., Vuilleumier, S., 2012. Measuring the effects of pesticides on bacterial communities in soil: a critical review. Eur. J. Soil Biol. 49:22–30. https://doi.org/10.1016/j.ejsobi.2011.11.010.

Jabarin, S.A., Lofgren, E.A., 1984. Thermal stability of polyethylene terephthalate. Polym. Eng. Sci. 24:1056–1063. https://doi.org/10.1002/pen.760241311.

Jager, T., 2016. Predicting environmental risk: a road map for the future. J. Toxicol. Environ. Health, Part A 79:572–584. https://doi.org/10.1080/15287394.2016.1171986.

Jessup, C.M., Kassen, R., Forde, S.E., Kerr, B., Buckling, A., Rainey, P.B., Bohannan, B.J.M., 2004. Big questions, small worlds: microbial model systems in ecology. Trends Ecol. Evol. 19, 189–197.

Katz, L.C., Iarovici, D.M., 1990. Green fluorescent latex microspheres: a new retrograde tracer. Neuroscience 34:511–520. https://doi.org/10.1016/0306-4522(90)90159-2.

Kawai, F., 2010. The biochemistry and molecular biology of xenobiotic polymer degradation by microorganisms. Biosci. Biotechnol. Biochem. 74:1743–1759. https://doi.org/10.1271/bbb.100394.

Kiyama, Y., Miyahara, K., Ohshima, Y., 2012. Active uptake of artificial particles in the nematode Caenorhabditis elegans. J. Exp. Biol. 215:1178–1183. https://doi.org/10.1242/jeb.067199.

Koelmans, A.A., Nowack, B., Wiesner, M.R., 2009. Comparison of manufactured and black carbon nanoparticle concentrations in aquatic sediments. Environ. Pollut. 157: 1110–1116. https://doi.org/10.1016/j.envpol.2008.09.006.

Koelmans, A.A., Besseling, E., Shim, W.J., 2015. Nanoplastics in the aquatic environment. In: Bergmann, M., Gutow, L., Klages, M. (Eds.), Critical Review BT - Marine Anthropogenic Litter. Springer International Publishing, Cham:pp. 325–340 https://doi.org/10.1007/978-3-319-16510-3_12.

Kole, C., Kole, P., Randunu, K.M., Choudhary, P., Podila, R., Ke, P.C., Rao, A.M., Marcus, R.K., 2013. Nanobiotechnology can boost crop production and quality: first evidence from increased plant biomass, fruit yield and phytomedicine content in bitter melon (Momordica charantia). BMC Biotechnol. 13. https://doi.org/10.1186/1472-6750-13-37.

Kyrikou, I., Briassoulis, D., 2007. Biodegradation of agricultural plastic films: a critical review. J. Polym. Environ. 15:125–150. https://doi.org/10.1007/s10924-007-0053-8.

Lambert, S., Wagner, M., 2016. Characterisation of nanoplastics during the degradation of polystyrene. Chemosphere 145:265–268. https://doi.org/10.1016/j.chemosphere.2015.11.078.

Lee, J.H., Khang, G., Lee, J.W., Lee, H.B., 1998. Interaction of different types of cells on polymer surfaces with wettability gradient. J. Colloid Interface Sci. 205:323–330. https://doi.org/10.1006/jcis.1998.5688.

Lin, S., Reppert, J., Hu, Q., Hudson, J.S., Reid, M.L., Ratnikova, T.A., Rao, A.M., Luo, H., Ke, P.C., 2009. Uptake, translocation, and transmission of carbon nanomaterials in rice plants. Small 5:1128–1132. https://doi.org/10.1002/smll.200801556.

Liu, Q., Chen, B., Wang, Q., Shi, X., Xiao, Z., Lin, J., Fang, X., 2009. Carbon nanotubes as molecular transporters for walled plant cells. Nano Lett. 9:1007–1010. https://doi.org/10.1021/nl803083u.

Liu, E.K., He, W.Q., Yan, C.R., 2014. “White revolution” to “white pollution” - agricultural plastic film mulch in China. Environ. Res. Lett. 9. https://doi.org/10.1088/1748-9326/9/9/091001.

Ma, X., Geiser-Lee, J., Deng, Y., Kolmakov, A., 2010. Interactions between engineered nanoparticles (ENPs) and plants: phytotoxicity, uptake and accumulation. Sci. Total Environ. 408:3053–3061. https://doi.org/10.1016/j.scitotenv.2010.03.031.

Maaß, S., Daphi, D., Lehmann, A., Rillig, M.C., 2017. Transport of microplastics by two collembolan species. Environ. Pollut. 225:456–459. https://doi.org/10.1016/j.envpol.2017.03.009.

Meeker, J.D., Sathyanarayana, S., Swan, S.H., 2009. Phthalates and other additives in plastics: human exposure and associated health outcomes. Philos. Trans. R. Soc. B Biol. Sci. 364:2097–2113. https://doi.org/10.1098/rstb.2008.0268.

Mohan, K., 2011. Microbial deterioration and degradation of polymeric materials. J. Biochem. Technol. 2, 210–215.

Mohapatra, D.P., Cledón, M., Brar, S.K., Surampalli, R.Y., 2016. Application of wastewater and biosolids in soil: occurrence and fate of emerging contaminants. Water Air Soil Pollut. 227. https://doi.org/10.1007/s11270-016-2768-4.

Morales-Díaz, A.B., Ortega-Ortíz, H., Juárez-Maldonado, A., Cadenas-Pliego, G., González-Morales, S., Benavides-Mendoza, A., 2017. Application of nanoelements in plant nutrition and its impact in ecosystems. Adv. Nat. Sci. Nanosci. Nanotechnol. 8. https://doi.org/10.1088/2043-6254/8/1/013001.

Nel, A.E., Mädler, L., Velegol, D., Xia, T., Hoek, E.M.V., Somasundaran, P., Klaessig, F., Castranova, V., Thompson, M., 2009. Understanding biophysicochemical interactions at the nano-bio interface. Nat. Mater. 8:543–557. https://doi.org/10.1038/nmat2442.

Nguyen, T.Q., 2008. Polymer degradation and stabilization. Handbook of Polymer Reaction Engineering. Wiley-VCH Verlag GmbH:pp. 757–831 https://doi.org/10.1002/9783527619870.ch15.

Nizzetto, L., Futter, M., Langaas, S., 2016. Are agricultural soils dumps for microplastics of urban origin? Environ. Sci. Technol. 50:10777–10779. https://doi.org/10.1021/acs.est.6b04140.

Nolte, T.M., Hartmann, N.B., Kleijn, J.M., Garnæs, J., van de Meent, D., Jan Hendriks, A., Baun, A., 2017a. The toxicity of plastic nanoparticles to green algae as influenced by surface modification, medium hardness and cellular adsorption. Aquat. Toxicol. 183:11–20. https://doi.org/10.1016/j.aquatox.2016.12.005.

Nolte, T.M., Peijnenburg, W.J.G.M., Hendriks, A.J., van de Meent, D., 2017b. Quantitative structure-activity relationships for green algae growth inhibition by polymer particles. Chemosphere 179:49–56. https://doi.org/10.1016/j.chemosphere.2017.03.067.

Oehlmann, J., Schulte-Oehlmann, U., Kloas, W., Jagnytsch, O., Lutz, I., Kusk, K.O., Wollenberger, L., Santos, E.M., Paull, G.C., VanLook, K.J.W., Tyler, C.R., 2009. A critical analysis of the biological impacts of plasticizers on wildlife. Philos. Trans. R. Soc. B Biol. Sci. 364:2047–2062. https://doi.org/10.1098/rstb.2008.0242.

Palma, G., Carenza, M., 1970. Degradation of poly(vinyl chloride). I. Kinetics of thermal and radiation-induced dehydrochlorination reactions at low temperatures. J. Appl. Polym. Sci. 14:1737–1754. https://doi.org/10.1002/app.1970.070140708.

Petersen, E.J., Diamond, S.A., Kennedy, A.J., Goss, G.G., Ho, K., Lead, J., Hanna, S.K., Hartmann, N.B., Hund-Rinke, K., Mader, B., Manier, N., Pandard, P., Salinas, E.R., Sayre, P., 2015. Adapting OECD aquatic toxicity tests for use with manufactured nanomaterials: key issues and consensus recommendations. Environ. Sci. Technol. 49:9532–9547. https://doi.org/10.1021/acs.est.5b00997.

Potts, J.E., Clendinning, R.A., Ackart, W.B., Niegisch, W.D., 1973. The biodegradability of synthetic polymers. In: Guillet, J. (Ed.), Polymers and Ecological Problems. Springer US, Boston, MA:pp. 61–79 https://doi.org/10.1007/978-1-4684-0871-3_4.

Rabek, J.F., Rånby, B., 1975. Role of singlet oxygen in photo-oxidative degradation and photostabilization of polymers. Polym. Eng. Sci. 15:40–43. https://doi.org/10.1002/pen.760150107.

Ramos, L., Berenstein, G., Hughes, E.A., Zalts, A., Montserrat, J.M., 2015. Polyethylene film incorporation into the horticultural soil of small periurban production units in Argentina. Sci. Total Environ. 523:74–81. https://doi.org/10.1016/j.scitotenv.2015.03.142.

Reed, A.M., Gilding, D.K., 1981. Biodegradable polymers for use in surgery — poly (glycolic)/poly(lactic acid) homo and copolymers: 2. In vitro degradation. Polymer (Guildf.) 22:494–498. https://doi.org/10.1016/0032-3861(81)90168-3.

Reisser, J., Shaw, J., Hallegraeff, G., Proietti, M., Barnes, D.K.A., Thums, M., Wilcox, C., Hardesty, B.D., Pattiaratchi, C., 2014. Millimeter-sized marine plastics: a new pelagic habitat for microorganisms and invertebrates. PLoS One 9. https://doi.org/10.1371/journal.pone.0100289.

Rembaum, A., Dreyer, W.J., 1980. Immunomicrospheres: reagents for cell labeling and separation. Science 80 (208), 364.

Rico, C.M., Majumdar, S., Duarte-Gardea, M., Peralta-Videa, J.R., Gardea-Torresdey, J.L., 2011. Interaction of nanoparticles with edible plants and their possible implications in the food chain. J. Agric. Food Chem. 59:3485–3498. https://doi.org/10.1021/jf104517j.

Rillig, M.C., 2012. Microplastic in terrestrial ecosystems and the soil? Environ. Sci. Technol. 46:6453–6454. https://doi.org/10.1021/es302011r.

Rillig, M.C., Ziersch, L., Hempel, S., 2017. Microplastic transport in soil by earthworms. Sci. Rep. 7:1362. https://doi.org/10.1038/s41598-017-01594-7.

Rochman, C.M., Browne, M.A., Underwood, A.J., van Franeker, J.A., Thompson, R.C., Amaral-Zettler, L.A., 2016. The ecological impacts of marine debris: unraveling the demonstrated evidence from what is perceived. Ecology 97:302–312. https://doi.org/10.1890/14-2070.1.

Rodriguez-Seijo, A., Lourenço, J., Rocha-Santos, T.A.P., da Costa, J., Duarte, A.C., Vala, H., Pereira, R., 2017. Histopathological and molecular effects of microplastics in Eisenia andrei Bouché. Environ. Pollut. 220:495–503. https://doi.org/10.1016/j.envpol.2016.09.092.

Rohr, J.R., Salice, C.J., Nisbet, R.M., 2016. The pros and cons of ecological risk assessment based on data from different levels of biological organization. Crit. Rev. Toxicol. 46: 756–784. https://doi.org/10.1080/10408444.2016.1190685.

Sandermann Jr., H., 1992. Plant metabolism of xenobiotics. Trends Biochem. Sci. 17: 82–84. https://doi.org/10.1016/0968-0004(92)90507-6.

Savoca, M.S., Wohlfeil, M.E., Ebeler, S.E., Nevitt, G.A., 2016. Marine plastic debris emits a keystone infochemical for olfactory foraging seabirds. Sci. Adv. 2.

Scandalios, J.G., 2001. Molecular responses to oxidative stress. In: Hawkesford, M.J., Buchner, P. (Eds.), Molecular Analysis of Plant Adaptation to the Environment. Springer, Netherlands, pp. 181–208.

Schettini, E., Stefani, L., Vox, G., 2014. Interaction between agrochemical contaminants and UV stabilizers for greenhouse EVA plastic films. Appl. Eng. Agric. 30:229–239. https://doi.org/10.13031/aea.30.10048.

Shen, C.-X., Zhang, Q.-F., Li, J., Bi, F.-C., Yao, N., 2010. Induction of programmed cell death in Arabidopsis and rice by single-wall carbon nanotubes. Am. J. Bot. 97:1602–1609. https://doi.org/10.3732/ajb.1000073.

Simpson, M.J., Hatcher, P.G., 2004. Overestimates of black carbon in soils and sediments. Naturwissenschaften 91:436–440. https://doi.org/10.1007/s00114-004-0550-8.

Singh, B., Sharma, N., 2008. Mechanistic implications of plastic degradation. Polym. Degrad. Stab. 93:561–584. https://doi.org/10.1016/j.polymdegradstab.2007.11.008.

Staples, C.A., Peterson, D.R., Parkerton, T.F., Adams, W.J., 1997. The environmental fate of phthalate esters: a literature review. Chemosphere 35:667–749. https://doi.org/10.1016/S0045-6535(97)00195-1.

Steinmetz, Z., Wollmann, C., Schaefer, M., Buchmann, C., David, J., Tröger, J., Muñoz, K., Frör, O., Schaumann, G.E., 2016. Plastic mulching in agriculture. Trading short-term agronomic benefits for long-term soil degradation? Sci. Total Environ. 550: 690–705. https://doi.org/10.1016/j.scitotenv.2016.01.153.

Syberg, K., Khan, F.R., Selck, H., Palmqvist, A., Banta, G.T., Daley, J., Sano, L., Duhaime, M.B., 2015. Microplastics: addressing ecological risk through lessons learned. Environ. Toxicol. Chem. 34:945–953. https://doi.org/10.1002/etc.2914.

Talsness, C.E., Andrade, A.J.M., Kuriyama, S.N., Taylor, J.A., Saal, F.S.V., 2009. Components of plastic: experimental studies in animals and relevance for human health. Philos. Trans. R. Soc. B Biol. Sci. 364:2079–2096. https://doi.org/10.1098/rstb.2008.0281.

Tan, X.-m., Lin, C., Fugetsu, B., 2009. Studies on toxicity of multi-walled carbon nanotubes on suspension rice cells. Carbon N. Y. 47:3479–3487. https://doi.org/10.1016/j.carbon.2009.08.018.

Taylor, M.L., Gwinnett, C., Robinson, L.F., Woodall, L.C., 2016. Plastic microfibre ingestion by deep-sea organisms. Sci. Rep. 6, 33997.

Teuten, E.L., Saquing, J.M., Knappe, D.R.U., Barlaz, M.A., Jonsson, S., Björn, A., Rowland, S.J., Thompson, R.C., Galloway, T.S., Yamashita, R., Ochi, D., Watanuki, Y., Moore, C., Viet, P.H., Tana, T.S., Prudente, M., Boonyatumanond, R., Zakaria, M.P., Akkhavong, K., Ogata, Y., Hirai, H., Iwasa, S., Mizukawa, K., Hagino, Y., Imamura, A., Saha, M., Takada, H., 2009. Transport and release of chemicals from plastics to the environment and to wildlife. Philos. Trans. R. Soc. B Biol. Sci. 364:2027–2045. https://doi.org/10.1098/rstb.2008.0284.

Thomas, N.L., Clarke, J., McLauchlin, A.R., Patrick, S.G., 2012. Oxodegradable plastics: degradation, environmental impact and recycling. Proc. Inst. Civ. Eng. Waste Resour. Manag. 165:133–140. https://doi.org/10.1680/warm.11.00014.

Torre-Roche, R.D.L., Hawthorne, J., Deng, Y., Xing, B., Cai, W., Newman, L.A., Wang, Q., Ma, X., Hamdi, H., White, J.C., 2013. Multiwalled carbon nanotubes and C60 fullerenes differentially impact the accumulation of weathered pesticides in four agricultural plants. Environ. Sci. Technol. 47. https://doi.org/10.1021/es4034809.

Toyota, K., Kimura, M., 2000. Microbial community indigenous to the earthworm Eisenia foetida. Biol. Fertil. Soils 31, 187–190.

Trapp, S., 2000. Modelling uptake into roots and subsequent translocation of neutral and ionisable organic compounds. Pest Manag. Sci. 56:767–778. https://doi.org/10.1002/1526-4998(200009)56:9<767::AID-PS198>3.0.CO;2-Q.

USEPA 40 CFR 503, 1993. Standards for the Use or Disposal of Sewage Sludge.

Van Cauwenberghe, L., Janssen, C.R., 2014. Microplastics in bivalves cultured for human consumption. Environ. Pollut. 193:65–70. https://doi.org/10.1016/j.envpol.2014.06.010.

Wan, Y., Wang, Y., Liu, Z., Qu, X., Han, B., Bei, J., Wang, S., 2005. Adhesion and proliferation of OCT-1 osteoblast-like cells on micro- and nano-scale topography structured poly(l-lactide). Biomaterials 26:4453–4459. https://doi.org/10.1016/j.biomaterials.2004.11.016.

Wang, J., Lv, S., Zhang, M., Chen, G., Zhu, T., Zhang, S., Teng, Y., Christie, P., Luo, Y., 2016. Effects of plastic film residues on occurrence of phthalates and microbial activity in soils. Chemosphere 151:171–177. https://doi.org/10.1016/j.chemosphere.2016.02.076.

Wang, P., Lombi, E., Zhao, F.-J., Kopittke, P.M., 2016. Nanotechnology: a new opportunity in plant sciences. Trends Plant Sci. 21:699–712. https://doi.org/10.1016/j.tplants.2016.04.005.

Wiesner, M.R., Lowry, G.V., Casman, E., Bertsch, P.M., Matson, C.W., Di Giulio, R.T., Liu, J., Hochella, M.F., 2011. Meditations on the ubiquity and mutability of nano-sized materials in the environment. ACS Nano 5:8466–8470. https://doi.org/10.1021/nn204118p.

Wright, S.L., Thompson, R.C., Galloway, T.S., 2013. The physical impacts of microplastics on marine organisms: a review. Environ. Pollut. 178:483–492. https://doi.org/10.1016/j.envpol.2013.02.031.

Yang, J., Yang, Y., Wu, W.-M., Zhao, J., Jiang, L., 2014. Evidence of polyethylene biodegradation by bacterial strains from the guts of plastic-eating waxworms. Environ. Sci. Technol. 48:13776–13784. https://doi.org/10.1021/es504038a.

Yoo, E.S., Im, S.S., 1999. Effect of crystalline and amorphous structures on biodegradability of poly(tetramethylene succinate). J. Environ. Polym. Degrad. 7:19–26. https://doi.org/10.1023/A:1021838017958.

Yoshida, S., Hiraga, K., Takehana, T., Taniguchi, I., Yamaji, H., Maeda, Y., Toyohara, K., Miyamoto, K., Kimura, Y., Oda, K., 2016. A bacterium that degrades and assimilates poly(ethylene terephthalate). Science 80 (351):1196–1199. https://doi.org/10.1126/science.aad6359.

Zhang, D., Liu, H., Hu, W., Qin, X., Ma, X., Yan, C., Wang, H., 2016. The status and distribution characteristics of residual mulching film in Xinjiang, China. J. Integr. Agric. 15: 2639–2646. https://doi.org/10.1016/S2095-3119(15)61240-0.

Zhang, S., Yang, X., Gertsen, H., Peters, P., Salánki, T., Geissen, V., 2018. A simple method for the extraction and identification of light density microplastics from soil. Sci. Total Environ. 616-617:1056–1065. https://doi.org/10.1016/j.scitotenv.2017.10.213.

Zhao, Q., Ma, C., White, J.C., Dhankher, O.P., Zhang, X., Zhang, S., Xing, B., 2017. Quantitative evaluation of multi-wall carbon nanotube uptake by terrestrial plants. Carbon N. Y. 114:661–670. https://doi.org/10.1016/j.carbon.2016.12.036.

Ziajahromi, S., Neale, P.A., Leusch, D.D.L., 2016. Wastewater treatment plant effluent as a source of microplastics: review of the fate, chemical interactions and potential risks to aquatic organisms. Water Sci. Technol. 74, 2253–2269.

Environment International 37 (2011) 226–247

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Review

Review of ‘emerging’ organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids

Bradley O. Clarke, Stephen R. Smith *

Department of Civil and Environmental Engineering, South Kensington Campus, Imperial College London, London, SW7 2AZ, United Kingdom

ARTICLE INFO

Article history:
Received 3 December 2009
Accepted 9 June 2010
Available online 24 August 2010

Keywords:
Sewage sludge
Biosolids
Land application
Antibiotics
Pharmaceuticals
Benzothiazoles
Bisphenol A
Organotins
Polybrominated diphenyl ethers
Polychlorinated alkanes
Polychlorinated naphthalenes
Polydimethylsiloxanes
Perfluorochemicals
Phthalate acid esters
Quaternary ammonium compounds
Steroids
Hormones
Synthetics musks
Triclosan
Triclocarban

ABSTRACT

A broad spectrum of organic chemicals is essential to modern society. Once discharged from industrial, domestic and urban sources into the urban wastewater collection system they may transfer to the residual solids during wastewater treatment and assessment of their significance and implications for beneficial recycling of the treated sewage sludge biosolids is required. Research on organic contaminants (OCs) in biosolids has been undertaken for over thirty years and the increasing body of evidence demonstrates that the majority of compounds studied do not place human health at risk when biosolids are recycled to farmland. However, there are 143,000 chemicals registered in the European Union for industrial use and all could be potentially found in biosolids. Therefore, a literature review of ‘emerging’ OCs in biosolids has been conducted for a selection of chemicals of potential concern for land application based upon human toxicity, evidence of adverse effects on the environment and endocrine disruption.

To identify monitoring and research priorities the selected chemicals were ranked using an assessment matrix approach. Compounds were evaluated based upon environmental persistence, human toxicity, evidence of bioaccumulation in humans and the environment, evidence of ecotoxicity and the number and quality of studies focussed on the contaminant internationally. The identified chemicals of concern were ranked in decreasing order of priority: perfluorinated chemicals (PFOS, PFOA); polychlorinated alkanes (PCAs), polychlorinated naphthalenes (PCNs); organotins (OTs), polybrominated diphenyl ethers (PBDEs), triclosan (TCS), triclocarban (TCC); benzothiazoles; antibiotics and pharmaceuticals; synthetic musks; bisphenol A, quaternary ammonium compounds (QACs), steroids; phthalate acid esters (PAEs) and polydimethylsiloxanes (PDMSs).

A number of issues were identified and recommendations for the prioritisation of further research and monitoring of 'emerging' OCs for the agricultural use of biosolids are provided. In particular, a number of ‘emerging’ OCs (PFOS, PFOA and PCAs) were identified for priority attention that are environmentally persistent and potentially toxic with unique chemical properties, or are present in large concentrations in sludge, that make it theoretically possible for them to enter human and ecological food-chains from biosolids-amended soil.

Abbreviations: <dl, Less than detection limit; ADBI, Synthetic polycyclic musk — Celestolide™; AHMI, Synthetic polycyclic musk — Phantolide™; AHTN, Synthetic polycyclic musk — Tonalide™; ATII, Synthetic polycyclic musks — Traseolide™; BFR, Brominated flame retardant; CAS, Chemical abstract service; CP, Chlorinated parrafin; DBT, Dibutyltin; DEHP, Di2-(ethylhexyl) phthalate; DPMI, Synthetic polycyclic musk — Cashmeran™; dw, Dry weight; GC, Gas chromatography; HBCB, Hexabromocyclododecane; HHCB, Synthetic polycyclic musk — Galaxolide™; HRGC, High resolution gas chromatography; IARC, International Agency for Research on Cancer; IPCS, International Programme on Chemical Safety; K_{OW}, Octanol–water partition coefficient; LCCP, Long-chain chlorinated parrafin; lPCA, Long-chain chlorinated alkane; MA, Musk ambrette; Max, Maximum concentration; MBT_{tin}, Monobutyltin; $MBT_{thiazole}$, Mercaptobenzothiazole; MCCP, Medium-chain chlorinated parrafin; Min, Minimum concentration; MK, Musk ketone; MM, Musk moskene; mPCA, Medium-chain chlorinated parrafin; MS, Mass spectrometer; MT, Musk tibetene; MX, Musk xlyene; n, Number of samples; OBT, 2-hydroxybenzothiazole; OC, Organic contaminant; OT, Organotin; PAE, Phthalate acid ester; PBB, Polybrominated biphenyl; PBDE, Polybrominated diphenyl ether; PCA, Polychlorinated alkane; PCB, Polychlorinated biphenyl; PCDD, Polychlorinated dibenzo-p-dioxin; PCDF, Polychlorinated dibenzofuran; PCN, Polychlorinated naphthalene; PDMS, Polydimethylsiloxane; PEC, Predicted environmental concentration; PFAC, Perfluoroalkyl carboxylate; PFAS, Perfluoroalkyl sulfonate; PFDA, Perfluorodecanoic acid; PFDoDA, Perfluorododecanoic acid; PFHxS, Perfluorohexane sulfonate; PFNA, Perfluorononanoic acid; PFOA, Perfluooctanoic acid; PFOS, Perfluorooctane sulfonate; PFOSA, Perfluorooctane sulfonamide; PFUnDA, Perfluoroundecanoic acid; PHS, Priority hazardous substance; PNEC, Predicted no-effect environmental concentration; POP, Persistent organic pollutant; PVC, Polyvinyl chloride; QAC, Quaternary ammonium compound; SCCP, Short-chain chlorinated parrafin; sPCA, Short-chain chlorinated parrafin; TBT, Tributyltin; TCC, Triclocarbam; TCDD, Tetrachloro dibenzo-ρ-dioxin; TCS, Triclosan; TEF, Toxicity equivalency factors; TEQ, Toxicity equivalency — TCDD equivalence; TPhT, Triphenyltin; UNEP, United Nations Environment Program; US EPA, United States Environmental Protection Agency; Vp, Vapour pressure; WFD, European Water Framework Directive; WHO, World Health Organization; WWTP, Wastewater treatment plant.

* Corresponding author. Tel.: +44 20 75946051; fax: +44 20 75941511.
E-mail address: s.r.smith@imperial.ac.uk (S.R. Smith).

0160-4120/$ – see front matter
doi:10.1016/j.envint.2010.06.004

Contents

1. Introduction

The land application of biosolids (treated sewage sludge) is the option favoured internationally for sludge management as it contributes positively to recycling nutrients, soil properties and fertility (CEC, 1986; CEC, 1991; US EPA, 1993; European Commission, 2010). Land application of biosolids is also likely to become an increasingly essential aspect of sustainable nutrient management as phosphorus resources become depleted (Steen, 1998).

Modern society depends on a large range of organic chemicals and these may ultimately enter urban wastewater. Degradation and attenuation during wastewater and sludge treatment remove significant amounts of organic contaminants (OCs). However, many OCs have lipophilic properties and hence transfer to sewages sludge and may be present in residual concentrations ranging from $<$ng kg^{-1} to % values in the dry solids depending on the initial amounts present, their lipophilicity and the extent of destruction during wastewater and sludge treatment.

Over the past thirty years a significant volume of research has been completed on this topic. Particular attention has been given to selected priority groups of persistent organic pollutants (POPs) such as chlorinated dioxins/furans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) (Wild et al., 1991; Alcock et al., 1996; Stevens et al., 2001). The body of published work on OCs in sludge covers: organochlorine pesticides (McIntyre and Lester, 1984; Clarke et al., 2010), PCBs (Alcock and Jones, 1993; Wilson et al., 1997), dioxin-like compounds (Sewart et al., 1995; Stevens et al., 2001; Clarke et al., 2008a); and more recently: chlorinated napthalenes (PCNs), PAHs, polychlorinated alkanes (PCAs), synthetic musks (Stevens et al., 2003), oestrogens (Gomes et al., 2009), organotin compounds (Voulvoulis et al., 2004; Voulvoulis and Lester, 2006) and nonyl phenol (NP) (Sjöström et al., 2008). The concentrations of 'traditional' POPs (eg PAHs, PCBs, PCDD/Fs) in sludge have declined substantially due to effective source control (Wild et al., 1990; Clarke et al., 2008a, 2010).

The 'traditional' POPs were considered as a risk to human health and the environment from biosolids land application due to their persistence, potential to bioaccumulate up foodwebs and toxicity (Chaney et al., 1996). However, hydrophobic non-ionic OCs are tightly sorbed to sludge and soil organic matter, thus reducing their bioavailablility to microorganisms and for plant uptake, but this characteristic also increases their persistence in soil (Alexander, 2000). Risk assessments also found that entry into the human foodchain resulting from biosolids land application was negligible because plant uptake is minimal (Briggs et al., 1982; O'Connor et al., 1990; Hundal et al., 2008), the strong sorption to the soil matrix prevents groundwater contamination (Wilson et al., 1996), while restrictions on surface application to pasture for grazing and the promotion of biosolids incorporation reduces the likelihood of OC accumulation by grazing animals. The assimilation of the available international research through risk assessment in the majority of studies concludes that the OCs examined do not pose a risk to human health when land applying biosolids (Dean and Suess, 1985; Jackson and Eduljee, 1994; Wild et al., 1994; Chaney et al., 1996; Schowanek et al., 2004; Eriksen et al., 2009). Nevertheless, it is recognised that continued vigilance is required to monitor and determine the significance and implications of 'emerging' OCs for the land application of biosolids.

The aim of this review is to identify research and monitoring priorities for 'emerging' OCs in biosolids, and particularly identify chemicals that may be potentially significant for agricultural use of biosolids, requiring further assessment and investigation. A list of compounds was selected and the available published information for these chemicals was critically examined and reviewed. The OCs were selected for evaluation on the basis that they exhibited one or more of the following properties: environmental persistence, bioaccumulation, toxicity or endocrine disruption. Research and monitoring priorities for the 'emerging' OCs considered have been evaluated using a matrix assessment approach to rank the chemicals of concern. The assessment of OCs was based on the following criteria:

- persistence of the OC in soil;
- potential risks to the human foodchain from biosolids land application;
- evidence of bioaccumulation in ecological receptors;
- evidence of ecotoxicity;
- the extent, quality and consistency of the research conducted.

The OCs selected for review were:

- antibiotics and pharmaceuticals
- benzothiazoles

- bisphenol A
- organotins (OTs)
- polybrominated diphenyl ethers (PBDEs)
- polychlorinated alkanes (PCAs)
- polychlorinated naphthalenes (PCNs)
- polydimethylsiloxanes (PDMSs)
- perfluorochemicals (PFCs)
- phthalate acid esters (PAEs)
- quaternary ammonium compounds (QACs)
- steroids
- synthetics musks
- triclosan (TCS) and triclocarban (TCC).

Chemical properties and structure of the selected compounds or class of compound are described in Table 1.

2. Review of emerging organic contaminants

2.1. Antibiotics and pharmaceuticals

The main transfer pathway for antibiotics and pharmaceuticals used in human medicine to enter the environment is via wastewater treatment plants (WWTPs). Antibiotics have been detected in sewage effluents (Golet et al., 2002), ground and river water (Hirsch et al., 1999; Golet et al., 2001; Kolpin et al., 2002), sewage sludge (Gobel et al., 2005), as well as soil and manure (due to veterinary use) (Golet et al., 2003). Studies on the fate of antibiotics and pharmaceuticals in wastewater, surface water and biosolids are primarily motivated by the question of whether antibiotics in the environment may contribute to the spread of antibiotic resistant bacterial pathogens (McArdell et al., 2003). However, concern regarding antibiotics and pharmaceuticals is also driven by understanding the ecological consequences of widespread environmental contamination and the possible entry of pharmaceuticals into the human foodchain (Daughton and Ternes, 1999; Thiele-Bruhn, 2003).

The chemical properties of antibiotics and pharmaceuticals can vary widely, however many contain a non-polar core with a polar functional moiety (Thiele-Bruhn, 2003). The varying chemical properties will influence the behaviour of the chemical through wastewater treatment as well as the mobility, persistence and bioavailability in the soil matrix. Antibiotics can be categorised into the following groups:

- fluoroquinolone (FQ)
- sulfonamide (SA)
- penicillin (PE)
- cephalosporin (CE)
- nitroimidazole (NI)
- tetracycline (TC)
- macrolide (MA)

In a study of antibiotics in Swedish WWTP, the most commonly detected antibiotics were: norfloxacin, ofloxacin, ciprofloxacin, trimethoprim, sulfamethoozole and doxycycline. Norfloxacin, ofloxacin, ciprofloxacin and doxycycline were the main antibiotics detected in sludge at the low mg kg^{-1} dry weight (dw) range (Lindberg et al., 2005). A mass balance study indicated that these chemicals passed unchanged through the WWTP and concentrations could be predicted based upon consumption and use data (Lindberg et al., 2005). Similar concentrations (low mg kg^{-1} dw) were reported in a Swiss study that detected ciprofloxacin and norfloxacin in sewage sludge (Golet et al., 2002). These compounds were also measured in biosolids-amended soil 21 months after application in the μg kg^{-1} dw range (Golet et al., 2003). The longer environmental persistence of antibiotics in biosolids-amended soil is apparently in contrast to aquatic environments, where degradation occurs in a matter of days (Andreozzi et al., 2003), and could be explained by increased sorption to the sludge/soil matrix reducing bioavailability for microbial biodegradation (Alexander, 2000; Drillia et al., 2005; Williams and Adamsen, 2006). Greenhouse plant uptake experiments have demonstrated that certain compounds, such as carbamazepine and sulfamethazine, can be translocated from the soil matrix and into the aerial plant components (Dolliver et al., 2007; Winker et al., 2010). However, the risk of human exposure via this pathway is considered low and unlikely to exceed acceptable daily intakes (Thiele-Bruhn, 2003; Boxall et al., 2006).

A recent Norwegian risk assessment (Eriksen et al., 2009) screened pharmaceutical compounds in sludge against consumption, estimated mass entering WWTP, human metabolism, biodegradation and behaviour in WWTP. Of the 1400 pharmaceutical compounds currently prescribed in Norway and screened in the risk assessment, only 14 were identified for further detailed investigation. The predicted environmental concentration (PEC) and the predicted no-effect environmental concentration (PNEC) of these compounds are presented in Table 2. The concentrations of drug substances in agricultural soils amended with biosolids were estimated to be <1 mg kg^{-1} dw and were significantly below the estimated soil PNEC values. The overall conclusion was that drug substances in sewage sludge constitute a low risk to the soil compartment (Eriksen et al., 2009).

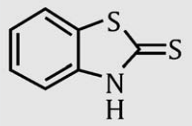
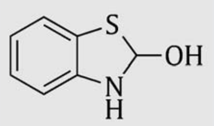
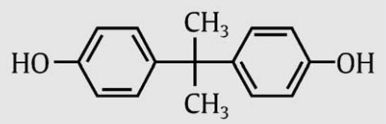
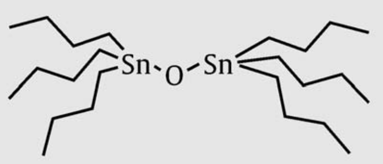
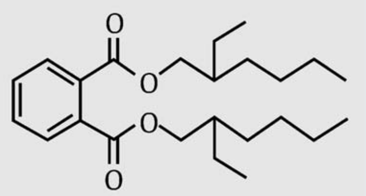
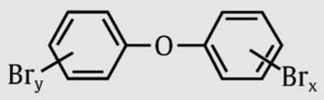
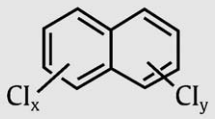
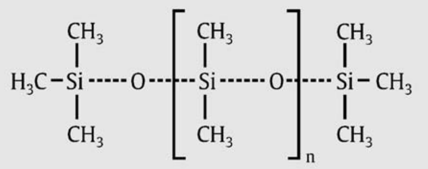
A survey of US biosolids found that, for 72 pharmaceuticals, two (viz. ciprofloxacin, diphenhydramine) were found in all samples ($n = 84$) and eight were found in at least 80 of the biosolids samples analysed. However, 15 pharmaceuticals were not found in any sample and 29 were present in fewer than three samples (US EPA, 2009). Many of the compounds identified as priorities in the Norwegian biosolids risk assessment were not included for analysis in the US biosolids survey. However, maximum concentrations of tetracycline (range: 0.04–5.3 and mean: 1.3 mg kg^{-1} dw) and ciprofloxacin (range: 0.08–41.0 and mean: 10.5 mg kg^{-1} dw) measured in the US survey (Table 3) were 12 and 24 times larger, respectively, than the amounts estimated in sludge for risk assessment by Eriksen et al. (2009). Nevertheless, applying these factors to the Norwegian $soil_{PEC}$ for the drug compounds (Eriksen et al., 2009) still results in a value that is well below the estimated $soil_{PNEC}$.

The potential implications for human health of increased antibiotic resistance in soil bacteria are clearly a matter of concern (Nwosu, 2001). A large variety of soil-borne saprophytes including actinomycetes, fungi and bacteria are capable of synthesizing antibiotics and resistance develops in soil microbial communities to overcome the effects of natural microbial antibiotics released into the soil. However, antibiotic resistance levels may rise due to inputs of anthropogenic sources (eg antibiotics in wastes from intensively reared livestock for instance). These are apparently short-lived and return to the background level once the selection pressure has been removed, through biodegradation of the antibiotic, as there is no competitive advantage in maintaining this characteristic, which is subsequently lost from the soil microbial community (Sengeløv et al., 2003; Rysz and Alvarez, 2004). The Panel on Contaminants in the Norwegian Scientific Committee for Food Safety (Eriksen et al., 2009) noted the fluoroquinolone antibiotic drug, ciprofloxacin, could potentially lead to the development of antibacterial resistance, due to its persistence and limited mobility in soil. However, the risk assessment of biosolids application to agricultural land indicated that it was unlikely that antibacterial resistance would be promoted in treated effluent from WWTP, sewage sludge or amended soil (Eriksen et al., 2009).

2.2. Benzothiazoles

The German Government has proposed limit values in biosolids for two rubber vulcanising agents: 2-mercaptobenzothiazole ($MBT_{thiazole}$) and 2-hydroxybenzothiazole (OBT) (BMU, 2007). These chemicals, referred to as accelerators, are used for the polymerisation of sulphur with rubber (vulcanisation). They have been detected in wastewater in

Table 1
Chemical structure and properties of 'emerging' organic contaminants.

Compound	Chemical structure	Chemical properties
Benzothiazoles		
2-Mercaptobenzothiazole (MBT$_{thiazole}$)		CAS No: 149-30-4 Formula: $C_7H_5NS_2$ Log K_{OW}: 2.42 Vp: $<$0.0014 Pa (25 °C) Half-life (soil): unknown (US EPA, 1984)
2-Hydroxybenzothiazole (OBT)		CAS No: 934-34-9 Formula: C_7H_5NOS Log K_{OW}: 1.76 Vp: 466 (25 °C) Half life (soil): unknown (Reddy and Quinn, 1997)
Bisphenol A		CAS No: 56-35-9 Formula: $C_{15}H_{16}O_2$ Log K_{OW}: 3.40 Vp: 1.15×10^{-5}-0.005 Pa (20 °C) Half life (soil): days Staples et al. (1998); Oehlmann et al. (2008)
Organotin compounds		
Tributyltin (TBT) oxide		CAS No: 56-35-9 Formula: $C_{24}H_{54}OSn_2$ Log K_{OW}: 3.19–3.84 Vp: 1×10^{-3} Pa (20 °C) Half life (soil): 70 days IPCS (1990)
Phthalate acid esters		
Di (2-ethylhexyl) phthalate		CAS No: 84-74-2 Formula: $C_{16}H_{22}O_4$ Log K_{OW}: 4.31–4.79 Vp: 0.01 Pa (25 °C) Half life (soil): 23–100 days IPCS (1992)
Polybrominated diphenyl ethers (PBDEs)		CAS No: varied Formula: $C_{12}H_{(10-x,y)}Br_{x,y}O$ Log K_{OW}: 4.28–9.9 Vp: 3.85–13.3 Pa (20–25 °C) Half life (soil): 4–20 years IPCS (1994); Sellstrom et al. (2005); Eljarrat et al. (2008)
Polychlorinated alkanes (PCAs)	Numerous isomers with varying degrees of chlorine substitution. Short-chain PCAs–C_{10-13} Medium-chain PCAs–C_{14-17} Long-chain PCAs–C_{18-30}	CAS No: varied Formula: $C_xH_{(2x+2)-y}Cl_y$ Log K_{OW}: varied Vp: varied Half life (soil): unknown
Polychlorinated naphthalenes (PCNs)		CAS No: varied Formula: $C_{12}H_{(8-x,y)}Cl_{x,y}$ Log K_{OW}: 6.42–10.11 Vp: 3×10^{-11}–4.2×10^{-9} Pa Half life (soil): unknown/persistent IPCS (2001)
Polydimethylsiloxanes (PDMSs)		CAS No: varied Formula: $Me_3SiO(SiMe_2O)_nSiMe_3$; n varies between 100 and >10,000 Log K_{OW}: non-polar Vp: variable Half life (soil): 2–28 days Griessbach and Lehmann (1999)

(continued on next page)

Table 1 (*continued*)

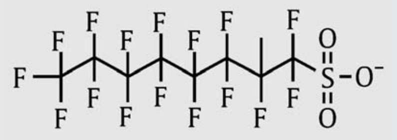
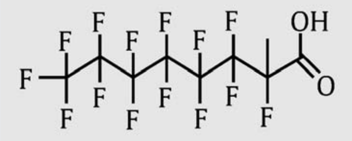
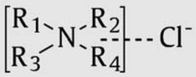
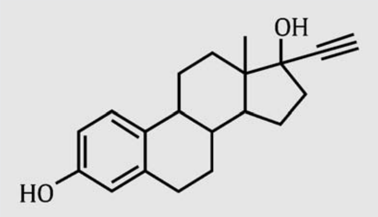
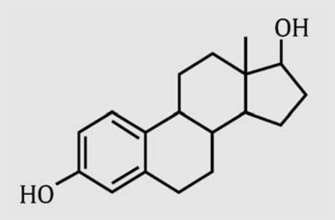
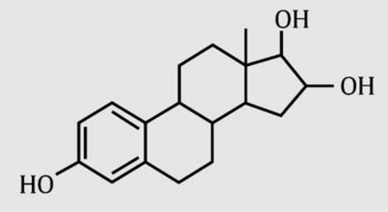
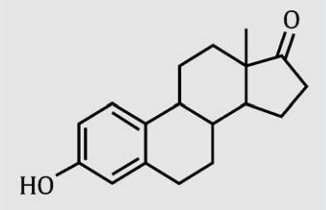
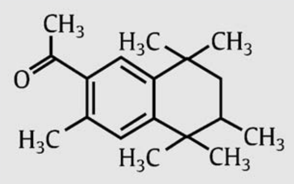
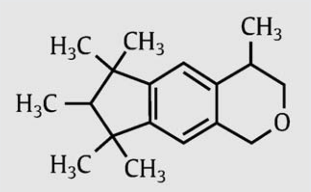
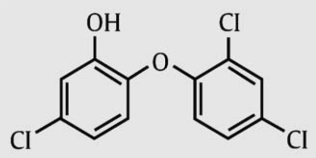
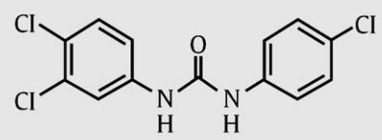
Compound	Chemical structure	Chemical properties
Perfluorochemicals		
Perfluorooctane sulphonate (PFOS)		CAS No: no specific number Formula: $C_8F_{17}SO_3^-$ Log K_{OW}: cannot be determined Vp: 3.31×10^{-4} Pa (20 °C) Half life (soil): unknown/persistent OECD (2002)
Perfluorooctanoic acid (PFOA)		CAS No: 335-67-1 Formula: $C_7F_{15}COOH$ Log K_{OW}: unknown Vp: unknown Half life (soil): unknown/persistent
Quaternary ammonium compounds (QACs)	 R1-4 represent alkyl or aryl substituents	Generalised structure of QACs. High variation in substitution and therefore, chemical properties IPCS (1999)
Steroids		
17 α-ethinyloestradiol		CAS No: 57-63-6 Formula: $C_{20}H_{24}O_2$ Log K_{OW}: 3.67 Vp: 6.0×10^{-9} Pa Half life (soil): a few days Ternes et al. (2002); Lai et al. (2002)
17 β-Oestradiol		CAS No: 50-28-2 Formula: $C_{18}H_{24}O_2$ Log K_{OW}: 4.01 Vp: 3.0×10^{-8} Pa Half life (soil): a few days Ternes et al. (2002); Lai et al. (2002)
Oestriol		CAS No: 5864-38-0 Formula: $C_{18}H_{24}O_2$ Log K_{OW}: 2.81 Vp: 9.0×10^{-13} Pa Half life (soil): a few days Ternes et al. (2002); Lai et al. (2002)
Oestrone		CAS No: 53-16-7 Formula: $C_{18}H_{22}O_2$ Log K_{OW}: 3.13 Vp: 3.0×10^{-8} Pa Half life (soil): a few days Ternes et al. (2002); Lai et al. (2002)

Table 1 (*continued*)

Compound	Chemical structure	Chemical properties
Synthetic musks		
AHTN (Tonalide™)		CAS No: 1506-02-1 Formula: $C_{18}H_{26}O$ Log Kow: 5.7 Vp: 0.0682 Pa Half life (soil): 180 days Balk and Ford (1999a)
HHCB (Galaxolide™)		CAS No: 1222-05-5 Formula: $C_{18}H_{26}O$ Log K_{OW}: 5.9 Vp: 0.0727 Pa Half life (soil): 180 days Balk and Ford (1999a)
Triclosan (TCS)		CAS No: 3380-34-5 Formula: $C_{12}H_7Cl_3O_2$ Log K_{OW}: 4.8 Vp: 0.00069 Pa (25 °C) Half life (soil): 266 days NICNAS (2008); Topp et al. (2008)
Triclocarban (TCC)		CAS No: 101-20-2 Formula: $C_{13}H_9Cl_3N_2O$ Log K_{OW}: 3.5–4.2 (22.6 °C) Vp: <100 Pa Half life (soil): unknown EC (2005); Snyder et al. (2010)

the low ng L^{-1} range (Kloepfer et al., 2004). Degradation rates are reported in days and there are contradictory studies claiming that the dominant removal mechanisms involved are biological (de Wever and Verachtert, 1997) or chemical (Gaja and Knapp, 1998). These compounds have a degree of aquatic toxicity and have also been employed as fungicide, herbicide and anti-algal agents (de Wever and Verachtert, 1997). Not only are there no studies reporting the concentrations of $MBT_{thiazole}$ or OBT in sludge, but there also few studies reporting their environmental distribution (Spies et al., 1987). Only once empirical measurements of $MBT_{thiazole}$ and OBT in sewage sludge have been completed will it be possible to assess whether these chemicals pose a risk to human health and/or the environment when land applying biosolids.

2.3. Bisphenol A

Bisphenol A (2,2-Bis-(4-hydroxyphenyl)propane) is a plasticiser manufactured in high quantities and is used as a monomer for the production of polycarbonate and epoxy resins, unsaturated polyester-

Table 2
Risk assessment evaluation concentrations (mg kg^{-1} dw) of selected pharmaceutical compounds in sludge-amended soil (Eriksen et al., 2009).

Therapeutical group	Drug substance	Predicted environmental concentration (PEC)		Predicted no-effect concentration (PNEC)
		Agricultural soil (60 t ha^{-1})	Park areas	
Alimentary tract and metabolism	Mesalazin	0.98	6.70	12
	Ranitidin	0.04	0.30	5277
Blood and blood forming organs	Dipyridamole	0.03	0.17	–
Cardiovascular system	Sotalol	0.02	0.15	4095
	Metoprolol	0.02	0.13	589
	Losartan	0.03	0.23	–
	Atorvastatin	0.05	0.34	11
Antibacterial drugs	Tetracycline	0.01	0.08	8.8
	Ciprofloxacin	0.04	0.29	26
Muscular–skeletal system	Carisoprodol	0.10	0.68	24368
Nervous system	Gabapentin	0.06	0.39	20460
	Levetiracetam	0.02	0.12	–
	Chlorprothixene	0.02	0.16	–
Respiratory organs	Fexofenadine	0.03	0.17	–

Table 3
Concentrations (mg kg^{-1} dw) of 'emerging' organic contaminants in sewage sludge/biosolids.

Contaminant	Country	Year	n	Mean	Min	Max	Reference
Antibiotics and pharmaceuticals							
4-Epitetracylcine	USA	2009	84	1.14	0.04	4.38	US EPA (2009)
Azithromycin	USA	2009	84	0.83	0.008	5.21	US EPA (2009)
Carbamazepine	USA	2009	84	0.14	0.009	6.03	US EPA (2009)
Cimetidine	USA	2009	84	1.33	0.004	8.33	US EPA (2009)
Ciprofloxacin	Germany	2002	2	2.35	2.27	2.42	Golet et al. (2002)
	Sweden	2005	10	2.5	0.5	4.8	Lindberg et al. (2005)
	USA	2009	84	10.5	0.075	40.8	US EPA (2009)
Diphenhydramine	USA	2009	84	0.871	0.037	5.73	US EPA (2009)
Doxycycline	Sweden	2005	10	1.4	<dl	1.5	Lindberg et al. (2005)
	USA	2009	84	0.877	0.034	5.09	US EPA (2009)
Erthromycin (Total)	USA	2009	84	0.036	0.002	0.18	US EPA (2009)
Fluoxetine	USA	2009	84	0.245	0.010	3.13	US EPA (2009)
Miconazole	USA	2009	84	1.239	0.007	9.21	US EPA (2009)
Norfloxacin	Germany	2002	2	2.25	2.13	2.37	Golet et al. (2002)
	Sweden	2005	10	1.51	0.1	4.2	Lindberg et al. (2005)
Ofloxacin	Sweden	2005	10	0.73	<0.1	2.0	Lindberg et al. (2005)
	USA	2009	84	8.573	0.025	58.10	US EPA (2009)
Tetracycline	USA	2009	84	1.278	0.038	5.27	US EPA (2009)
Bisphenol A							
	Germany	2002	38	*	0.004	1.363	Fromme et al. (2002)
	Germany	2002	18	*	~40	~325	Meesters and Schroder (2002)
	Australia	2007	4	0.089	0.004	0.158	Tan et al. (2007)
	Greece	2007	1	0.62	*	*	Gatidou et al. (2007)
	Greece	2008	1	0.03	*	*	Pothitou and Voutsa (2008)
	Greece	2008	27	0.53	<0.56	1.75	Stasinakis et al. (2008)
	China	2009	2	0.11	0.10	0.13	Nie et al. (2009)
	Overall		91	0.28	0.004	~325	
Organotins							
Monobutyltin (MBT_{tin})	Switzerland	1987	4	3.3	0.2	6	Mueller (1987)
	Switzerland	1991	3	0.78	0.10	0.97	Fent et al. (1991)
	Canada	1992	36	0.02	*	*	Chau et al. (1992)
	Switzerland	1996	25	0.5	*	*	Fent (1996b)
	France	2000	1	0.24	*	*	Bancon-Montigny et al. (2000)
	UK	2004	40	0.71	*	*	Voulvoulis et al. (2004)
	Overall		109	0.93	0.10	6	
Dibutyltin (DBT)	Switzerland	1987	4	5	0.7	7.5	Mueller (1987)
	Switzerland	1987	4	0.98	0.41	1.24	Fent et al. (1991)
	Canada	1991	3	0.04	*	*	Chau et al. (1992)
	Switzerland	1992	36	1.5	*	*	Fent (1996b)
	France	1996	25	0.08	*	*	Bancon-Montigny et al. (2000)
	UK	2004	40	0.06	*	*	Voulvoulis et al. (2004)
	Overall		112	1.28	0.41	7.5	
Tributyltin (TBT)	Switzerland	1987	4	3.5	0.3	6	Mueller (1987)
	Switzerland	1991	3	0.99	0.28	1.51	Fent et al. (1991)
	Canada	1992	36	0.1	*	*	Chau et al. (1992)
	Switzerland	1996	25	1.1	*	*	Fent (1996b)
	France	2000	1	0.05	*	*	Bancon-Montigny et al. (2000)
	Switzerland	2004	24	0.15	0.02	0.65	Plagellat et al. (2004)
	UK	2004	40	0.13	*	*	Voulvoulis et al. (2004)
	Overall		133	0.86	0.02	6	
Triphenyltin (TPhT)	Switzerland	1987	4	2.3	<0.02	9	Mueller (1987)
	Canada	1991	36	0.3	*	*	Chau et al. (1992)
	Switzerland	1992	25	0.5	*	*	Fent (1996b)
	France	1996	1	0.01	*	*	Bancon-Montigny et al. (2000)
	Switzerland	2000	24	0.02	<dl	0.28	Plagellat et al. (2004)
	Overall		90	0.63	<0.02	9	
Phthalate acid esters (PAEs)							
DEHP	Canada	1989	6	65	3	176	Webber and Lesage (1989)
	Germany	2002	15	~67	~28	~154	Fromme et al. (2002)
	Canada	2003	20	2.7	<0.02	11	Bright and Healey (2003)
	Finland	2003	13	95	28	122	Marttinen et al. (2003a)
	Spain	2005	134	67	2	3514	Abad et al. (2005)
	UK	2005	1	62	*	*	Gibson et al. (2005)
	UK	2005	*	30	*	*	Oliver et al. (2005)
	Denmark	2007	*	67	61	78	Roslev et al. (2007)
	Australia	2007	5	11.2	0.26	45.1	Tan et al. (2007)
	Australia	2008	14	17	2	44	Clarke et al. (2008b)
	France	2009	10	72.1	*	*	Dargnat et al. (2009)
	Spain	2009	4	159	13	345	Aparicio et al. (2009)
	USA	2009	84	53	<dl	310	US EPA (2009)
	Overall		306	58	<0.02	3514	

Table 3 (*continued*)

Contaminant	Country	Year	n	Mean	Min	Max	Reference
Polybrominated diphenyl ethers (PBDEs)							
BDE47	Sweden	1992	2	0.015	0.015	0.015	Nylund et al. (1992)
	Sweden	1999	3	0.065	0.036	0.080	Sellstrom et al. (1999)
	USA	2001	11	0.568	0.359	0.754	Hale et al. (2001)
	Netherlands	2003	3	0.020	0.010	0.040	de Boer et al. (2003)
	Spain	2004	6	0.037	0.002	0.050	Fabrellas et al. (2004)
	Germany	2004	8	0.047	0.025	0.088	Hamm (2004)
	USA	2004	1	0.757	*	*	(North, 2004)
	Sweden	2006	50	0.049	0.007	0.100	Law et al. (2006)
	Germany	2007	19	0.052	0.020	0.115	Knoth et al. (2007)
	China	2007	31	0.005	0.0004	0.059	Wang et al. (2007)
	Australia	2008	16	0.126	<0.001	0.410	Clarke et al. (2008c)
	Kuwait	2008	21	0.002	0.0002	0.008	Gevao et al. (2008)
	Antarctica	2008	2	0.776	0.132	1.420	Hale et al. (2008)
	USA	2009	84	0.709	0.073	5.000	US EPA (2009)
	USA	2010	15	0.161	0.128	0.238	Andrade et al. (2010)
	Overall		272	0.226	0.0002	5.000	
BDE99	Sweden	1992	2	0.019	0.019	0.019	Nylund et al. (1992)
	Sweden	1999	3	0.085	0.056	0.100	Sellstrom et al. (1999)
	USA	2001	11	0.661	0.391	1.157	Hale et al. (2001)
	Netherlands	2003	3	0.021	0.011	0.038	de Boer et al. (2003)
	Spain	2004	6	0.037	0.023	0.064	Fabrellas et al. (2004)
	Germany	2004	8	0.070	0.037	0.127	Hamm (2004)
	USA	2004	1	0.940	*	*	North (2004)
	Sweden	2006	50	0.060	0.008	0.150	Law et al. (2006)
	Germany	2007	39	0.057	0.024	0.124	Knoth et al. (2007)
	China	2007	31	0.005	0.003	0.068	Wang et al. (2007)
	Australia	2008	14	0.141	0.0004	0.400	Clarke et al. (2008c)
	Kuwait	2008	21	0.005	0.0004	0.015	Gevao et al. (2008)
	Antarctica	2008	2	0.735	0.200	1.270	Hale et al. (2008)
	USA	2009	84	0.716	0.064	4.000	US EPA (2009)
	USA	2010	15	0.169	0.128	0.245	Andrade et al. (2010)
	Overall		290	0.248	0.0004	4.000	
BDE209	Sweden	1999	3	0.220	0.170	0.270	Sellstrom et al. (1999)
	USA	2001	11	1.370	0.085	4.890	Hale et al. (2001)
	Netherlands	2003	3	0.096	0.009	0.190	de Boer et al. (2003)
	Spain	2004	6	5.968	0.756	18.632	Fabrellas et al. (2004)
	Germany	2004	8	0.326	0.100	0.639	Hamm (2004)
	USA	2004	1	1.183	*	*	North (2004)
	Sweden	2006	50	0.120	0.006	1.000	Law et al. (2006)
	Germany	2007	39	0.442	0.113	1.339	Knoth et al. (2007)
	China	2007	31	0.069	<0.001	1.109	Wang et al. (2007)
	Australia	2008	14	0.705	0.003	3.780	Clarke et al. (2008c)
	Kuwait	2008	21	0.182	0.005	1.596	Gevao et al. (2008)
	Antarctica	2008	2	0.770	0.219	1.320	Hale et al. (2008)
	USA	2009	84	2.180	0.150	17.000	US EPA (2009)
	USA	2010	15	0.920	0.792	1.220	Andrade et al. (2010)
	Overall		288	1.039	0.003	18.632	
ΣPBDEs	USA	2004	1	3.381	*	*	North (2004)
	Germany	2007	39	0.555	0.142	2.491	Knoth et al. (2007)
	China	2007	31	0.094	0.005	1.115	Wang et al. (2007)
	Australia	2008	14	1.137	0.005	4.230	Clarke et al. (2008c)
	Kuwait	2008	21	0.191	0.006	1.600	Gevao et al. (2008)
	Antarctica	2008	2	2.664	0.637	4.690	Hale et al. (2008)
	USA	2010	15	1.496	1.330	1.820	Andrade et al. (2010)
	Overall		123	1.360	0.005	4.690	
Polychlorinated alkanes (PCAs)							
sPCA	Germany	1995	2	56	47	65	Rieger and Ballschmiter (1995)
	UK	2003	14	42	7	200	Stevens et al. (2003)
	Overall		16	49	7	200	
mPCA	UK	2001	9	19.6	1.8	93	Nicholls et al. (2001)
	UK	2003	14	1800	30	9700	Stevens et al. (2003)
	Overall		23	910	1.8	9700	
Polychlorinated napthalenes (PCNs)							
	Sweden	1992	2	0.005	0.003	0.006	Nylund et al. (1992)
	UK	2003	14	0.083	0.050	0.190	Stevens et al. (2003)
	China	2008	8	*	0.001	0.028	Guo et al. (2008)
	Overall		24	0.044	0.001	0.190	
Polydimethylsiloxanes (PDMSs)							
	Japan	1984	1	144	*	*	Watanabe et al. (1984)
	USA	1997	12	1120	122	5155	Fendinger et al. (1997)
	Overall		13	632	122	5155	

(*continued on next page*)

Table 3 (*continued*)

Contaminant	Country	Year	n	Mean	Min	Max	Reference
Perfluorochemicals							
PFOS	USA	2001	12	0.58	0.06	3.12	3M Environmental Laboratory (2001)
	USA	2006	*	0.100	0.081	0.160	Schultz et al. (2006)
	USA	2006	10	0.031	<0.010	0.065	Sinclair and Kannan (2006)
	USA	2007	8	0.073	0.008	0.110	Loganathan et al. (2007)
	Denmark	2008	7	*	0.005	0.074	Bossi et al. (2008)
	Overall		37	0.196	0.005	3.12	
PFOA	USA	2001	5	0.049	0.002	0.244	3M Environmental Laboratory (2001)
	USA	2006	*	<0.003	*	*	Schultz et al. (2006)
	USA	2006	10	0.107	0.018	0.241	Sinclair and Kannan (2006)
	USA	2007	8	0.068	0.0083	0.219	Loganathan et al. (2007)
	Denmark	2008	7	*	0.001	0.020	Bossi et al. (2008)
	Overall		30	0.075	0.001	0.244	
Quaternary ammonium compounds (QACs)							
DTDMAC	Switzerland	1991	5	3670	2570	5870	Fernandez et al. (1996)
	Switzerland	1992	5	960	730	1510	Fernandez et al. (1996)
	Switzerland	1993	5	470	300	570	Fernandez et al. (1996)
	Switzerland	1994	5	210	150	300	Fernandez et al. (1996)
Total QACs	Austria	2007	6	*	22	103	MartÌnez-Carballo et al. (2007)
	Overall		26	1328	22	5870	
Steroids							
Beta stigmastanol	USA	2009	84	168	3.44	1330	US EPA (2009)
Campesterol	USA	2009	84	101	2.84	524	US EPA (2009)
Cholestanol	USA	2009	84	680	3.86	4590	US EPA (2009)
Cholesterol	USA	2009	84	1129	2.34	5390	US EPA (2009)
Coprostanol	USA	2009	84	4367	7.72	43700	US EPA (2009)
Epicoprostanol	USA	2009	84	1703	0.87	6030	US EPA (2009)
Stigmasterol	USA	2009	84	321	0.46	569	US EPA (2009)
17α-Ethinyloestradiol	Germany	2002	4	0.005	<0.004	0.017	Ternes et al. (2002)
	China	2009	2	*	<dl	<dl	Nie et al. (2009)
	USA	2009	84	*	<dl	0.355	US EPA (2009)
17β-Oestradiol	Germany	2002	4	0.020	0.005	0.049	Ternes et al. (2002)
	China	2009	2	*	<dl	<dl	Nie et al. (2009)
	USA	2009	84	*	<dl	0.355	US EPA (2009)
Oestriol	China	2009	2	0.010	0.010	0.011	Nie et al. (2009)
	USA	2009	84	*	<dl	0.232	US EPA (2009)
Oestrone	Germany	2002	4	0.027	<0.002	0.037	Ternes et al. (2002)
	China	2009	2	0.016	0.011	0.022	Nie et al. (2009)
	USA	2009	84	*	<dl	0.965	US EPA (2009)
Synthetic musks							
AHTN (tonalid)	Switzerland	2000	12	1.54	0.74	4.16	Herren and Berset (2000)
	Germany	2002	4	3.56	2.52	5.07	Heberer (2002)
	Spain	2003	1	0.052			Llompart et al. (2003)
	UK	2003	14	4.7	0.12	16	Stevens et al. (2003)
	Switzerland	2004	16	7.3	2.5	11.2	Kupper et al. (2004)
	China	2005	3	2.56	0.72	6.20	Zeng et al. (2005)
	Hong Kong	2008	30	5.85	0.475	13.9	Shek et al. (2008)
	Overall		80	3.65	0.12	16	
HHCB (galaxolide)	Switzerland	2000	12	4.85	2.29	12.16	Herren and Berset (2000)
	Germany	2002	4	8.26	6.03	11.45	Heberer (2002)
	Spain	2003	1	0.162			Llompart et al. (2003)
	UK	2003	14	27	1.9	81	Stevens et al. (2003)
	Switzerland	2004	16	20.3	7.4	36.0	Kupper et al. (2004)
	China	2005	3	10.76	5.42	21.21	Zeng et al. (2005)
	Hong Kong	2008	30	27.1	3.58	78.6	Shek et al. (2008)
	Overall		80	14.06	1.9	81	
Triclosan							
	USA	2002	10	4.55	0.53	15.6	McAvoy et al. (2002)
	Germany	2003	20	*	0.40	8.80	Bester (2003)
	Spain	2005	7	2.83	0.42	5.40	Morales et al. (2005)
	Canada	2007	12	3.21	0.62	11.55	Chu and Metcalfe (2007)
	Australia	2007	19	5.58	0.09	16.79	Ying and Kookana (2007)
	Greece	2007	1	1.84	*	*	Gatidou et al. (2007)
	Greece	2008	5	0.46	*	*	Pothitou and Voutsa (2008)
	Greece	2008	27	3.21	0.19	9.85	Stasinakis et al. (2008)
	USA	2009	4	1.87	0.09	7.06	Cha and Cupples (2009)
	USA	2009	84	16.10	0.33	133	US EPA (2009)
	Overall		189	4.41	0.09	133	
Triclocarban							
	USA	2006	3	51	*	*	Heidler et al. (2006)
	Canada	2007	12	4.17	2.17	5.97	Chu and Metcalfe (2007)

Table 3 (*continued*)

Contaminant	Country	Year	n	Mean	Min	Max	Reference
Triclocarban	USA	2007	5	19.3	7.5	25.9	Sapkota et al. (2007)
	USA	2009	4	7.19	4.89	9.28	Cha and Cupples (2009)
	USA	2009	84	39.43	0.19	441	US EPA (2009)
	Overall		108	24.2	0.19	441	

*No data; <dl — less than detection limit.

styrene resins and flame retardants (Staples et al., 1998). The final products are used as coatings on cans, as powder paints, as additives in thermal paper, in dental fillings and as antioxidants in plastics (Staples et al., 1998). Release into the environment is possible during manufacturing processes and by leaching from final products (Fromme et al., 2002). Bisphenol A has been shown to be weakly oestrogenic and to possess some anti-androgenic activity (Sohoni and Sumpter, 1998). However, the relative potency ranges are approximately 1×10^{-6} to 5×10^{-7} times less than 17β-oestradiol (Harris et al., 1997). Based on *in vitro* receptor-interaction studies, the oestrogenic activity was estimated to be 2×10^{-3} fold lower than for oestradiol. Bisphenol A has been implicated as an endocrine disrupting chemical and laboratory studies (using mice) indicate that development problems can be associated with environmentally relevant exposure (Newbold et al., 2009). The chemical structure of bisphenol A is given in Table 1.

Bisphenol A is regularly detected in surface waters primarily because it is continuously released into the environment (Heemken et al., 2001; Fromme et al., 2002; Oehlmann et al., 2008) and not because it is environmentally persistent (Dorn et al., 1987). While there is no direct evidence to confirm a detrimental causal link from exposure to bisphenol A (human or environmental) concern exists about this compound due to reports of adverse reproductive and developmental effects in wildlife that are possibly mediated *via* endocrine disruptive pathways (Fürhacker et al., 2000; Vandenberg et al., 2007; Oehlmann et al., 2008; Newbold et al., 2009).

Bisphenol A is widely used in households and industry, therefore, it can be expected to be present in raw sewage (Fürhacker et al., 2000). A German study identified that the paper industry was the major contributor of bisphenol A in wastewater (Fürhacker et al., 2000). WWTP mass balance studies have detected bisphenol A in raw water, sewage sludge and effluents (Meesters and Schroder, 2002). Significant reductions (up to 99%) during wastewater treatment have been reported (Fürhacker et al., 2000; Tan et al., 2007) and biodegradation is thought to be the principal removal mechanism (Pothitou and Voutsa, 2008).

There is a large variation in reported bisphenol A concentrations in sludges internationally, with values ranging from low μg kg^{-1} dw (Fromme et al., 2002; Gatidou et al., 2007; Tan et al., 2007; Pothitou and Voutsa, 2008; Nie et al., 2009) to mid mg kg^{-1} dw (Meesters and Schroder, 2002). Bisphenol A is a bulk chemical manufactured in similar quantities to phthalates acid esters (PAEs), however, concentrations of bisphenol A are two orders of magnitude smaller in sludge than PAEs. This suggests that bisphenol A is considerably more degradable during wastewater and sludge treatment compared to phthalates. Similarly, bisphenol A is reported to rapidly dissipate in soil and has an estimated half-life of <3 days (Fent et al., 2003). A study of the toxic effects of bisphenol A to soil isopods has been reported, however, the concentrations used (10–300 mg kg^{-1} dw) were far higher than environmentally relevant values and the toxicity was associated with the delivery solvent rather than bisphenol A solely (Lemos et al., 2009). Few studies have examined the ecotoxicological effects of bisphenol A in soil and this requires further attention. Studies are also required to more accurately determine the concentrations of bisphenol A in sludge. Nevertheless, the concentrations of bisphenol A reported in sludge are not high and, coupled with its rapid biodegradation during wastewater treatment, this compound is unlikely to pose an issue when land applying biosolids. Bisphenol A is under review for possible identification as a European Water Framework Directive (WFD) Priority Substance or Priority Hazardous Substance (PHS) to control emission sources (EPCEU, 2008). While evidence is indicating that bisphenol A is an endocrine disrupting chemical (Li et al., 2009; Newbold et al., 2009) that can be found in the human body (Lee et al., 2008), exposure primarily occurs in the domestic environment and via direct ingestion (Vandenberg et al., 2007). Transfer to humans from biosolids-amended soil, by contrast, is extremely unlikely since there is little evidence that bisphenol A is environmentally persistent or bioaccumulates via food-chain mediated pathways.

2.4. Organotins (OTs)

Organotin compounds (OTs) have been used since the 1960s for industrial and agricultural purposes viz., polyvinyl chloride (PVC) stabilisers, fungicides, bactericides, insecticides, industrial catalysts and wood preservatives (Hoch, 2001). This includes the use of monobutyltin (MBT_{tin}) and dibutyltin (DBT) as heat and light stabilisers in PVC processing, the use of tributyltin (TBT) in antifouling formulations and as a general-purpose wood preservative, as well as the use of triphenyltins (TPhT) in agriculture. The use of TBT as an antifouling agent for ship hulls and as a general wood preservative has ceased in the UK and internationally because of high toxicity in aquatic ecosystems (Alzieu, 1991; Fent, 1996a; Voulvoulis et al., 2004).

Mass balances for OTs in WWTP demonstrate that they are effectively removed during wastewater treatment and are concentrated in the sludge. Reported removal rates of MBT_{tin}, DBT and TBT are 95%, 84% and 86%, respectively (Voulvoulis et al., 2004). OT concentrations in wastewater show diurnal fluctuations, however there is no explanation for this apparent behaviour (Voulvoulis et al., 2004).

There is contradictory evidence from laboratory studies concerning the biodegradation of TBT and TPhT by the activated sludge process. For example, Stasinakis et al. (2005) showed these compounds were degraded by biological wastewater treatment, whereas Voulvoulis and Lester (2006) found minimal degradation. In a laboratory study, 50% of TBT and 20% of TPhT applied to soil in biosolids remained in the soil after 2 months (Marcic et al., 2006). The biodegradability of OTs in soil is also reported to decline with increasing substitution (Heroult et al., 2008).

The concentration of OT compounds in sewage sludge (Table 3) has been reported from Switzerland (Mueller, 1987; Fent and Mueller, 1991; Fent, 1996b), Canada (Chau et al., 1992), France (Bancon-Montigny et al., 2000) and the UK (Voulvoulis et al., 2004; Voulvoulis and Lester, 2006). There is no consistent trend in the concentration data, however, values for the main OTs rarely exceed 1 mg kg^{-1} dw in contemporary sludge samples, which may reflect the declining use of these compounds (Table 3).

2.5. Phthalate acid esters (PAEs)

Phthalate acid esters (PAEs) have been in use for over 50 years, mainly in the manufacture of resins and plastics such as PVC (Fromme et al., 2002). PAEs are also used in other non-PVC applications such as paints, rubber products, adhesives and some cosmetics. PAEs soften plastic resins without chemically binding with them and as a consequence leach from plastic products into the surrounding environment. The PAE content of plastic generally ranges from 20 to 40%, but in some cases is as high as 55% (Fatoki and Vernon, 1990). The most common PAE is di(2-ethylhexyl)phthalate (DEHP) and approximately 95% of DEHP production is directed towards plasticizer use, particularly in PVC products such as tubing and medical device components. The chemical structure and properties of DEHP are given in Table 1. Recently, use of DEHP has declined to an extent, due to concerns that it may disrupt endocrine systems, and the use of other phthalate plasticizers has increased, in particular diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP), which may, in fact be more environmentally persistent (Cadogan, 2002). There is contradictory information published regarding the impact and significance of phthalates for human health and the environment. A recent Chinese study found that significant contamination of the aerial components of vegetable plants occurred from a plastic based mulch with a DEHP concentration of 16.5% (Du et al., 2009). The results of this study appear contrary to currently accepted models of organic pollutants movement into plants (Briggs et al., 1982; Travis and Arms, 1988) and other experimental investigations that show there is minimal uptake of DEHP by crop plants (Schmitzer et al., 1988; Yin et al., 2003). Given that Du et al. (2009) report that the DEHP concentration was smaller in the roots of the plant it is possible that volatilisation or direct contamination might have played a significant role in the accumulation of DEHP in leaves and stems in this case. However, evidence from biosolids-amended systems indicates the minimal uptake of DEHP into plants (Aranda et al., 1989). In contrast to the apparent uptake of DEHP by vegetables from plastic in direct contact with the soil and crop, the sorption of DEHP onto the sludge matrix may thus control its bioavailability preventing movement and transfer into crops. Nevertheless, further research is warranted to clarify the bioavailability of DEHP to plants and whether contamination of aerial plant components can occur from contaminated soil. There is no reported evidence that DEHP has a negative impact upon the soil ecosystem (Kirchmann et al., 1991; Cartwright et al., 2000; Jensen et al., 2001).

PAEs are not environmentally persistent and are readily degraded in soils and sewage sludge under both aerobic and anaerobic conditions (Keyser et al., 1976; Walker et al., 1984; Shanker et al., 1985; Group, 1986; Staples et al., 1997). They are readily metabolised and do not accumulate in mammals even when fed artificially in diets high in PAEs (Giam et al., 1984). Organisms ingesting high doses of PAEs were quickly able to remove phthalate compounds from their body tissues once the chemical was excluded from the feed (Giam et al., 1984).

Only a relatively small number of international studies were found reporting PAE concentrations in sewage sludge. It may be expected that PAEs would increase in sewage sludge and the environment generally in proportion to their use within society, however, there is no evidence indicating that this is the case. The concentration of PAEs in sludge is reported from Canada (Webber and Lesage, 1989; Bright and Healey, 2003), Germany (Fromme et al., 2002), Finland (Marttinen et al., 2003a,b), Spain (Abad et al., 2005), the UK (Gibson et al., 2005; Oliver et al., 2005), Australia (Tan et al., 2007; Clarke et al., 2008b) and the USA (US EPA, 2009). A summary of DEHP concentration data is compiled in Table 3.

Abad et al. (2005) reported the concentration of DEHP in Spanish sewage sludge ($n=139$) over a number of years and for different WWTPs ($n=20$). The concentration of DEHP was highly variable ranging from 1.5 to 3513.8 mg kg^{-1} dw. DEHP concentrations varied from $18.4 \rightarrow 16.9 \rightarrow 76.8 \rightarrow 3513.8 \rightarrow 157.4 \rightarrow 11.4$ mg kg^{-1} dw over a two-year period at one WWTP demonstrating the high variability in the DEHP content of sewage sludge. Nevertheless, the DEHP concentration was typically between 10 and 50 mg kg^{-1} dw (Abad et al., 2005) and was consistent with other survey data for DEHP in sewage sludge (Marttinen et al., 2004; Bago et al., 2005; Gibson et al., 2005; Oliver et al., 2005).

PAEs are well known to degrade during wastewater treatment and degradation under both aerobic and anaerobic conditions increases with water solubility (Shelton et al., 1984; Ziogou et al., 1989; Jianlong et al., 2000; Fauser et al., 2003; Marttinen et al., 2004; Amir et al., 2005). PAEs characteristically have high log K_{ow} values >4 and therefore partition strongly to the sewage sludge during wastewater treatment (Table 1). They are rapidly degraded by aerobic sludge treatment processes, such as composting (Cheng et al., 2008; Pakou et al., 2009), but reported removals by anaerobic digestion vary from no observed anaerobic biodegradation up to 23–61% removal of DEHP in digested sludge (Fountoulakis et al., 2006). Consequently DEHP is typically present in sewage sludge from the low mg kg^{-1} to <200 mg kg^{-1} dw range (Table 3).

2.6. Polybrominated diphenyl ethers (PBDEs)

PBDEs are a class of brominated fire retardants (BFRs) that were used in plastics, textiles, electronic circuitry, and other materials. There are 209 PBDE congeners and they are numbered according to the IUPAC system for PCBs (Ballscmitter and Zell, 1980). PBDEs were sold in three commercial formulations; each named for the prominent homologue in the mixture viz., pentaBDE (BDE 47, 99, 100, 153, 154), octaBDE (BDE 183), and decaBDE (BDE 209) (Sjödin et al., 1998). Despite the commercial formulation names each contains many BDE congeners (BSEF, 2005). PBDEs have low vapour pressures ($4.69 \times 10^{-5} - 6.59 \times 10^{-6}$ Pa) and are highly lipophilic (log K_{ow} values of 5.9–10) (IPCS, 1994; Braekevelt et al., 2003). Due to the potential threat to human health and the environment, PBDEs (specifically pentaBDE and octaBDE) were listed as United Nations Environment Programme (UNEP) Persistent Organic Pollutants (POPs) in 2008 (UNEP, 2001; UNEP, 2009).

Assessment of health risks associated with human exposure and accumulation of PBDEs is complicated and has not been adequately characterized. However, the potential risks associated with exposure to the most bioactive congeners (tri- to octa-BDE) include thyroid hormone disruption, neuro-developmental defects and cancer. Several studies have shown that PBDEs share similar general properties to organo-halogenated compounds as *in vivo* exposure of rodents resulted in reduction of serum total and free thyroid hormone (thyroxine T4) levels (Darnerud et al., 2001; McDonald, 2002). Altered thyroid hormone function, particularly during development, is profound and has been hypothesized to lead to disrupted brain development and permanent neurological damage (Legler and Brouwer, 2003).

PBDEs are routinely detected in sewage sludge in the low mg kg^{-1} dw range (Table 3) and values have been reported from Sweden (Nylund et al., 1992; Sellstrom et al., 1999; Law et al., 2006), USA (de Carlo, 1979; Hale et al., 2001; North, 2004), Germany (Knoth et al., 2007), The Netherlands (de Boer et al., 2003), China (Wang et al., 2007), Australia (Clarke et al., 2008c), Kuwait (Gevao et al., 2008) and Antarctica (Hale et al., 2008).

Three congeners account for the majority of ΣPBDEs in sewage sludge and include: BDE47, 99 (pentaBDE) and BDE209 (decaBDE); the concentrations of these congeners are summarised in Table 3. PBDE congeners representative of the pentaBDE (BDE47, 99, 100, 153, 154) formulations are often present at similar concentrations regardless of the catchment type indicating domestic origin (Hale et al., 2001; Hale et al., 2008). The primary congener of the decaBDE formulation, BDE209, is consistently detected in the highest concentrations in sewage sludge and, in national surveys, its concentrations are also highly variable, suggesting important industrial inputs (Clarke et al., 2008c). Trace PBDE amounts (ng L^{-1}) have also been detected in treated effluent (de Boer et al., 2000; Hamm, 2004; North, 2004; Knoth et al., 2007) and recent studies have demonstrated this as a point source of environmental PBDE contamination (Toms et al., 2006; Toms et al., 2008). The contamination of sludges and effluents with PBDEs could therefore have potential implications for disposal and beneficial reuse strategies. However, action has been taken in Europe to significantly restrict the use of pentaBDE and octaBDE and the placing on the market of articles containing one or both of these substances taking effect from 15 August 2004 (EPCEU, 2003). PentaBDE is also a WFD PHS (EPCEU, 2001). Therefore, emissions to wastewater and presence in sludge are expected to decrease through source controls thus reducing the significance of these compounds for agricultural recycling of biosolids.

2.7. Polychlorinated alkanes (PCAs)

Technical mixtures of polychlorinated alkanes (PCAs), often referred to as chlorinated paraffins (CPs), are a class of industrial chemicals comprising of chlorinated straight-chain hydrocarbons. They have been produced since the 1930s for use as extreme pressure lubricant additives, plasticizers, flame retardants, and paint additives (IPCS, 1996). World production of PCAs was estimated to be 300,000 t in 1985 (IPCS, 1996) and a similar amount was produced in 2009 (Eurochlor, 2009). They are manufactured in the European Union, North America, South Africa, Australia, India, China, Taiwan and Japan (Eurochlor, 2009). Following their widespread and unrestricted use, PCAs are now present in a range of environmental compartments (Campbell and McConnell, 1980). They have been detected in human milk (Thomas et al., 2006), environmental samples (Campbell and McConnell, 1980; Bayen et al., 2006) and in air over the UK, including remote regions (Peters et al., 2000). The International Agency for Research into Cancer (IARC) has classified PCAs as Class 2B “possibly carcinogenic to humans” (IARC, 1998).

PCAs are chlorinated linear chain alkanes with the general formula $C_xH_{(2x+2)-y}Cl_y$. They are produced from the n-alkane fractions derived from petroleum distillation by chlorination, with the degree of chlorination ranging between 30% and 72% by weight (IPCS, 1996). They are divided into three groups: short-chain PCAs (noted as sPCAs or SCCPs) comprising 10 to 13 carbon atoms, medium-chain PCAs (mPCAs or MCCPs) comprising 14 to 17 carbon atoms and long-chain PCAs (lPCAs or LCCPs) with 18 or more carbon atoms. PCAs are viscous liquid or yellowish dense oils, except for some lPCAs (C20- to C30- with a chlorine content of >70%) which are solid and are practically insoluble in water (IPCS, 1996). There are many possible positions for the chlorine atoms and presence of chiral carbon atoms lead to a large number of potential positional isomers, enantiomers and diastereoisomers. PCAs therefore represent a difficult analytical problem because of the complexity inherent in industrial mixtures. The total number of possible congeners is unknown, but far exceeds 10,000 (Eljarrat and Barceló, 2006).

Reports of PCA concentrations in sewage sludge samples are very limited in the literature (Table 3). In the early 1990s sPCAs were measured in two German sludge samples from an industrial area, which contained 65 and 47 mg kg^{-1} dw of sPCAs (Rieger and Ballschmiter, 1995). Concentrations of mPCAs in samples of digested sludge ($n=9$) from the UK were in the range 1.8 to 93 mg kg^{-1} dw (Nicholls et al., 2001). In another UK survey ($n=14$), sPCAs and mPCAs concentrations were between 7–200 mg kg^{-1} dw and 30–9700 mg kg^{-1} dw, respectively (Stevens et al., 2003). Comparison of data from the limited amount of information available is difficult.

sPCAs are an identified WFD PHS and are therefore subject to controls that should ultimately lead to the cessation or phasing out of discharges, emissions and losses to the environment (EPCEU, 2001). Nevertheless, concentrations of PCAs reported in sludge remain significantly higher than the regulated PCBs, which are typically <1 mg kg^{-1} dw in sludge.

A preliminary human health exposure assessment, comparing the ratio of the PCA contaminant concentration in biosolids to the tolerable daily intake of 100 μg kg^{-1} day^{-1}, demonstrated that PCAs could potentially represent a risk to human health from worse case exposure by the direct ingestion pathway for biosolids (IPCS, 1996). The mean concentration in UK sludge was used for the calculations (1800 mg kg^{-1} dw from Stevens et al., 2003). Thus, the direct ingestion of 100 mg day^{-1} of sludge (US EPA, 1997) by a child with a body weight of 15 kg would contribute 12% of the child's tolerable daily intake of PCAs. By contrast, a 15 kg child suffering from the pica medical condition (deliberate ingestion of soil) is assumed to ingest 10 g of soil per day (US EPA, 1997) and would therefore be exposed to 514% of their tolerable daily exposure to PCAs. The concentrations of PCAs in sewage sludge, evidence of accumulation in human and environmental biota, as well as toxicity data indicate that further research is necessary to assess the risk to human health and the environment from the industrial use of this chemical group.

2.8. Polychlorinated naphthalenes (PCNs)

Technical mixtures of PCNs have been used since the early 1900s as dielectric fluids, engine oil additives, electroplating masking compounds, wood preservatives, lubricants, and for dye production (Falandysz, 1998). The historical use of PCNs precedes PCBs, however their applications are similar. They are also structurally similar and have similar physico-chemical properties. There are 75 PCN congeners, substituted with one to eight chlorine atoms per naphthalene molecule (Table 1). They were voluntarily phased out in the 1970s in the USA, but global production of PCN mixtures was estimated to be approximately 150,000 t in the 1990s (Falandysz, 1998).

PCNs are ubiquitous environmental contaminants sharing many of the characteristics of UNEP POPs (Alcock and Jones, 1999): bioaccumulation (Falandysz, 1998), toxicity (Blankenship et al., 2000), long-range atmospheric transport (Harner et al., 1998) and environmental persistence. Several PCN congeners exhibit dioxin-like toxicity and have been assigned TEF values similar to the coplanar PCBs (Blankenship et al., 2000; Villeneuve et al., 2000). There are three known main sources of PCNs in the environment: technical PCN formulations, technical PCB formulations, and thermal (e.g. combustion, roasting, metal reclamation) and other processes (e.g. chloro-alkali industry) in the presence of chlorine (Falandysz, 1998).

Very limited data on PCN concentrations in sludge was found in the literature (Table 3), with reports from Sweden (Nylund et al., 1992), the UK (Stevens et al., 2003) and recently, China (Guo et al., 2008). In the early 1990s, the ΣPCN (9 congeners) concentration in sewage sludge from Sweden ranged between 3.2 and 5.9 μg kg^{-1} dw (Nylund et al., 1992). Slightly higher concentrations were reported in the UK where the mean ΣPCN value was 83 μg kg^{-1} dw and range was 50 to 190 μg kg^{-1} dw (Stevens et al., 2003). Total PCN concentrations in sludge samples from eight Chinese WWTPs, measured for >70 of the 75 PCN congeners, were between 1.48 and 21.21 μg kg^{-1} dw, and the ‘dioxin’ toxicity equivalence (TEQ) was in the range 0.11–2.45 ng WHO_{05} kg^{-1} dw (Guo et al., 2008). This contribution of dioxin-like PCNs is not high when compared to recently reported dioxin-like compound concentrations in English and European sludges (Stevens et al., 2001).

2.9. Polydimethylsiloxanes (PDMSs)

Polydimethylsiloxanes (PDMSs) are man-made organosilicone compounds that range from low molecular weight volatile materials to high molecular weight polymeric substances (Fendinger et al., 1997). They are widely used in industrial applications and consumer products, such as textile treatments, household and personal care products and antifoams for food processing or WWTP (Griessbach and Lehmann, 1999). These applications all result in discharges to WWTP and the potential to enter the environment as a component of effluents and in sewage sludge (Fendinger et al., 1997). PDMSs have been detected in environmental samples such as surface water, sediments and fish tissue (Watanabe et al., 1984, 1988). PDMSs have low ecological toxicity, which occurs at higher concentrations than those observed in the environment (Hobbs et al., 1975), and are not considered to pose an ecologically significant threat (Frye, 1988).

PDMSs have a very low water solubility and are primarily removed by sorption to solids during wastewater treatment (Varaprath et al., 1996; Fendinger et al., 1997). At least 94% of PDMSs are unchanged during wastewater treatment because of high chemical and thermal stabilities (Watts et al., 1995; Fendinger et al., 1997). PDMSs are not toxic to wastewater microbial communities and do not affect treatment performance (Watts et al., 1995). PDMSs not removed on the sludge solids are present in wastewater treatment effluent as a component of the suspended solids (Fendinger et al., 1997) and this accounts for their environmental distribution in sediments and surface waters (Watanabe et al., 1988).

PDMSs degrade in the soil environment as a result of abiotic processes rather than biodegradation, and have a half-life estimated to range from 4 to 28 days (Carpenter et al., 1995; Lehmann and Miller, 1996; Lehmann et al., 1998; Griessbach and Lehmann, 1999). Increased soil moisture retards the degradation of PDMSs in soil (Griessbach and Lehmann, 1999). Clays appear to be the component responsible for catalysing oligomerization and hydrolysis reactions of PDMSs in soil (Buch and Ingebrigtson, 1979; Xu et al., 1998). A multiyear field dissipation study and laboratory studies, to evaluate the persistence or degradation of PDMSs in biosolids-amended soils, found that soil moisture was the factor controlling the persistence or degradation of PDMSs and that there was no direct effect of biosolids on PDMS persistence or degradation (Traina et al., 2002). As may be expected, the half-life for PDMS determined under field conditions (876 to 1443 days) was longer than that estimated in laboratory studies and this was attributed to the higher moisture contents of the field soils (Traina et al., 2002). PDMSs eventually mineralise in soil to carbon dioxide and silicic acid (Stevens, 1998). A study examining the ecotoxicity of PDMS found no effects on seed germination, seed survival, plant yields or soil microorganisms (Tolle et al., 1995).

Few studies have reported the concentrations of PDMSs present in sewage sludge (Table 3). The most comprehensive study available (Fendinger et al., 1997) indicated PDMS concentrations in US sludges were in the range 290 and 5155 mg kg^{-1} dw with a mean value of 1120 mg kg^{-1} dw. This is approaching a magnitude higher than the concentration (144 mg kg^{-1} dw) reported in a Japanese sludge (Watanabe et al., 1984). Further work would appear to be necessary to determine the concentrations of PDMSs in sewage sludges internationally.

2.10. Perfluorochemicals (PFCs)

Perfluorochemicals (PFCs) are a family of anthropogenic chemicals that have been used since the late 1950s to make products resistant to heat, oil, stains, grease and water. Common applications include non-stick cookware, breathable membranes for clothing, stain-resistant carpets and fabrics, components of fire fighting foam, surfactants and other industrial applications (US EPA, 2008). They have been used in many industry sectors, including the aerospace, automotive, building/construction, chemical processing, electronics, semiconductors, and textile industries (US EPA, 2008).

PFCs are persistent and widely dispersed in the environment (Giesy and Kannan, 2001; Kannan et al., 2001). Accumulation of PFCs has been detected in ocean animals, such as birds and mammals, and in human tissues throughout the world (Olsen et al., 2003; Kannan et al., 2004). The human and environmental toxicological response to such exposure is not known, but could include endocrine disruption (Lau et al., 2004).

The chemical structures of PFCs make them very resistant to degradation in the environment; the carbon–fluorine bonds are extremely strong and are stronger relative to other commonly used halogens viz., bromine and chlorine. Consequently, perfluorocarbon chains do not readily biodegrade and any biodegradation may be limited to attached hydrocarbon moieties. The two most common groups of PFCs that are measured and detected in environmental matrices are:

- Perfluoroalkyl sulphonates (PFASs) — perfluorooctane sulphonate (PFOS), perfluorohexane sulphonate (PFHxS), perfluorooctane sulphonamide (PFOSA)
- Perfluoroalkyl carboxylates (PFACs) — perfluorooctanoic acid (PFOA), perflurorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA)

PFASs and PFACs are synthetic chemicals that do not occur naturally in the environment (US EPA, 2008). They are employed as a base chemical in the preparation of fluoropolymers and upon degradation can release the environmentally persistent monomers (Boulanger et al., 2005).

Directive 2006/122/EC (EPCEU, 2006) places restrictions on the marketing and use of PFOS and there are also voluntary reductions on PFOA although it is still manufactured. PFOS is also under review for possible identification as a WFD Priority Substance or PHS (EPCEU, 2008). The EU is currently assessing PFOA and, whilst there are no restrictions in place in the EU at present, a ban could be imposed in the future. However, these substances have been extensively used in the built environment and therefore could represent a significant, long-term diffuse input into wastewater and sludge.

The earliest available report of PFCs in sewage sludge is a study of sludges collected from six USA cities (3M Environmental Laboratory, 2001). PFOS and PFOA were the most common PFCs present and were detected in all samples analysed at the low μg kg^{-1} dw range (Table 3). A sludge sample was tested from a WWTP serving a fluorochemical manufacturer and this correlated with substantial increases in PFOS (2980 μg kg^{-1} dw) and PFOA (173 μg kg^{-1} dw) concentrations. This study demonstrated that PFCs, in particular PFOS and PFOA, are likely to be present in sludge in Western countries where PFCs are manufactured and used. Domestic sources are also likely to be a major contributor of PFCs in sewage sludge.

Other studies in the USA (Schultz et al., 2006; Sinclair and Kannan, 2006; Loganathan et al., 2007) and Europe (Bossi et al., 2008) report similar concentration ranges. No differences in PFC levels were apparent in sludges from urban and rural WWTPs, however, major seasonal variations in concentrations were observed (Loganathan et al., 2007). Whilst PFCs have been investigated at WWTPs in other countries (Alzaga and Bayona, 2004; Boulanger et al., 2005), sewage sludge concentrations have mainly been reported in the US. This is largely a consequence of the analytical difficulties associated with quantification of PFCs in sewage sludge matrices.

Mass balance studies of PFCs at WWTP commonly report higher mass loadings of PFOA and PFOS in WWTP effluent compared to raw influent (Schultz et al., 2006; Sinclair and Kannan, 2006; Loganathan et al., 2007). This suggests the degradation of other fluorinated organic compounds (i.e. fluoropolymers) into PFOA and PFOS may take place during wastewater treatment (Loganathan et al., 2007).

Field investigations have demonstrated that PFCs in sludge-amended soil can be mobilised by rainfall (Gottschall et al., 2010).

2.11. Quaternary ammonium compounds (QACs)

Quaternary ammonium compounds (QACs) are cationic surfactants. The molecules contain at least one hydrophobic hydrocarbon alkyl chain linked to a positively charged nitrogen atom. The other alkyl groups are typically short-chain substituents such as methyl or benzyl groups. Cationic surfactants are positively charged in aqueous solutions (Madsen et al., 2001; Ying, 2006). QACs are commonly used in domestic products such as fabric softeners, hair conditioners and other hair preparations. Other applications of cationic surfactants include disinfectants and biocides, emulsifiers, wetting agents, and processing additives. By volume, the most important cationic surfactants in household products are the alkyl ester ammonium salts that are used in fabric softeners (Madsen et al., 2001).

Ditallow dimethyl ammonium chloride (DTDMAC) was the most widely used active ingredient in fabric softeners. However DTDMAC is toxic to aquatic organisms (Roghair et al., 1992; Versteeg et al., 1992) and was therefore voluntarily phased out by industry following an ecological risk assessment (van Leeuwen et al., 1992) in preference of more biodegradable QACs, such as diethyl ester dimethyl ammonium chloride (DEEDMAC) (Giolando et al., 1995). Fernandez et al. (1996) monitored the DTDMAC concentrations in sewage sludge in Switzerland, which declined from 3.67 g kg^{-1} dw in 1991 to 0.21 g kg^{-1} dw in 1994 due to its replacement with the alternative QACs.

Domestic use of QACs is the primary source of these compounds entering WWTPs. Due to their positive charge, cationic surfactants sorb strongly to the negatively charged surfaces of sludge, soil and sediments (Madsen et al., 2001; Ying, 2006; Clara et al., 2007), and it is estimated that ~90% of QACs associate with sludge during wastewater treatment (van Leeuwen et al., 1992). Removal of QACs in wastewater treatment can also be attributed to biodegradation (Nishiyama et al., 1995), where degradation rates are typically reported in days or hours (Giolando et al., 1995; Sütterlin et al., 2008). WWTP discharges can result in environmental contamination of marine sediments with QACs (Li and Brownawell, 2009).

There are very few reports of QAC concentrations in sludge in the scientific peer-reviewed literature (Table 3). A recent study from Austria reported that the total QAC concentration was in the range 22 to 103 mg kg^{-1} dw (MartÌnez-Carballo et al., 2007), suggesting further substantial reductions in QACs have taken place compared to earlier work addressing the impact of phasing out DTDMAC (Fernandez et al., 1996).

It has been controversially argued that QACs have biocidal properties that may confer antibiotic resistance to bacteria (Gaze et al., 2005; Gaze, 2008). However, it is difficult to reconcile this firstly because QACs are not disinfectants, but are in fact surfactants with low toxicity and ecotoxicity (Giolando et al., 1995). Secondly, modern QAC formulations are designed to rapidly biodegrade during wastewater treatment and anaerobic digestion, and are almost completely removed by these processes (Giolando et al., 1995). In soil QACs rapidly degrade with short half-lives (17–40 d) (Giolando et al., 1995).

2.12. Steroids

Natural endogenous (17β-oestradiol, oestrone, oestriol) and synthetic steroids (17α-ethinyloestradiol, mestranol) are excreted by humans and WWTP effluent is the primary source of synthetic steroids entering the environment (Snyder et al., 2001). Livestock (particularly lactating cows) are also a major source of endogenous oestrogen inputs to soil (Kolodziej et al., 2004). Over 99% of oestrogenic activity in sewage effluents and surface waters may be attributable to the presence of 17β-oestradiol (E2) and 17α-ethinyloestradiol (EE2) at concentrations in the ng L^{-1} range (Snyder et al., 2001). Oestrogenic activity in WWTP effluents has resulted in adverse effects on environmental biota (Jobling et al., 1998). Natural and synthetic steroids are excreted from the human body as inactive polar conjugates, but are present in sewage influent and effluent as free, active steroids (Belfroid et al., 1999). Once released from the body conjugated oestrogens undergo chemical or enzymatic dissociation in bacterial sludge and re-form as active oestrogens (Belfroid et al., 1999; Reddy et al., 2005).

Several investigations have examined the fate of oestrogens in WWTPs, however, few studies have measured the concentrations of oestrogenic compounds in sludge due to the analytical difficulties involved (Gomes et al., 2004). The presence of 'free' oestrogens in WWTP effluents and receiving waters is commonly reported (Shore et al., 1993; Desbrow et al., 1998; Ternes et al., 1999b), demonstrating that the conversion of oestrogen metabolites into active forms occurs somewhere between the domestic discharge and WWTP outlet. However, the degradation of all steroid-like compounds (natural and synthetic) occurs rapidly and typically within a few days or less (Ternes et al., 1999a; Korner et al., 2000; Layton et al., 2000; Hashimoto and Murakami, 2009). Natural oestrogens biodegrade in the order: 17β-oestradiol → oestrone → oestriol and at a faster rate compared to synthetic mestranol and 17α-ethinyloestradiol (Ternes et al., 1999a). Research at full-scale WWTPs indicates that operational retention times may only allow partial degradation as concentrations of oestrone measured in treated effluent are frequently increased compared to the influent raw wastewater (Barontri et al., 2000).

Mass balance studies of WWTPs consistently show high removal rates of oestrogens during wastewater treatment, equivalent to: 64–99.9% for 17β-oestradiol, and 78–83% for oestrone and 17α-ethinyloestradiol (Ternes et al., 1999b). While many studies do not distinguish between degradation and sludge partitioning (Schlusener and Bester, 2008), laboratory experiments indicate the high biodegradability of steroids (Ternes et al., 1999a). Such laboratory studies indicate that degradation processes contribute significantly to steroid removal (Ternes et al., 1999a). The removal rate of the natural hormones 17β-oestradiol, oestrone and 17α-ethinyloestradiol during wastewater treatment was >90% and only 5% of the mass of oestrogens entering the WWTP was sorbed to the final digested sewage sludge, indicating high biodegradability in the WWTP (Andersen et al., 2003).

Few studies have reported steroid concentrations in sewage sludge due to analytical difficulties, as well as high degradation rates. The concentrations of oestrone (<2–37 μg kg^{-1} dw), 17β-oestradiol (5–49 μg kg^{-1} dw), 17α-ethinyloestradiol (<4–17 μg kg^{-1} dw) and mestranol (<2 μg kg^{-1} dw) were measured by Ternes et al. (2002) in German sludges (Table 3). A recent survey of US sludges (n = 84) quantified 25 steroids (US EPA, 2009), but only three steroid compounds (i.e., campesterol, cholestanol, and coprostanol) were found (US EPA, 2009). 17α-ethinyloestradiol was not detected in any sample and five hormones were found in fewer than six samples. Other oestrogenic steroids were not frequently detected and when detected were in the low μg kg^{-1} dw concentration range (US EPA, 2009).

These low concentrations, combined with fast biodegradation rates in WWTP mass balance and laboratory studies suggest that steroids are unlikely to pose a risk to human health or the environment when land applying biosolids.

2.13. Synthetic musks

Synthetic musks are inexpensive substitutes for natural musks and have been used since the 1930s as fragrances in a variety of domestic and industrial products viz., detergent, cosmetics, shampoo, perfume, food and cigarette additives (Rimkus, 1999). Synthetic musks can be broadly categorised into two groups: nitromusks and polycyclic musks. Nitro musks were the first commonly used synthetic musks, but their use was reduced in the 1950s due to evidence of toxicity to humans and the environment (Tas et al., 1997). They were largely replaced with the polycyclic musks, which account for approximately 85% of worldwide production, while nitro musks account for the remaining 15% (Tas et al., 1997).

The most commonly used synthetic musks are:

- nitromusks — musk moskene (MM), musk tibetene (MT), musk xylene (MX), musk ketone (MK) and musk ambrette (MA).
- polycyclic musks — Galaxolide™ (HHCB), Tonalide™ (AHTN), Celestolide™ (ADBI), Phantolide™ (AHMI), Cashmeran™ (DPMI) and Traseolide™ (ATII).

The majority of synthetic musk applications occur in the domestic environment and are found in personal care products that will be released into the sewer after use and, consequently, the principal source of synthetic musks to the environment is thought to be WWTP effluents and sludges (Rimkus, 1999). WWTP mass balance studies indicate removal rates of between 83 and 91%, whereas approximately 40% of AHTN and HHCB were eliminated during anaerobic sludge digestion (Balk and Ford, 1999a). The concentrations of synthetic musks in sewage sludge have been reported from Switzerland (Herren and Berset, 2000), Germany (Heberer, 2002), Spain (Llompart et al., 2003), UK (Stevens et al., 2003), China (Zeng et al., 2005) and Hong Kong (Shek et al., 2008).

The nitromusks (MA, MX, MM, and MT) were generally not detected in these studies and when present were found at low µg kg^{-1} dw values. This is consistent with use patterns of nitromusks that have largely been replaced by the polycyclic musks (Rimkus, 1999). MX is currently under review for possible identification as a WFD Priority Substance or PHS (EPCEU, 2008).

The polycyclic musks most frequently detected and at the highest concentrations in sludge are HHCB (0.1–81 mg kg^{-1} dw) and AHTN (0.03–16 mg kg^{-1} dw) (Table 3). Again, this is consistent with use patterns as, together, HHCB and AHTN account for >95% of the market share of polycyclic musks (Tas et al., 1997). Current German proposals are to set biosolids limits for HHCB and AHTN of 10 mg kg^{-1} dw and 15 mg kg^{-1} dw, respectively (BMU, 2007). Other polycyclic musks (ADBI, DPMI) are typically present in lower concentration ranges (<1 mg kg^{-1} dw). The mean HHCB concentration in UK sewage sludges (27 mg kg^{-1} dw) was larger than in other European sludges, such as Switzerland (4.85 mg kg^{-1} dw), Germany (8.26 mg kg^{-1} dw) or Spain (0.16 mg kg^{-1} dw). However, concentrations of HHCB measured in sludge in China and Hong Kong are similar to the UK. Soil ecotoxicity studies report a PNEC for HHCB and AHTN of 0.32 mg kg^{-1} dw that incorporates a fifty fold safety factor and is based upon earthworm and springtail no observable effects concentrations of 45 mg kg^{-1} dw for both chemicals (Balk and Ford, 1999b). The concentrations of these compounds found in biosolids are relatively high when compared to other POPs and therefore, further investigation is warranted to elucidate their fate, behaviour, and persistence in biosolids-amended soils (Stevens et al., 2003).

2.14. Triclosan and triclocarban

Triclosan (TCS; 5-chloro-2-[2,4-dichloro-phenoxy]-phenol) and triclocarban (TCC; 3,4,4′-trichlorocarbanilide) are antimicrobial agents widely used in personal care products such as shampoos, soaps, deodorants, cosmetics, skin-care lotions and creams, mouth rinses, and toothpastes. These domestic applications are likely to be the major source of TCS and TCC to WWTPs (Bester, 2003). The amount of TCS and TCC used in consumer products typically ranges from 0.1 to 0.3% (w/w). At these levels they exhibit a broad-spectrum activity against bacteria, molds and yeasts (McAvoy et al., 2002).

TCS and TCC are both relatively hydrophobic, with log K_{OW} values at neutral pH of 3.5–4.8 and 4.9, respectively (Halden and Paull, 2005; Snyder et al., 2010). The octanol–water distribution of TCS, however, depends on the pH of the environmental matrix that the compounds are exposed to, since the hydroxyl groups (–OH) in the molecule are capable of deprotonation allowing water solubility.

Mass balance studies at WWTP show the incomplete removal of TCC and TCS during wastewater treatment (Heidler et al., 2006; Sapkota et al., 2007). Therefore, TCS and TCC are released into the environment in WWTP effluents and by land application of biosolids. Consequently, they are regularly detected in surface waters receiving WWTP inputs (Halden and Paull, 2004; Halden and Paull, 2005). However, they can also be found upstream of WWTP discharges indicating environmental persistence (Sapkota et al., 2007). Potential environmental problems from the release of TCC and TCS from WWTP effluent in surface water include bioaccumulation in algae and snails (Coogan et al., 2007; Coogan and La Point, 2008), algal growth inhibiting effects (Yang et al., 2008) and endocrine disruption (Ahn et al., 2008).

A mass balance for TCC at a WWTP showed that approximately 75% of the initial mass of TCC was recovered in sludge, with a concentration of 51 mg kg^{-1} dw (Heidler and Halden, 2007). It is commonly reported that TCS and TCC partition to sludge during wastewater treatment (Ying and Kookana, 2007). Mass balance studies indicate that losses of between 48 and 65% occur possibly due to volatilization or biodegradation (Bester, 2003; Heidler and Halden, 2007), but biodegradation is the more likely removal mechanism (Ying and Kookana, 2007). Laboratory studies have also confirmed the degradation of TCS (Federle et al., 2002; Stasinakis et al., 2007). Biosolids were identified as a source of TCS in agricultural soil contributing to the bioaccumulation of TCS in earthworm tissue with bioaccumulation factors ranging from 0.05 to 27 (Kinney et al., 2008). Furthermore, two recent studies have detected the movement of several pharmaceuticals and personal care products from agricultural areas amended with biosolids into tile drainage water (Lapen et al., 2008) and runoff (Topp et al., 2008). Water run-off experiments found that TCS leached only from surface applied biosolids and not

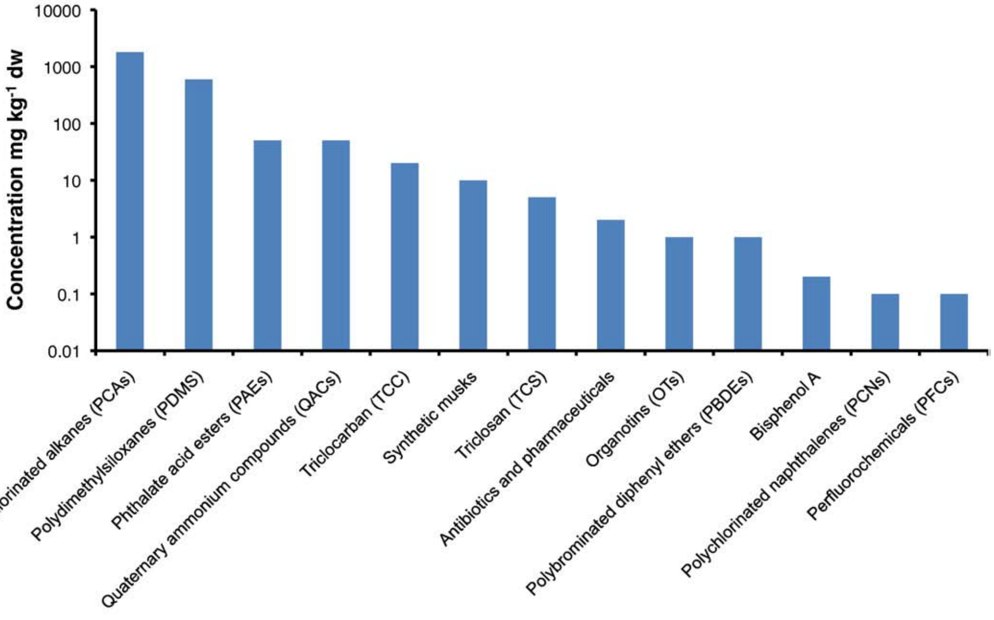


Fig. 1. Typical concentrations of selected 'emerging' organic contaminants in sewage sludge (mg kg^{-1} dw).

Table 4
Assessment matrix to determine research priorities for selected 'emerging' organic contaminants in sewage sludge with respect to their potential significance for agricultural utilisation.

Emerging organic contaminant	Persistent in soil (>6 months) 2 – yes 1 – uncertain 0 – no	Human food chain 2 – possible 1 – uncertain 0 – no	Ecological bioaccumulation 2 – yes 1 – possible 0 – no	Soil ecotoxicity 2 – yes 1 – uncertain 0 – no	Research quality 3 – lack of empirical data 2 – few reported studies 1 – a number of consistent studies 0 – many consistent studies	Score (/11)
Antibiotics and pharmaceuticals[a]	0	2	0	1	2	5
Benzothiazoles	1	1	0	1	3	6
Bisphenol A	0	0	0	0	2	2
Organotins	1	1	2	1	2	7
Phthalate acid esters (PAEs)	0	0	0	0	1	1
Polybrominated diphenyl ethers (PBDEs)	2	2	2	1	0	7
Polychlorinated alkanes (PCAs)	2	2	1	1	3	9
Polychlorinated naphthalenes (PCNs)	2	2	1	1	3	9
Polydimethylsiloxanes (PDMSs)	0	0	0	0	1	1
Perfluorochemicals (PFCs)	2	2	2	1	3	10
Quaternary ammonium compounds (QACs)	0	0	0	0	2	2
Steroids	0	0	0	0	2	2
Synthetic musks	1	0	1	0	1	3
Triclosan	1	0	2	2	2	7
Triclocarban	1	0	2	2	2	7

[a] The chemical properties of antibiotics and pharmaceuticals and subsequent behaviour in the environment can vary greatly. The scores are considered generally for antibiotics and pharmaceuticals, certain exceptions such as carbamazepine may exhibit longer soil persistence.

from subsurface application. Therefore, land application practices for biosolids in the UK are likely to prevent surface water contamination from TCS or TCC, although a potential risk to groundwater by leaching has been suggested (Topp et al., 2008).

Reports of TCS and TCC concentrations in activated sludges and biosolids have been reported from the USA (McAvoy et al., 2002; Heidler et al., 2006; Kinney et al., 2006; Sapkota et al., 2007; US EPA, 2009), Germany (Bester, 2003), Spain (Morales et al., 2005), Canada (Chu and Metcalfe, 2007), Australia (Ying and Kookana, 2007) and Greece (Gatidou et al., 2007; Pothitou and Voutsa, 2008; Stasinakis et al., 2008). The ranges of concentrations reported for TCS and TCC are 0.5–16 mg kg^{-1} dw and 4–50 mg kg^{-1} dw, respectively (Table 3). Recent biosolids surveys in the USA show that TCC and TCS are routinely detected in biosolids and that the concentrations are higher than previously reported (McAvoy et al., 2002; Heidler et al., 2006; Kinney et al., 2006; Sapkota et al., 2007; US EPA, 2009).

3. Assessment and ranking of emerging contaminants

3.1. Typical concentrations of organic contaminants in sewage sludge

A summary of reported concentrations of the selected 'emerging' contaminants examined here is presented in Fig. 1. The concentrations in Fig. 1 are presented on a logarithmic scale in descending order of reported mean concentrations, ranging from PCAs (g kg^{-1} dw) to PFCs (μg kg^{-1} dw). The concentrations of the industrial chemical PCAs are much higher compared to contaminants from domestic sources i.e., QACs, TCS. These concentrations suggest significant industrial discharges of PCAs occur into the wastewater collection system. Chemicals utilized in the domestic environment were in the next 'high-level' concentration range (PAEs, QACs, TCC, synthetic musks, TCS), followed by less commonly used industrial and domestic chemicals (OTs, PBDEs, PCNs, PFCs).

3.2. Matrix assessment

Research and monitoring priorities were identified from an assessment matrix consisting of five criteria applied to the selected 'emerging' contaminants (Table 4). These included:

- environmental persistence in soil environment (>6 months);
- potential for human health impacts resulting from the land application biosolids;
- evidence or likelihood of bioaccumulation in humans or the environment;
- evidence of ecotoxicity, and
- the quality of empirical data and trends on the contaminant in biosolids internationally.

3.3. Assessment results

The 'emerging' contaminants were ranked in decreasing order of priority as follows (maximum possible score of 11):

- perfluorinated chemicals (10)
- polychlorinated alkanes (9), polychlorinated naphthalenes (9)
- polybrominated diphenyl ethers (7), organotins (7), triclosan (7), triclocarban (7)
- benzothiazoles (6)
- antibiotics and pharmaceuticals (5)
- synthetic musks (3)
- bisphenol A (2), quaternary ammonium compounds (2), steroids (2)
- phthalate acid esters (1), polydimethylsiloxanes (1).

PFCs represent a potentially major environmental uncertainty. They have been detected in human blood (Olsen et al., 2003) and environmental samples (Giesy and Kannan, 2001) throughout the world. They have a unique chemistry that facilitates a degree of water solubility, which is not observed with other POPs. Thus, the barriers that normally prevent human and ecological exposures to POPs in biosolids-amended soil may not prevent movement of PFCs. For example, increased water solubility raises the likelihood of exposure through all pathways – water contamination, plant accumulation and grazing animal accumulation (Chaney et al., 1996). Water contamination and plant accumulation are considered to be the priority pathways of concern, as grazing animal accumulation is not unique to PFCs. Whilst measures are in place in Europe to restrict the major exposure risks to PFOS (EPCEU, 2006), and could be extended to PFOA in future, transfer to biosolids could continue to occur over a long period due to the ubiquitous use of these substances within the built environment.

PCAs and PCNs were both detected in recent surveys of UK biosolids (Stevens et al., 2003). PCAs were found at relatively high concentrations (mean concentration 1800 mg kg^{-1} dw), while PCNs were typically less than 1 mg kg^{-1} dw. By comparing the concentrations of these compounds to PCBs and PCDD/Fs it is apparent that PCAs warrant further investigation, as the concentrations of PCAs are three orders of magnitude higher than those of PCBs found in contemporary sewage sludge. Also, there is mounting evidence that PCAs are accumulating in the human population and the impact of these chemicals on human health and the environment has not yet been explored (Nicholls et al., 2001; Thomas et al., 2006). A preliminary human health exposure assessment indicated that the concentrations of PCAs in sludge could be harmful to human health through the direct ingestion exposure pathway. The concentrations of PCNs are small in contrast and are unlikely to pose a threat to human health or the environment at the concentrations measured in sewage sludge internationally.

PBDEs have been the subject of increasing international research (Clarke et al., 2008c). PBDE concentrations in biosolids may be similar throughout the world, however, manufacturing can add significant quantities of PBDEs to the burden derived from domestic sources (Fabrellas et al., 2004). Furthermore, restrictions applied to the penta- and octa-PBDE commercial formulations may increase demand and consumption of the decaBDE formulation. The deca-formulation is the source of BDE 209, the major congener detected in sludges internationally and field studies have shown that this compound is persistent in the environment (Eljarrat et al., 2008).

Antimicrobial agents TCS and TCC have received increasing research attention internationally (Singer et al., 2002; Ying and Kookana, 2007) and are capable of ecological toxicity (Yang et al., 2008) and bioaccumulation in environmental biota (Kinney et al., 2008). However, a recent risk assessment (Reiss et al., 2009) showed that TCS was unlikely to pose a significant problem for sensitive environmental compartments from the agricultural use of biosolids. Nevertheless, field studies have demonstrated that TCS and TCC may exhibit some environmental persistence in biosolids-amended soil (Topp et al., 2008; Cha and Cupples, 2009). The biodegradation of these compounds is reported in laboratory (McAvoy et al., 2002) and WWTP studies (Ying and Kookana, 2007), but further evaluation of the persistence and toxicity of TCS and TCC in biosolids-amended soil is required. It is also important to recognise that the primary route of human exposure to TCS and TCC will occur in the domestic environment and not as a result of land applying biosolids.

Organotin compounds were present in small concentrations in biosolids in the studies reported, but are potentially ecotoxic. There are limited empirical biosolids measurements internationally, so it is difficult to draw definitive conclusions about typical biosolids concentrations. Furthermore, they warrant further investigation to determine their significance in biosolids-amended soil.

Limit values for benzothiazoles in sludge are proposed and under consideration by the German Government. However, there are insufficient data concerning these chemicals to make an informed assessment of their potential significance. Nevertheless, benzothiazoles have not been detected in environmental media and laboratory studies indicate that they are biodegradable (de Wever and Verachtert, 1997; Gaja and Knapp, 1998). Therefore, it would appear that there are no specific scientific grounds for regulating this group of OCs in biosolids. Nevertheless, further research is required to determine typical concentrations in sewage sludge, environmental persistence, ecological toxicity and persistence in biosolids-amended soil.

A recent risk assessment completed in Norway evaluated over 1400 pharmaceutical compounds based upon a tired approach where chemicals were screened against consumption, volume wastewater of influent, human metabolism, biodegradation and behaviour in WWTP (Eriksen et al., 2009). Fourteen pharmaceuticals were identified for further risk assessment investigation as the only compounds that potentially may pose risk to human health or the environment. These were: atorvastatin, carisoprodol, chlorprothixene, ciprofloxacin, dipyridamole, fexofenadinesotalol, gabapentin, levetiracetam, losartan, mesalazin, metoprolol, ranitidin and tetracycline. The estimated soil concentrations of drug substances (PEC) were low (concentration range 0.01–1 mg kg^{-1} dw) and well below the estimated PNEC values. Therefore Eriksen et al. (2009) concluded that drug substances in sewage sludge constitute a low risk to the soil compartment.

The polycyclic musks are unlikely to pose a risk to human health from land application of biosolids and the majority of human exposure will occur in the domestic environment. The environmental risk assessment of AHTN and HHCB indicates that these substances are unlikely to pose a significant hazard to the ecosystem at the concentrations likely to be found in biosolids-amended soil (Balk and Ford, 1999a,1999b). Therefore, proposals for AHTN and HHCB contaminant limits in biosolids appear unfounded. However, further research is warranted to understand the ecological risk of polycyclic musks with respect to fate, mobility and persistence given the relatively high concentrations of these compounds detected in sludge.

Four high-volume production chemicals were included for assessment and all were indicated as having a low research priority. Concern has been raised over QACs due to potential development of antibiotic resistance and endocrine disruption for bisphenol A and phthalates. However, these chemicals are not environmentally persistent, they biodegrade rapidly and humans are routinely exposed to these compounds through more important pathways via dermal and ingestion routes in the domestic environment. PDMS is another high-volume production chemical that is not considered to pose a risk to humans or the environment when land applying biosolids due to low toxicity.

Steroid concentrations in sludge were only found in two international studies. There are analytical difficulties that may prevent the detection and measurement of this group of compounds, however, they are also readily degradable and are therefore not present in significant quantities in stabilised biosolids.

4. Conclusions

There are 50 million chemicals entered in the Chemical Abstracts Registry and of these 143,000 chemicals are registered with the European Chemicals Agency for industrial use (ECHA, 2009; Toussant, 2009). Once discharged from industrial, domestic and urban sources into the urban wastewater collection system they may transfer to the residual sewage sludge during wastewater treatment. Continued vigilance is therefore required to monitor and determine the significance and implications of ‘emerging’ OCs for the land application of treated wastewater biosolids. The significance of a selection of key contaminants for the agricultural use of biosolids was examined here based upon persistence, human health impacts, bioaccumulation, ecotoxicity and quality of published research for the given chemicals. The concentrations of the 'emerging' OCs in biosolids were also considered.

Two chemical classes warrant particular note. These are the PFCs and PCAs. PFCs are an emerging environmental concern as they have been detected in human blood (Olsen et al., 2003) and environmental samples (Giesy and Kannan, 2001) throughout the world. They have a unique chemistry for a chemical defined as a POP that facilitates a degree of water solubility, and therefore, there is an increased likelihood of exposure through all pathways (water contamination, plant accumulation and grazing animal accumulation) compared to other POPs (Chaney et al., 1996). PCAs were found at relatively high concentrations in sludge (mean concentration 1800 mg kg^{-1} dw). Comparison of the concentrations of these compounds to PCBs and PCDD/Fs shows that the PCA content in sludge is three orders of magnitude higher than PCB values for instance, and signals the importance of further investigations into the significance of PCAs in biosolids for land application.

Recycling biosolids on land is recognised internationally as the most sustainable option for managing the residual sludge from urban wastewater treatment and most risk assessments demonstrate that this practice does not place human health at risk from the OCs studied.

However, continued vigilance in assessing the significance and implications of ‘emerging’ OCs in sludge is necessary to support and ensure the long-term sustainability and security of the beneficial agricultural route for biosolids management. The research and monitoring priorities for 'emerging' OCs in sludge we have identified and discussed here would further contribute to the technical evidence base to protect human health and the environment when sewage sludge biosolids are recycled in agriculture as soil improvers and fertilisers.

References

3M Environmental Laboratory (2001) Environmental Monitoring — Multi-City Study Water, Sludge, Sediment, POTW Effluent and Landfill Leachate Samples 3M, United States.

Abad E, Martinez K, Planas C, Palacios O, Caixach J, Rivera J. Priority organic pollutant assessment of sludges for agricultural purposes. Chemosphere 2005;61:1358.

Ahn KC, Zhao B, Chen J, Cherednichenko G, Sanmarti E, Denison MS, et al. In vitro biologic activities of the antimicrobials triclocarban, its analogs, and triclosan in bioassay screens: receptor-based bioassay screens. Environ Health Perspect 2008;116:1203–10.

Alcock RE, Jones KC. Polychlorinated biphenyls in digested UK sewage sludges. Chemosphere 1993;26:2199.

Alcock R, Jones K. New directions: “new” organic compounds in the environment. Atmos Environ 1999;33:1645–6.

Alcock RE, Bacon J, Bardget RD, Beck AJ, Haygarth PM, Lee RGM, et al. Persistence and fate of polychlorinated biphenyls (PCBs) in sewage sludge-amended agricultural soils. Environ Pollut 1996;93:83.

Alexander M. Aging, bioavailability, and overestimation of risk from environmental pollutants. Environ Sci Technol 2000;34:4259–65.

Alzaga R, Bayona JM. Determination of perfluorocarboxylic acids in aqueous matrices by ion-pair solid-phase microextraction-in-port derivatization–gas chromatography–negative ion chemical ionization mass spectrometry. J Chromatogr A 2004;1042: 155–62.

Alzieu C. Environmental problems caused by TBT in France: assessment, regulations, prospects. Mar Environ Res 1991;32:7-17.

Amir S, Hafidi M, Merlina G, Hamdi H, Jouraiphy A, El Gharous M, et al. Fate of phthalic acid esters during composting of both lagooning and activated sludges. Process Biochem 2005;40:2183–90.

Andersen H, Siegrist H, Halling-Sorensen B, Ternes TA. Fate of estrogens in a municipal sewage treatment plant. Environ Sci Technol 2003;37:4021–6.

Andrade NA, Mcconnell LL, Torrents A, Ramirez M. Persistence of polybrominated diphenyl ethers in agricultural soils after biosolids applications. J Agric Food Chem 2010;58:3077–84.

Andreozzi R, Raffaele M, Nicklas P. Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. Chemosphere 2003;50:1319–30.

Aparicio I, Santos JL, Alonso E. Limitation of the concentration of organic pollutants in sewage sludge for agricultural purposes: a case study in South Spain. Waste Manage 2009;29:1747–53.

Aranda JM, O'connor GA, Eiceman GA. Effects of sewage sludge on di-(2-ethylhexyl) phthalate uptake by plants. J Environ Qual 1989;18:45–50.

Bago B, Martin Y, Mejia G, Broto-Puig F, Diaz-Ferrero J, Agut M, et al. Di-(2-ethylhexyl) phthalate in sewage sludge and post-treated sludge: quantitative determination by HRGC-MS and mass spectral characterization. Chemosphere 2005;59:1191–5.

Balk F, Ford RA. Environmental risk assessment for the polycyclic musks AHTN and HHCB in the EU: I. Fate and exposure assessment. Toxicol Lett 1999a;111:57–79.

Balk F, Ford RA. Environmental risk assessment for the polycyclic musks, AHTN and HHCB: II. Effect assessment and risk characterisation. Toxicol Lett 1999b;111: 81–94.

Ballscmitter K, Zell M. Analysis of polyhlorinated biphenyls (PCB) by glass capillary gas chromatography. Fresenius J Anal Chem 1980;302:20–31.

Bancon-Montigny C, Lespes G, Potin-Gautier M. Improved routine speciation of organotin compounds in environmental samples by pulsed flame photometric detection. J Chromatogr A 2000;896:149–58.

Barontri CRC, D'ascenzo G, Di Corcia A, Gentili A, Samperi R. Monitoring natural and synthetic estrogens at activated sludge sewage treatment plants and in a receiving river water. Environ Sci Technol 2000;34:5059–66.

Bayen S, Obbard JP, Thomas GO. Chlorinated paraffins: a review of analysis and environmental occurrence. Environ Int 2006;32:915–29.

Belfroid AC, van der Horst A, Vethaak AD, Schafer AJ, Rijs GBJ, Wegener J, et al. Analysis and occurrence of estrogenic hormones and their glucuronides in surface water and waste water in The Netherlands. Sci Total Environ 1999;225:101–8.

Bester K. Triclosan in a sewage treatment process — balances and monitoring data. Water Res 2003;37:3891–6.

Blankenship AL, Kannan K, Villalobos SA, Villeneuve DL, Falandysz J, Imagawa T, et al. Relative potencies of individual polychlorinated naphthalenes and halowax mixtures to induce Ah receptor-mediated responses. Environ Sci Technol 2000;34:3153–8.

BMU (2007) BUNDESMINISTREIUM FUER UMWELT (BMU), *Novellierung der Klaerschlammverordnung,* http://www.bmu.de/files/pdfs/allgemein/application/pdf/novellierung_klaerschlammverordnung.pdf. Accessed 20 July 2010.

Bossi R, Strand J, Sortkjær O, Larsen MM. Perfluoroalkyl compounds in Danish wastewater treatment plants and aquatic environments. Environ Int 2008;34:443–50.

Boulanger B, Vargo JD, Schnoor JL, Hornbuckle KC. Evaluation of perfluorooctane surfactants in a wastewater treatment system and in a commercial surface protection product. Environ Sci Technol 2005;39:5524–30.

Boxall ABA, Johnson P, Smith EJ, Sinclair CJ, Stutt E, Levy LS. Uptake of veterinary medicines from soils into plants. J Agric Food Chem 2006;54:2288–97.

Braekevelt E, Tittlemier SA, Tomy GT. Direct measurement of octanol–water partition coefficients of some environmentally relevant brominated diphenyl ether congeners. Chemosphere 2003;51:563–7.

Briggs GG, Bromilow RH, Evans AA. Relationships between lipophilicity and root uptake and translocation of non-ionised chemicals by barley. Pesticide Sci 1982;13: 495–504.

Bright DA, Healey N. Contaminant risks from biosolids land application: contemporary organic contaminant levels in digested sewage sludge from five treatment plants in Greater Vancouver, British Columbia. Environ Pollut 2003;126:39–49.

BSEF (2005) Bromine Science and Environmental Forum Bromine Science and Environment forum, Accessed 9th July 2008 <www.bsef.com>.

Buch RR, Ingebrigtson DN. Rearrangement of poly (dimethylsiloxane) fluids on soil. Environ Sci Technol 1979;13:676–9.

Cadogan D. Health and environmental impact of phthalates. Plastics Addit Compounding 2002;4:28–9.

Campbell I, McConnell G. Chlorinated paraffins and the environment. 1. Environmental occurrence. Environ Sci Technol 1980;14:1209–14.

Carpenter JC, Cella JA, Dorn SB. Study of the degradation of polydimethylsiloxanes on soil. Environ Sci Technol 1995;29:864–8.

Cartwright CD, Thompson IP, Burns RG. Degradation and impact of phthalates plasticizers on soil microbial communities. Environ Toxicol Chem 2000;19:1253–61.

CEC (1986) *Council Directive of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (86/278/EEC).* Official Journal of the European Communities No. L 181/6–12, Brussels.

CEC (1991) *Council Directive of 21 May 1991 concerning urban waste water treatment (91/271/EEC).* Official Journal of the European Communities No. L 135/40–52, Brussels.

Cha J, Cupples AM. Detection of the antimicrobials triclocarban and triclosan in agricultural soils following land application of municipal biosolids. Water Res 2009;43:2522–30.

Chaney RL, Ryan JA, O'Connor GA. Organic contaminants in municipal biosolids: risk assessment, quantitative pathways analysis, and current research priorities. Sci Total Environ 1996;185:187–216.

Chau YK, Zhang S, Maguire RJ. Occurrence of butyltin species in sewage and sludge in Canada. Sci Total Environ 1992;121:271–81.

Cheng H-F, Kumar M, Lin J-G. Degradation kinetics of di-(2-ethylhexyl) phthalate (DEHP) and organic matter of sewage sludge during composting. J Hazard Mater 2008;154:55–62.

Chu S, Metcalfe CD. Simultaneous determination of triclocarban and triclosan in municipal biosolids by liquid chromatography tandem mass spectrometry. J Chromatogr A 2007;1164:212–8.

Clara M, Scharf S, Scheffknecht C, Gans O. Occurrence of selected surfactants in untreated and treated sewage. Water Res 2007;41:4339–48.

Clarke B, Porter N, Symons R, Blackbeard J, Ades P, Marriott P. Dioxin-like compounds in Australian sewage sludge — review and national survey. Chemosphere 2008a;72: 1215–28.

Clarke B, Porter N, Symons R, Blackbeard J, Ades P, Marriott P. Persistent organic pollutants in Australian sewage sludge. AWA biosolids speciality conference. Adelaide, Australia; 2008b.

Clarke B, Porter N, Symons R, Marriott P, Ades P, Stevensen G, et al. Polybrominated diphenyl ethers and polybrominated biphenyls in Australian sewage sludge. Chemosphere 2008c;73:980–9.

Clarke BO, Porter NA, Marriott PJ, Blackbeard JR. Investigating the levels and trends of organochlorine pesticides and polychlorinated biphenyl in sewage sludge. Environ Int 2010;36:323–9.

Coogan MA, Edziyie RE, La Point TW, Venables BJ. Algal bioaccumulation of triclocarban, triclosan, and methyl-triclosan in a North Texas wastewater treatment plant receiving stream. Chemosphere 2007;67:1911–8.

Coogan MA, La Point TW. Snail boaccumulation of triclocarban, triclosan, and methyltriclosan in a North Texas, USA, stream affected by wastewater treatment plant runoff. Environ Toxicol Chem 2008;27:1788–93.

Dargnat C, Teil M-J, Chevreuil M, Blanchard M. Phthalate removal throughout wastewater treatment plant: case study of Marne Aval station (France). Sci Total Environ 2009;407:1235–44.

Darnerud PO, Eriksen GS, Johannesson T, Larsen PB, Viluksela M. Polybrominated diphenyl ethers: occurances, dietary exposure, and toxicology. Environ Health Perspect 2001;109(suppl 1):48–68.

Daughton CG, Ternes TA. Pharmaceuticals and personal care products in the environment: agents of subtle change? Environ Health Perspect 1999;107: 907–38.

de Boer J, Horst A, Wester PG. PBDEs and PBBs in suspended particulate matter, sediments, sewage treatment plant in- and effluents and biota from the Netherlands. Organohalogen Comp 2000;27:85–8.

de Boer J, Wester PG, van der Horst A, Leonards PEG. Polybrominated diphenyl ethers in influents, suspended particulate matter, sediments, sewage treatment plant and effluents and biota from the Netherlands. Environ Pollut 2003;122:63–74.

de Carlo VJ. Studies of brominanted chemicals in the environment. Ann NY Acad Sci 1979;320:678–81.

de Wever H, Verachtert TH. Biodegradation and toxicity of benzothiazoles. Water Res 1997;31:2673–84.

Dean RB, Suess MJ. The risk to health of chemicals in sewage sludge applied to land. Waste Manage Res 1985;3:251–78.

Desbrow C, Routledge E, Brighty G, Sumpter J, Waldock M. Identification of estrogenic chemicals in STW effluent. 1. Chemical fractionation and in vitro biological screening. Environ Sci Technol 1998;32:1549–58.

Dolliver H, Kumar K, Gupta S. Sulfamethazine uptake by plants from manure-amended soil. J Environ Qual 2007;36:1224–30.

Dorn PB, Chou C-S, Gentempo JJ. Degradation of bisphenol A in natural waters. Chemosphere 1987;16:1501–7.

Drillia P, Stamatelatou K, Lyberatos G. Fate and mobility of pharmaceuticals in solid matrices. Chemosphere 2005;60:1034–44.

Du QZ, Fu XW, Xia HL. Uptake of di-(2-ethylhexyl)phthalate from plastic mulch film by vegetable plants. Food Addit Contam A Chem Anal Control Expo Risk Assess 2009;26:1325–9.

EC. Scientific committee on consumer products opinion on triclocarban. Brussels: European Commission, Health & Consumer Protection Directorate-General; 2005.

ECHA (2009) List of pre-registered substances. European Chemicals Agency (ECHA), Helsinki, Accessed 22nd October 2009 <http://echa.europa.eu/home_en.asp>.

Eljarrat E, Barceló D. Quantitative analysis of polychlorinated n-alkanes in environmental samples. TrAC Trends Anal Chem 2006;25:421–34.

Eljarrat E, Marsh G, Labandeira A, Barcelo D. Effect of sewage sludges contaminated with polybrominated diphenylethers on agricultural soils. Chemosphere 2008;71:1079–86.

EPCEU (2001) *Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC.* The European Parliament and the Council of the European Union, Official Journal of the European Communities L 331/1-5, Brussels.

EPCEU (2003) *Directive 2003/11/EC of the European Parliament and of the Council of 6 February 2003 amending for the 24th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (pentabromodiphenyl ether, octabromodiphenyl ether).* The European Parliament and the Council of the European Union, Official Journal of the European Union L42/45–46., Brussels.

EPCEU (2006) *Directive 2006/122/EC of The European Parliament and of the Council of 12 December 2006 amending for the 30th time Council Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations (perfluorooctane sulfonates).* The European Parliament and the Council of the European Union, Official Journal of the European Communities L 372/32–34, Brussels.

EPCEU (2008) *Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council.* The European Parliament and the Council of the European Union, Official Journal of the European Union L348/84–93, Brussels.

Eriksen GS, Amundsen CE, Bernhoft A, Eggen T, Grave K, Halling-Sørensen B, et al. Risk assessment of contaminants in sewage sludge applied on Norwegian soils. Norway: Panel on Contaminants in the Norwegian Scientific Committee for Food Safety; 2009.

Eurochlor (2009) Chlorinated paraffins. Chlorine Online Information Resource, Euro Chlor, Accessed 1st September 2009 <http://www.eurochlor.org/paraffins>.

European Commission (2010) Sewage sludge. European Commission, Brussels. Accessed 25th May 2010 <http://ec.europa.eu/environment/waste/sludge/index.htm>.

Fabrellas B, Larrazabal D, Martinez MA, Eljarrat E, Barcelo D. Presence of polybrominated diphenyl ethers in Spanish sewage sludges: important contribution of deca-BDE. Organohalogen Comp 2004;66:3755–60.

Falandysz J. Polychlorinated naphthalenes: an environmental update. Environ Pollut 1998;101:77–90.

Fatoki OS, Vernon F. Phthalate esters in rivers of the greater Manchester area, U.K. Sci Total Environ 1990;95:227–32.

Fauser P, Vikelsoe J, Sorensen PB, Carlsen L. Phthalates, nonylphenols and LAS in an alternately operated wastewater treatment plant—fate modelling based on measured concentrations in wastewater and sludge. Water Res 2003;37:1288–95.

Federle TW, Kaiser SK, Nuck BA. Fate and effects of triclosan in activated sludge. Environ Toxicol Chem 2002;21:1330–7.

Fendinger NJ, McAvoy DC, Eckhoff WS, Price BB. Environmental occurrence of polydimethylsiloxane. Environ Sci Technol 1997;31:1555–63.

Fent K. Ecotoxicology of organotin compounds. Crit Rev Toxicol 1996a;26:3-117.

Fent K. Organotin compounds in municipal wastewater and sewage sludge: contamination, fate in treatment process and ecotoxicological consequences. Sci Total Environ 1996b;185:151–9.

Fent K, Mueller MD. Occurrence of organotins in municipal wastewater and sewage sludge and behavior in a treatment plant. Environ Sci Technol 1991;25:489–93.

Fent K, Hunn J, Renggli D, Siegrist H. Fate of tributyltin in sewage sludge treatment. Mar Environ Res 1991;32:223–31.

Fent G, Hein WJ, Moendel MJ, Kubiak R. Fate of 14C-bisphenol A in soils. Chemosphere 2003;51:735–46.

Fernandez P, Alder AC, Suter MJF, Giger W. Determination of the quaternary ammonium surfactant ditallowdimethylammonium in digested sludges and marine sediments by supercritical fluid extraction and liquid chromatography with postcolumn ion-pair formation. Anal Chem 1996;68:921–9.

Fountoulakis MS, Stamatelatou K, Batstone DJ, Lyberatos G. Simulation of DEHP biodegradation and sorption during anaerobic digestion of secondary sludge. Water Sci Technol 2006;54:119–28.

Fromme H, Kuchler T, Otto T, Pilz K, Muller J, Wenzel A. Occurrence of phthalates and bisphenol A and F in the environment. Water Res 2002;36:1429.

Frye CL. The environmental fate and ecological impact of organosilicon materials: a review. Sci Total Environ 1988;73:17–22.

Fürhacker M, Schard S, Weber H. Bisphenol A: emissions from point sources. Chemosphere 2000;41:751–6.

Gaja MA, Knapp JS. Removal of 2-mercaptobenzothiazole by activated sludge: a cautionary note. Water Res 1998;32:3786–9.

Gatidou G, Thomaidis NS, Stasinakis AS, Lekkas TD. Simultaneous determination of the endocrine disrupting compounds nonylphenol, nonylphenol ethoxylates, triclosan and bisphenol A in wastewater and sewage sludge by gas chromatography–mass spectrometry. J Chromatogr A 2007;1138:32–41.

Gaze WH. Is pollution driving antibiotic resistance? Planet Earth (quarterly magazine of the Natural Environment Research Council); 2008. p. 14–5. Winter.

Gaze WH, Abdouslam N, Hawkey PM, Wellington EMH. Incidence of class 1 integrons in a quaternary ammonium compound-polluted environment. Antimicrob Agents Chemother 2005;49:1802–7.

Gevao B, Muzaini S, Helaleh M. Occurrence and concentrations of polybrominated diphenyl ethers in sewage sludge from three wastewater treatment plants in Kuwait. Chemosphere 2008;71:242–7.

Giam CS, Powers MA, Leonard JE. Phthalic acid esters. In: Hutzinger, editor. Handbook of environmental chemistry 3 part C. Springer; 1984.

Gibson R, Wang M-J, Padgett E, Beck AJ. Analysis of 4-nonylphenols, phthalates, and polychlorinated biphenyls in soils and biosolids. Chemosphere 2005;61: 1336–44.

Giesy JP, Kannan K. Global distribution of perfluorooctane sulfonate in wildlife. Environ Sci Technol 2001;35:1339–42.

Giolando ST, Rapaport RA, Larson RJ, Federle TW, Stalmans M, Masscheleyn P. Environmental fate and effects of DEEDMAC: a new rapidly biodegradable cationic surfactant for use in fabric softeners. Chemosphere 1995;30:1067–83.

Gobel A, Thomsen A, Mcardell CS, Alder AC, Giger W, Theif N, et al. Extraction and determination of sulfonamides, macrolides, and trimethoprim in sewage sludge. J Chromatogr A 2005;1085:179–89.

Golet EM, Alder AC, Hartmann A, Ternes TA, Giger W. Trace determination of fluoroquinolone antibacterial agents in urban wastewater by solid-phase extraction and liquid chromatography with fluorescence detection. Anal Chem 2001;73:3632–8.

Golet EM, Strehler A, Alder AC, Giger W. Determination of fluoroquinolone antibacterial agents in sewage sludge and sludge-treated soil using accelerated solvent extraction followed by solid-phase extraction. Anal Chem 2002;74:5455–62.

Golet EM, Xifra I, Siegrist H, Alder AC, Giger W. Environmental exposure assessment of fluoroquinolone antibacterial agents from sewage to soil. Environ Sci Technol 2003;37:3243–9.

Gomes RL, Avcioglu E, Scrimshaw MD, Lester JN. Steroid-estrogen determination in sediment and sewage sludge: a critique of sample preparation and chromatographic/mass spectrometry considerations, incorporating a case study in method development. TrAC Trends Anal Chem 2004;23:737–44.

Gomes RL, Scrimshaw MD, Lester JN. Fate of conjugated natural and synthetic steroid estrogens in crude sewage and activated sludge batch studies. Environ Sci Technol 2009;43:3612–8.

Gottschall N, Topp E, Edwards M, Russell P, Payne M, Kleywegt S, et al. Polybrominated diphenyl ethers, perfluorinated alkylated substances, and metals in tile drainage and groundwater following applications of municipal biosolids to agricultural fields. Sci Total Environ 2010;408:873–83.

Griessbach EFC, Lehmann RG. Degradation of polydimethylsiloxane fluids in the environment — a review. Chemosphere 1999;38:1461–8.

Group EF. Environmental fate and aquatic toxicology studies on phthalate esters. Environ Health Perspect 1986;65:337–40.

Guo L, Zhang B, Xiao K, Zhang Q, Zheng M. Levels and distributions of polychlorinated naphthalenes in sewage sludge of urban wastewater treatment plants. Chin Sci Bull 2008;53:508–13.

Halden RU, Paull DH. Analysis of triclocarban in aquatic samples by liquid chromatography electrospray ionization mass spectrometry. Environ Sci Technol 2004;38:4849–55.

Halden RU, Paull DH. Co-occurrence of triclocarban and triclosan in U.S. water resources. Environ Sci Technol 2005;39:1420–6.

Hale R, Guardia ML, Harvey E, Gaylor M, Mainor T, Duff W. Persistent pollutants in land-applied sludges. Nature 2001;412:140–1.

Hale RC, Kim SL, Harvey E, La Guardia MJ, Mainor TM, Bush EO, et al. Antarctic research bases: local sources of polybrominated diphenyl ether (PBDE) flame retardants. Environ Sci Technol 2008;42:1452–7.

Hamm S. Polybrominated diphenyl ethers in sewage sludge and effluents of sewage plants from a central region of Germany. Organohalogen Comp 2004;66:1629–34.

Harner T, Kylin H, Bidleman TF, Halsall C, Strachan WMJ, Barrie LA, et al. Polychlorinated naphthalenes and coplanar polychlorinated biphenyls in Arctic air. Environ Sci Technol 1998;32:3257–65.

Harris CA, Henttu P, Parker MG, Sumpter JP. The estrogenic activity of phthalate esters In vitro. Environ Health Perspect 1997;105:802–11.

Hashimoto T, Murakami T. Removal and degradation characteristics of natural and synthetic estrogens by activated sludge in batch experiments. Water Res 2009;43:573–82.

Heberer T. Occurrence, fate, and assessment of polycyclic musk residues in the aquatic environment of urban areas — a review. Acta Hydrochim Hydrobiol 2002;30:227–43.

Heemken OP, Reincke H, Stachel B, Theobald N. The occurrence of xenoestrogens in the Elbe river and the North Sea. Chemosphere 2001;45:245–59.

Heidler J, Halden RU. Mass balance assessment of triclosan removal during conventional sewage treatment. Chemosphere 2007;66:362–9.

Heidler J, Sapkota A, Halden RU. Partitioning, persistence, and accumulation in digested sludge of the topical antiseptic triclocarban during wastewater treatment. Environ Sci Technol 2006;40:3634–9.

Heroult J, Nia Y, Denaix L, Bueno M, Lespes G. Kinetic degradation processes of butyl- and phenyltins in soils. Chemosphere 2008;72:940–6.

Herren D, Berset JD. Nitro musks, nitro musk amino metabolites and polycyclic musks in sewage sludges: quantitative determination by HRGC-ion-trap-MS/MS and mass spectral characterization of the amino metabolites. Chemosphere 2000;40:565–74.

Hirsch R, Ternes T, Haberer K, Kratz K-L. Occurrence of antibiotics in the aquatic environment. Sci Total Environ 1999;225:109–18.

Hobbs EJ, Keplinger ML, Calandra JC. Toxicity of polydimethylsiloxanes in certain environmental systems. Environ Res 1975;10:397–406.

Hoch M. Organotin compounds in the environment - an overview. Appl Geochem 2001;16:719–43.

Hundal LS, Cox A, Granato TC, Abedin Z. Levels of dioxins in soil and corn tissues after 30 years of biosolids application. J Environ Qual 2008;37:1497–500.

IARC (1998) *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans; Volume 48 Some Flame Retardants and Textile Chemicals, and Exposures in the Textile Manufacturing Industry*. World Health Organization, International Agency for Research on Cancer, Lyon, France. <http://monographs.iarc.fr/ENG/Monographs/vol18/volume18.pdf>.

IPCS (1990) *Environmental Health Criteria 116: Tributyltin Compounds*. International Programme on Chemical Safety, Geneva, Switzerland. <http://www.inchem.org/documents/ehc/ehc/ehc116.htm#SectionNumber:1.1>.

IPCS (1992) Environmental Health Criteria 131: Diethylhexyl phthalate. International Programme on Chemical Safety, Switzerland, Geneva. <http://www.inchem.org/documents/ehc/ehc/ehc131.htm>.

IPCS. Environmental health criteria 162: brominated diphenyl ethers. Geneva, Switzerland: International Programme on Chemical Safety; 1994.

IPCS. Environmental health criteria 181: chlorinated paraffins. Geneva, Switzerland: International Programme on Chemical Safety; 1996.

IPCS. Poisons information monograph G022 (Group PIM): quaternary ammonium compounds. Switzerland, Geneva: International Programme on Chemical Safety; 1999.

IPCS. Concise international chemical assessment document (CICAD) chlorinated napthalenes no. 34. Geneva: World Health Organisation, International Program on Chemical Safety; 2001.

Jackson AP, Eduljee GH. An assessment of the risks associated with PCDDs and PCDFs following the application of sewage sludge to agricultural land in the UK. Chemosphere 1994;29:2523–43.

Jensen J, Langevelde JV, Pritzl G, Krogh PH. Effects of di(2-ethylhexyl) phthalate and dibutyl phthalate on the collembolan *Folsomia fimetaria*. Environ Toxicol Chem 2001;20:1085–91.

Jianlong W, Lujun C, Hanchang S, Yi Q. Microbial degradation of phthalic acid esters under anaerobic digestion of sludge. Chemosphere 2000;41:1245–8.

Jobling S, Nolan M, Tyler C, Brightly G, Sumpter J. Widespread sexual disruption in wild fish. Environ Sci Technol 1998;32:2498–506.

Kannan K, Franson JC, Bowerman WW, Hansen KJ, Jones PD, Giesy JP. Perfluorooctane sulfonate in fish-eating water birds including bald eagles and albatrosses. Environ Sci Technol 2001;35:3065–70.

Kannan K, Corsolini S, Falandysz J, Fillmann G, Kumar KS, Loganathan BG, et al. Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries. Environ Sci Technol 2004;38:4489–95.

Keyser P, Pujar BG, Eaton RW, Ribbons DW. Biodegradation of the phthalates and their esters by bacteria. Environ Health Perspect 1976;18:159–66.

Kinney CA, Furlong ET, Zaugg SD, Burkhardt MR, Werner SL, Cahill JD, et al. Survey of organic wastewater contaminants in biosolids destined for land application. Environ Sci Technol 2006;40:7207–15.

Kinney CA, Furlong ET, Kolpin DW, Burkhardt MR, Zaugg SD, Werner SL, et al. Bioaccumulation of pharmaceuticals and other anthropogenic waste indicators in earthworms from agricultural soil amended with biosolid or swine manure. Environ Sci Technol 2008;42:1863–70.

Kirchmann H, Åström H, Jönsäll G. Organic pollutants in sewage sludge 1. Effect of toluene, naphthalene, 2-metholnaphthalene, 4-n-nonylphenol and di-2-ethylhexyl phthalate on soil biological processes and their decomposition in soil. Swed J Agric Res 1991;21:107–13.

Kloepfer A, Jekel M, Reemtsma T. Determination of benzothiazoles from complex aqueous samples by liquid chromatography–mass spectrometry following solid-phase extraction. J Chromatogr A 2004;1058:81–8.

Knoth W, Mann W, Meyer R, Nebhuth J. Polybrominated diphenyl ether in sewage sludge in Germany. Chemosphere 2007;67:1831–7.

Kolodziej EP, Harter T, Sedlak DL. Dairy wastewater, aquaculture, and spawning fish as sources of steroid hormones in the aquatic environment. Environ Sci Technol 2004;38:6377–84.

Kolpin DW, Furlong ET, Meyer MT, Thurman EM, Zaugg SD, Barber LB, et al. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. Streams, 1999–2000: a national reconnaissance. Environ Sci Technol 2002;36:1202–11.

Korner W, Bolz U, Süssmut W, Hiller G, Schuller W, Hanf V, et al. Input/output balance of estrogenic active compounds in a major municipal sewage plant in Germany. Chemosphere 2000;40:1131–42.

Kupper T, Berset JD, Etter-Holzer R, Furrer R, Tarradellas J. Concentrations and specific loads of polycyclic musks in sewage sludge originating from a monitoring network in Switzerland. Chemosphere 2004;54:1111–20.

Lai KM, Scrimshaw MD, Lester JN. Prediction of the bioaccumulation factors and body burden of natural and synthetic estrogens in aquatic organisms in the river systems. Sci Total Environ 2002;289:159–68.

Lapen DR, Topp E, Metcalfe CD, LI H, Edwards M, Gottschall N, et al. Pharmaceutical and personal care products in tile drainage following land application of municipal biosolids. Sci Total Environ 2008;399:50–65.

Lau C, Butenhoff JL, Rogers JM. The developmental toxicity of perfluoroalkyl acids and their derivatives. Toxicol Appl Pharmacol 2004;198:231–41.

Law RJ, Allchin CR, de Boer J, Covaci A, Herzke D, Lepom P, et al. Levels and trends of brominated flame retardants in the European environment. Chemosphere 2006;64:187–208.

Layton AC, Gregory BW, Seward JR, Schultz TW, Sayler GS. Mineralization of steroidal hormones by biosolids in wastewater treatment systems in Tennessee U.S.A. Environ Sci Technol 2000;34:3925–31.

Lee YJ, Ryu H-Y, Kim H-K, Min CS, Lee JH, Kim E, et al. Maternal and fetal exposure to bisphenol A in Korea. Reprod Toxicol 2008;25:413–9.

Legler J, Brouwer A. Are brominated flame retardants endocrine disruptors? Environ Int 2003;29:879–85.

Lehmann RG, Miller JR. Volatilization and sorption of dimethylsilanediol in soil. Environ Toxicol Chem 1996;15:1455–60.

Lehmann RG, Miller JR, Xu S, Singh UB, Reece CF. Degradation of silicone polymer at different soil moistures. Environ Sci Technol 1998;32:1260–4.

Lemos M, van Gestel C, Soares A. Endocrine disruption in a terrestrial isopod under exposure to bisphenol A and vinclozolin. J Soils Sed 2009;9:492–500.

Li X, Brownawell BJ. Analysis of quaternary ammonium compounds in estuarine sediments by LC–ToF–MS: very high positive mass defects of alkylamine ions as powerful diagnostic tools for identification and structural elucidation. Anal Chem 2009;81:7926–35.

Li Y-J, Song T-B, Cai Y-Y, Zhou J-S, Song X, Zhao X, et al. Bisphenol A exposure induces apoptosis and upregulation of Fas/FasL and caspase-3 expression in the testes of mice. Toxicol Sci 2009;108:427–36.

Lindberg RH, Wennberg P, Johansson MI, Tysklind M, Andersson BAV. Screening of human antibiotic substances and determination of weekly mass flows in five sewage treatment plants in sweden. Environ Sci Technol 2005;39:3421–9.

Llompart M, Garcìa-Jares C, Salgado C, Polo M, Cela R. Determination of musk compounds in sewage treatment plant sludge samples by solid-phase microextraction. J Chromatogr A 2003;999:185–93.

Loganathan BG, Sajwan KS, Sinclair E, Senthil Kumar K, Kannan K. Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia. Water Res 2007;41:4611–20.

Madsen, T., Boyd, H. B., Nylen, D., Rathmann-Pedersen, A., Petersen, G. I. & Simonsen, F. (2001) Environmental and health assessment of substances in household detergents and cosmetic detergent products. Environmental Project No. 615, Final Report. IN DANISH ENVIRONMENTAL PROTECTION AGENCY (Ed.).

Marcic C, Le Hecho I, Denaix L, Lespes G. TBT and TPhT persistence in a sludged soil. Chemosphere 2006;65:2322–32.

Martìnez-Carballo E, Gonzalez-Barreiro C, Sitka A, Kreuzinger N, Scharf S, Gans O. Determination of selected quaternary ammonium compounds by liquid chromatography with mass spectrometry. Part II. Application to sediment and sludge samples in Austria. Environ Pollut 2007;146:543–7.

Marttinen SK, Kettunen RH, Rintala JA. Occurrence and removal of organic pollutants in sewages and landfill leachates. Sci Total Environ 2003a;301:1-12.

Marttinen SK, Kettunen RH, Sormunen KM, Rintala JA. Removal of bis(2-ethylhexyl) phthalate at a sewage treatment plant. Water Res 2003b;37:1385–93.

Marttinen SK, Hanninen K, Rintala JA. Removal of DEHP in composting and aeration of sewage sludge. Chemosphere 2004;54:265–72.

McArdell CS, Molnar E, Suter MJF, Giger W. Occurrence and fate of macrolide antibiotics in wastewater treatment plants and in the Glatt Valley Watershed, Switzerland. Environ Sci Technol 2003;37:5479–86.

McAvoy DC, Schatowitz B, Jacob M, Hauk A, Eckhoff WS. Measurement of triclosan in wastewater treatment systems. Environ Toxicol Chem 2002;21:1323–9.

McDonald TA. A perspective on the potential health risks of PBDEs. Chemosphere 2002;46:745–55.

McIntyre A, Lester J. Occurrence and distribution of persistent organochlorine compounds in U.K. sewage sludges. Water Air Soil Pollut 1984;23:397–415.

Meesters RJW, Schroder HF. Simultaneous determination of 4-nonylphenol and bisphenol A in sewage sludge. Anal Chem 2002;74:3566–74.

Morales S, Canosa P, Rodrìguez I, Rubì E, Cela R. Microwave assisted extraction followed by gas chromatography with tandem mass spectrometry for the determination of triclosan and two related chlorophenols in sludge and sediments. J Chromatogr A 2005;1082:128–35.

Mueller MD. Comprehensive trace level determination of organotin compounds in environmental samples using high-resolution gas chromatography with flame photometric detection. Anal Chem 1987;59:617–23.

Newbold RR, Jefferson WN, Padilla-Banks E. Prenatal exposure to bisphenol A at environmentally relevant soses adversely affects the murine female reproductive tract later in life. Environ Health Perspect 2009;117:879–85.

Nicholls CR, Allchin CR, Law RJ. Levels of short and medium chain length polychlorinated n-alkanes in environmental samples from selected industrial areas in England and Wales. Environ Pollut 2001;114:415–30.

NICNAS. Triclosan. Canberra: Australian Government, Department of Health and Ageing, National Industrial Chemicals Notification and Assessment Scheme; 2008.

Nie Y, Qiang Z, Zhang H, Adams C. Determination of endocrine-disrupting chemicals in the liquid and solid phases of activated sludge by solid phase extraction and gas chromatography–mass spectrometry. J Chromatogr A 2009;1216:7071–80.

Nishiyama N, Toshima Y, Ikeda Y. Biodegradation of alkyltrimethylammonium salts in activated sludge. Chemosphere 1995;30:593–603.

North KD. Tracking polybrominated diphenyl ether releases in a wastewater treatment plant effluent, Palo Alto, California. Environ Sci Technol 2004;38:4484–8.

Nwosu VC. Antibiotic resistance with particular reference to soil microorganisms. Res Microbiol 2001;152:421–30.

Nylund K, Asplund L, Jansson B, Jonsson P, Litzen K, Sellstrom U. Analysis of some polyhalogenated organic pollutants in sediment and sewage sludge. Chemosphere 1992;24:1721–30.

O'Connor GA, Kiehl D, Eiceman GA, Ryan JA. Plant uptake of sludge-borne PCBs. J Environ Qual 1990;19:113–8.

OECD. Co-operation on existing chemicals hazard assessment of perfluorooctane sulfonate (PFOS) and its salts. Paris: Organisation for Economic Co-operation and Development; 2002.

Oehlmann J, Oetken M, Schulte-Oehlmann U. A critical evaluation of the environmental risk assessment for plasticizers in the freshwater environment in Europe, with special emphasis on bisphenol A and endocrine disruption. Environ Res 2008;108:140–9.

Oliver R, May E, Williams J. The occurrence and removal of phthalates in a trickle filter STW. Water Res 2005;39:4436–44.

Olsen GW, Church TR, Miller JP, Burris JM, Hansen KJ, Lundberg JK, et al. Perfluorooctanesulfonate and other fluorochemicals in the serum of American Red Cross adult blood donors. Environ Health Perspect 2003;111:1892–901.

Pakou C, Kornaros M, Stamatelatou K, Lyberatos G. On the fate of LAS, NPEOs and DEHP in municipal sewage sludge during composting. Bioresour Technol 2009;100:1634–42.

Peters AJ, Tomy GT, Jones KC, Coleman P, Stern GA. Occurrence of C10–C13 polychlorinated n-alkanes in the atmosphere of the United Kingdom. Atmos Environ 2000;34:3085–90.

Plagellat C, Kupper T, de Alencastro LF, Grandjean D, Tarradellas J. Biocides in sewage sludge: quantitative determination in some swiss wastewater treatment plants. Bull Environ Contam Toxicol 2004;73:794–801.

Pothitou P, Voutsa D. Endocrine disrupting compounds in municipal and industrial wastewater treatment plants in Northern Greece. Chemosphere 2008;73:1716–23.

Reddy CM, Quinn JG. Environmental chemistry of benzothiazoles derived from rubber. Environ Sci Technol 1997;31:2847–53.

Reddy S, Iden CR, Brownawell BJ. Analysis of steroid conjugates in sewage influent and effluent by liquid chromatography–tandem mass spectrometry. Anal Chem 2005;77:7032–8.

Reiss R, Lewis G, Griffin J. An ecological risk assessment for triclosan in the terrestrial environment. Environ Toxicol Chem 2009;28:1546–56.

Rieger R, Ballschmiter K. Semivolatile organic compounds – polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF), biphenyls (PCB), hexachlorobenzene (HCB), 4, 4'-DDE and chlorinated paraffins (CP) – as markers in sewer films. Fresenius J Anal Chem 1995;352:715–24.

Rimkus GG. Polycyclic musk fragrances in the aquatic environment. Toxicol Lett 1999;111:37–56.

Roghair CJ, Buijze A, Schoon HNP. Ecotoxicological risk evaluation of the cationic fabric softener DTDMAC. I. Ecotoxicological effects. Chemosphere 1992;24:599–609.

Roslev P, Vorkamp K, Aarup J, Frederiksen K, Nielsen PH. Degradation of phthalate esters in an activated sludge wastewater treatment plant. Water Res 2007;41:969–76.

Rysz M, Alvarez PJJ. Amplification and attenuation of tetracycline resistance in soil bacteria: aquifer column experiments. Water Res 2004;38:3705–12.

Sapkota A, Heidler J, Halden RU. Detection of triclocarban and two co-contaminating chlorocarbanilides in US aquatic environments using isotope dilution liquid chromatography tandem mass spectrometry. Environ Res 2007;103:21–9.

Schlusener MP, Bester Kai. Behavior of steroid hormones and conjugates during wastewater treatment — a comparison of three sewage treatment plants. CLEAN Soil Air Water 2008;36:25–33.

Schmitzer JL, Scheunert I, Korte F. Fate of bis(2-ethylhexyl) [14C]phthalate in laboratory and outdoor soil-plant systems. J Agric Food Chem 1988;36:210–5.

Schowanek D, Carr R, David H, Douben P, Hall J, Kirchmann H, et al. A risk-based methodology for deriving quality standards for organic contaminants in sewage sludge for use in agriculture — conceptual framework. Regul Toxicol Pharmacol 2004;40:227–51.

Schultz MM, Higgins CP, Huset CA, Luthy RG, Barofsky DF, Field JA. Fluorochemical mass flows in a municipal wastewater treatment facility. Environ Sci Technol 2006;40:7350–7.

Sellstrom U, Kierkegaard A, Alsberg T, Jonsson P, Wahlberg C, Wit CD. Brominated flame retardants in sediments from European estuaries, the Baltic Sea and in sewage sludge. Organohalogen Comp 1999;40:383–6.

Sellstrom U, de Wit CA, Lundgren N, Tysklind M. Effect of sewage-sludge application on concentrations of higher-brominated diphenyl ethers in soils and earthworms. Environ Sci Technol 2005;39:9064–70.

Sengeløv G, Agersø Y, Halling-Sørensen B, Baloda SB, Andersen JS, Jensen LB. Bacterial antibiotic resistance levels in Danish farmland as a result of treatment with pig manure slurry. Environ Int 2003;28:587–95.

Sewart A, Harrad SJ, McLachlan MS, Mcgrath SP, Jones KC. PCDD/Fs and non-o-PCBs in digested U.K. sewage sludges. Chemosphere 1995;30:51.

Shanker R, Ramakrishma C, Seth PK. Degradation of some phthalic acid esters in soil. Environ Pollut A Ecol Biol 1985;39:1–7.

Shek WM, Murphy MB, Lam JCW, Lam PKS. Synthetic polycyclic musks in Hong Kong sewage sludge. Chemosphere 2008;71:1241–50.

Shelton DR, Boyd SA, Tiedje JM. Anaerobic biodegradation of phthalic acid esters in sludge. Environ Sci Technol 1984;18:93–7.

Shore LS, Gurevitz M, Shemesh M. Estrogen as an environmental pollutant. Bull Environ Contam Toxicol 1993;51:361–6.

Sinclair E, Kannan K. Mass loading and fate of perfluoroalkyl surfactants in wastewater treatment plants. Environ Sci Technol 2006;40:1408–14.

Singer H, Muller S, Tixier C, Pillonel L. Triclosan: Occurrence and fate of a widely used biocide in the aquatic environment: field measurements in wastewater treatment plants, surface waters, and lake sediments. Environ Sci Technol 2002;36:4998–5004.

Sjödin A, Jakobsson E, Kierkegaard A, Marsh G, Sellstrom U. Gas chromatographic identification and quantification of polybrominated diphenyl ethers in a commercial product, Bromkal 70-5DE. J Chromatogr A 1998;822:83–9.

Sjöström E, Collins CD, Smith SR, Shaw G. Degradation and plant uptake of nonylphenol (NP) and nonylphenol-12-ethoxylate (NP12EO) in four contrasting agricultural soils. Environ Pollut 2008;156:1284–9.

Snyder SA, Villeneuve DL, Snyder EM, Giesy JP. Identification and quantification of estrogen receptor agonists in wastewater effluents. Environ Sci Technol 2001;35:3620–5.

Snyder EH, O'Connor GA, McAvoy DC. Measured physicochemical characteristics and biosolids-borne concentrations of the antimicrobial triclocarban (TCC). Sci Total Environ 2010;408:2667–73.

Sohoni P, Sumpter J. Several environmental oestrogens are also anti-androgens. J Endocrinol 1998;158:327–39.

Spies RB, Anderesen BD, JR DWR. Benzothiazoles in estuarine sediments as indicators of street runoff. Nature 1987;327:697.

Staples CA, Peterson DR, Parkerton TF, Adams WJ. The environmental fate of phthalate esters: a literature review. Chemosphere 1997;35:667.

Staples CA, Dome PB, Klecka GM, Oblock ST, Harris LR. A review of the environmental fate, effects, and exposures of bisphenol A. Chemosphere 1998;36:2149–73.

Stasinakis AS, Thomaidis NS, Nikolaou A, Kantifes A. Aerobic biodegradation of organotin compounds in activated sludge batch reactors. Environ Pollut 2005;134:431–8.

Stasinakis AS, Petalas AV, Mamais D, Thomaidis NS, Gatidou G, Lekkas TD. Investigation of triclosan fate and toxicity in continuous-flow activated sludge systems. Chemosphere 2007;68:375–81.

Stasinakis AS, Gatidou G, Mamais D, Thomaidis NS, Lekkas TD. Occurrence and fate of endocrine disrupters in Greek sewage treatment plants. Water Res 2008;42:1796–804.

Steen I. Phosphorus recovery — phosphorus availability in the 21st century, management of a non-renewable resource. Phosphorus Potassium 1998;217.

Stevens C. Environmental degradation pathways for the breakdown of polydimethylsiloxanes. J Inorg Biochem 1998;69:203–7.

Stevens J, Green NJL, Jones KC. Survey of PCDD/Fs and non-ortho PCBs in UK sewage sludges. Chemosphere 2001;44:1455.

Stevens JL, Northcott GL, Stern GA, Tomy GT, Jones KC. PAHs, PCBs, PCNs, organochlorine pesticides, synthetic musks, and polychlorinated n-alkanes in U.K. sewage sludge: Survey results and implications. Environ Sci Technol 2003;37:462–7.

Sütterlin H, Alexy R, Coker A, Kümmerer K. Mixtures of quaternary ammonium compounds and anionic organic compounds in the aquatic environment: elimination and biodegradability in the closed bottle test monitored by LC–MS/MS. Chemosphere 2008;72:479–84.

Tan BLL, Hawker DW, Müller JF, Leusch FDL, Tremblay LA, Chapman HF. Comprehensive study of endocrine disrupting compounds using grab and passive sampling at selected wastewater treatment plants in South East Queensland, Australia. Environ Int 2007;33:654–69.

Tas JW, Balk F, Ford RA, van de Plassche EJ. Environmental risk assessment of musk ketone and musk xylene in the Netherlands in accordance with the EU-TGD. Chemosphere 1997;35:2973–3002.

Ternes TA, Kreckel P, Mueller J. Behaviour and occurrence of estrogens in municipal sewage treatment plants—II. Aerobic batch experiments with activated sludge. Sci Total Environ 1999a;225:91–9.

Ternes TA, Stumpf M, Mueller J, Haberer K, Wilken RD, Servos M. Behavior and occurrence of estrogens in municipal sewage treatment plants—I. Investigations in Germany, Canada and Brazil. Sci Total Environ 1999b;225:81–90.

Ternes TA, Andersen H, Gilberg D, Bonerz M. Determination of estrogens in sludge and sediments by liquid extraction and GC/MS/MS. Anal Chem 2002;74:3498–504.

Thiele-Bruhn S. Pharmaceutical antibiotic compounds in soils — a review. J Plant Nutr Soil Sci 2003;166:145–67.

Thomas GO, Farrar D, Braekevelt E, Stern G, Kalantzi OI, Martin FL, et al. Short and medium chain length chlorinated paraffins in UK human milk fat. Environ Int 2006;32:34–40.

Tolle DA, Frye CL, Lehmann RG, Zwick TC. Ecological effects of PDMS-augmented sludge amended to agricultural microcosms. Sci Total Environ 1995;162:193–207.

Toms L, Mueller J, Mortimer M, Symons R, Stevenson G, Gaus C. Assessment of concentrations of polybrominated diphenyl ether flame retardants in aquatic environments in Australia. Canberra: Australian Government, Department of the Environment and Water Resources; 2006.

Toms LL, Mortimer M, Symons RK, Paepke O, Mueller JF. Polybrominated diphenyl ethers (PBDEs) in sediment by salinity and land-use type from Australia. Environ Int 2008;34:58–66.

Topp E, Monteiro SC, Beck A, Coelho BB, Boxall ABA, Duenk PW, et al. Runoff of pharmaceuticals and personal care products following application of biosolids to an agricultural field. Sci Total Environ 2008;396:52–9.

Toussant M. Editorial: a scientific milestone. Chem Eng News 2009;87:3.

Traina SJ, Fendinger NJ, Mcavoy DC, Kerr KM, Gupta S. Fate of polydimethylsilicone in biosolids-amended field plots. J Environ Qual 2002;31:247–55.

Travis CC, Arms AD. Bioconcentration of organics in beef, milk, and vegetation. Environ Sci Technol 1988;22:271–4.

UNEP. Stockholm convention of persistent organic pollutants. Stockholm, Sweden: United Nations Environment Programme; 2001.

UNEP (2009) *Governments unite to step-up reduction on global DDT reliance and add nine new chemicals under international treaty.* United Nations Environment Programme, Geneva, Accessed 3rd July 2009 <http://chm.pops.int/Convention/Pressrelease/COP4Geneva8May2009/tabid/542/language/en-US/Default.aspx>.

US EPA (1984) Fifteenth Report of the Interagency Testing Committee to the Administrator; Receipt of Report and Request for Comments Regarding Priority List of Chemicals, US Environmental Protection Agency, Washington.

US EPA (1993) *Federal Register: Vol 58, No. 32. 40 CFR Part 257* et al. *Standards for the Use or Disposal of Sewage sludge; Final Rules* United States Environmental Protection Agency, Washington.

US EPA. Exposure factors handbook. Washington: National Center for Environmental Assessment; 1997.

US EPA (2008) Perfluorooctanoic acid (PFOA) and fluorinated telomers: Basic information US EPA, Washington, 19th March 2010 <http://www.epa.gov/oppt/pfoa/pubs/pfoainfo.html>.

US EPA (2009) Targeted National Sewage Sludge Survey Statistical Analysis Report. United States Environmental Protection Agency Office of Water. EPA-822-R-08-018. Washington, DC.

Van Leeuwen K, Roghair C, De Nijs T, De Greef J. Ecotoxicological risk evaluation of the cationic fabric softener DTDMAC. III. Risk assessment. Chemosphere 1992;24:629–39.

Vandenberg LN, Hauser R, Marcus M, Olea N, Welshons WV. Human exposure to bisphenol A (BPA). Reprod Toxicol 2007;24:139–77.

Varaprath S, Frye CL, Hamelink J. Aqueous solubility of permethylsiloxanes (silicones). Environ Toxicol Chem 1996;15:1263–5.

Versteeg DJ, Feijtel TCJ, Cowan CE, Ward TE, Rapaport RA. An environmental risk assessment for DTDMAC in The Netherlands. Chemosphere 1992;24:641–62.

Villeneuve DL, Kannan K, Khim JS, Falandysz J, Nikiforov VA, Blankenship AL, et al. Relative potencies of individual polychlorinated naphthalenes to induce dioxin-like responses in fish and mammalian in vitro bioassays. Arch Environ Contam Toxicol 2000;39:273–81.

Voulvoulis N, Lester JN. Fate of organotins in sewage sludge during anaerobic digestion. Sci Total Environ 2006;371:373–82.

Voulvoulis N, Scrimshaw MD, Lester JN. Removal of organotins during sewage treatment: a case study. Environ Technol 2004;25:733–40.

Walker WW, Cripe CR, Pritchard PH, Bourquin AW. Dibutylphthalate degradation in estuarine and freshwater sites. Chemosphere 1984;13:1283–94.

Wang Y, Zhang Q, Lv J, Li A, Liu H, Li G, et al. Polybrominated diphenyl ethers and organochlorine pesticides in sewage sludge of wastewater treatment plants in China. Chemosphere 2007;68:1683–91.

Watanabe N, Nakamura T, Watanabe E, Sato E, Ose Y. Distribution of organosiloxanes (silicones) in water, sediments and fish from the Nagara River watershed, Japan. Sci Total Environ 1984;35:91–7.

Watanabe N, Nagase H, Ose Y. Distribution of silicones in water, sediment and fish in Japanese rivers. Sci Total Environ 1988;73:1–9.

Watts RJ, Kong S, Haling CS, Gearhart L, Frye CL, Vigon BW. Fate and effects of polydimethylsiloxanes on pilot and bench-top activated sludge reactors and anaerobic/aerobic digesters. Water Res 1995;29:2405–11.

Webber MD, Lesage S. Organic contaminants in canadian municipal sludges. Waste Manage Res 1989;7:63–82.

Wild SR, Waterhouse KS, McGrath SP, Jones KC. Organic contaminants in an agricultural soil with a known history of sewage sludge amendments: polynuclear aromatic hydrocarbons. Environ Sci Technol 1990;24:1706–11.

Wild SR, Berrow ML, Jones KC. The persistence of polynuclear aromatic hydrocarbons (PAHs) in sewage sludge amended agricultural soils. Environ Pollut 1991;72:141–57.

Wild SR, Harrad SJ, Jones KC. The influence of sewage sludge applications to agricultural land on human exposure to polychlorinated dibenzo-p-dioxins (PCDDs) and -furans (PCDFs). Environ Pollut 1994;83:357.

Williams CF, Adamsen FJ. Sorption–desorption of carbamazepine from irrigated soils. J Environ Qual 2006;35:1779–83.

Wilson SC, Duarte-Davidson R, Jones KC. Screening the environmental fate of organic contaminants in sewage sludges applied to agricultural soils: 1. The potential for downward movement to groundwaters. Sci Total Environ 1996;185:45–57.

Wilson SC, Alcock RE, Sewart AP, Jones KC. Organic chemicals in the environment — persistence of organic contaminants in sewage sludge-amended soil: a field experiment. J Environ Qual 1997;26:1467–77.

Winker M, Clemens J, Reich M, Gulyas H, Otterpohl R. Ryegrass uptake of carbamazepine and ibuprofen applied by urine fertilization. Sci Total Environ 2010;408:1902–8.

Xu S, Lehmann RG, Miller JR, Chandra G. Degradation of polydimethylsiloxanes (silicones) as influenced by clay minerals. Environ Sci Technol 1998;32:1199–206.

Yang L-H, Ying G-G, Su H-C, Stauber JL, Adams MS, Binet MT. Growth-inhibiting effects of 12 anitbacterial agents and their mixtures on the freshwater microbial GA pseudokirchneriella subcapitata. Environ Toxicol Chem 2008;27:1201–8.

Yin R, Lin XG, Wang SG, Zhang HY. Effect of DBP/DEHP in vegetable planted soil on the quality of capsicum fruit. Chemosphere 2003;50:801–5.

Ying G-G. Fate, behavior and effects of surfactants and their degradation products in the environment. Environ Int 2006;32:417–31.

Ying G-G, Kookana RS. Triclosan in wastewaters and biosolids from Australian wastewater treatment plants. Environ Int 2007;33:199–205.

Zeng X, Sheng G, Xiong Y, Fu J. Determination of polycyclic musks in sewage sludge from Guangdong, China using GC–EI–MS. Chemosphere 2005;60:817–23.

Ziogou K, Kirk PWW, Lester JN. Behaviour of phthalic acid esters during batch anaerobic digestion of sludge. Water Res 1989;23:743.

STATE OF MAINE
DEPARTMENT OF ENVIRONMENTAL PROTECTION

JANET T. MILLS
GOVERNOR

GERALD D. REID
COMMISSIONER

Memorandum

To: Licensed facilities that land apply, compost, or process sludge in Maine
From: David Burns, P.E., Acting Director, Bureau of Remediation and Waste Management
Date: March 22, 2019
Re: Requirement to analyze for PFAS compounds

David Burns

Background:

Per- and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals that includes PFOA, PFOS, PFBS, and many other compounds. PFAS have been manufactured and used by a variety of industries around the globe, including in the United States since the 1940s. PFOA and PFOS have been the most extensively produced and studied of these chemicals. Both chemicals are persistent in the environment and in the human body – meaning they don't readily break down and can accumulate over time. Additionally, there is evidence that exposure to PFAS can lead to adverse human health effects.[1] PFAS can be found in many places including food packaging, water and stain resistant products, non-stick products, certain firefighting foams, and many others. Because these chemicals are so prevalant and don't easily break down, they can be concentrated through the wastewater treatment process. In 2016, the US Environmental Protection Agency (EPA) established a health advisory level in drinking water of 70 parts per trillion (ppt) combined for two PFAS compounds – PFOA and PFOS.

In late 2016, the Department became aware that a monitoring well located at a dairy farm in southern Maine which had previously agronomically utilized residuals had groundwater which exceeded the EPA health advisory level. The Department sampled drinking water, groundwater, surface water, soil, manure, hay, feed, and milk at this farm. Although not conclusive, results of this testing indicate that the land application of wastewater treatment plant sludge/biosolids may have contributed to the contamination of this farm with PFAS compounds.

On July 8, 2018, the *Solid Waste Management Rules: Beneficial Use of Solid Wastes*, 06-096 C.M.R. ch. 418, Appendix A was revised to include screening concentrations for three PFAS compounds: PFOA (0.0025 mg/kg), PFOS (0.0052 mg/kg), and PFBS (1.9 mg/kg).

Pertinent Regulations and Licensing Authority:

The *Solid Waste Management Rules: Agronomic Utilization of Residuals*, 06-096 C.M.R. ch. 419, § 4(A) requires that a residual must be physically and chemically suitable for the intended utilization activity, must be non-hazardous, and must be of a known and consistent quality. 06-096 C.M.R. ch. 419, § 4(C) further requires that the residual generator must develop and implement a waste characterization sampling and analytical work plan in accordance with the *Solid Waste Management Rules: Water Quality Monitoring, Leachate Monitoring, and Waste Characterization*, 06-096 C.M.R. ch. 405.

AUGUSTA
17 STATE HOUSE STATION
AUGUSTA, MAINE 04333-0017
(207) 287-7688 FAX: (207) 287-7826

BANGOR
106 HOGAN ROAD, SUITE 6
BANGOR, MAINE 04401
(207) 941-4570 FAX: (207) 941-4584

PORTLAND
312 CANCO ROAD
PORTLAND, MAINE 04103
(207) 822-6300 FAX: (207) 822-6303

PRESQUE ISLE
1235 CENTRAL DRIVE, SKYWAY PARK
PRESQUE ISLE, MAINE 04769
(207) 764-0477 FAX: (207) 760-3143

website: www.maine.gov/dep

06-096 C.M.R. ch. 405, § 6(B)(2) requires the development of a waste characterization sampling and analytical work plan for initial and ongoing characterization. Further, 06-096 C.M.R. ch. 405, § 6(D) requires that solid wastes proposed for agronomic utilization must be characterized based on specific characteristics. The group of parameters that the generator may be required to analyze for depends upon the processes that generate the residual and inputs to that process. 06-096 C.M.R. ch. 405, § 6(D)(2)(o) further requires that in addition to specific parameters already identified in 06-096 C.M.R. ch. 405, § 6(D)(2), the Department may require analysis for other parameters that, based on a description of the process generating the residual, may be in the residual in significant concentrations to adversely impact the utilization program. Standard Condition 3 to all solid waste facility licenses requires a licensee to submit all reports and information requested by the Department demonstrating that the licensee has complied or will comply with all terms and conditions of their approval. License terms and conditions include compliance with all applicable operating rules in accordance with 06-096 C.M.R. ch. 400, § 3(E).

Sampling and Analysis Required:

The Department is now requiring all sludge/biosolids program licensees and sludge/biosolids composting facilities to test their material for PFOA, PFOS, and PFBS. Your Sampling and Analytical Work Plan (SAWP) must be updated to include sampling and analysis for these compounds on an ongoing basis. We recommend you follow the Department's PFAS sampling guidance (Attachment 1) and update your SAWP accordingly. Please pay particular attention to the summary of prohibited and acceptable items for use in PFAS sampling (appended as Attachment 1). PFAS sampling requires specific procedures to prevent inadvertent cross-contamination of samples. Your updated SAWP must be submitted to the Department for review and approval by April 12, 2019 and all initial sampling must be conducted in accordance with the Department's guidance no later than May 7, 2019. You must use one of the laboratories approved by the Department to test for these compounds. A list of prequalified laboratories is appended as Attachment 2. All data must be submitted to the Department in Electronic Data Deliverable (EDD) format, Version 6.0, along with a .pdf copy of the complete laboratory report including quality control and quality assurance information within 10 days of receipt. Results from this initial round of testing will provide the Department with critical data which will inform our determination regarding the need for and frequency of additional testing for these compounds.

Prohibition:

Pursuant to the provisions of 06-096 C.M.R. ch. 419, § 5(A), sludge/biosolids and sludge/biosolids-derived compost or products may not be land applied if the screening concentrations for PFOA, PFOS or PFBS in 06-096 C.M.R. ch. 418, Appendix A are exceeded unless and until the provisions of 06-096 C.M.R. ch. 419, § 5(B) are met. The land application and/or distribution of sludge or sludge-derived products cannot resume until approved by the Department.

Questions:

If you have any questions, please contact Carla Hopkins at Carla.J.Hopkins@maine.gov or 207-215-3314.

---

[1] https://www.epa.gov/pfas/basic-information-pfas

ATTACHMENT 1

DEPARTMENT OF ENVIRONMENTAL PROTECTION · STATE OF MAINE ·

COVER SHEET
STANDARD OPERATING PROCEDURE-ADDENDUM

OPERATION TITLE: **DEVELOPMENT OF A SAMPLING AND ANALYSIS PLAN-**

ADDENDUM - A – ADDITIONAL REQUIREMENTS FOR THE SAMPLING OF PERFLUORINATED ALKYLATED SUBSTANCES (PFASs), PERFLUOROOCTANOIC ACID (PFOA) and PERFLUOROOCTANE SULFONATE (PFOS).

1.0 APPLICABILITY

This Standard Operating Procedure (SOP) ADDENDUM applies to all programs in the Maine Department of Environmental Protection's (MEDEP) Division of Remediation (DR). It is also applicable to all parties that may submit data that will be used by the DEP/DR.

This SOP ADDENDUM is not a rule and is not intended to have the force of law, nor does it create or affect any legal rights of any individual, all of which are determined by applicable statutes and law. This SOP does not supersede statutes or rules.

2.0 PURPOSE

The purpose of this document is to describe the MEDEP/DRs requirements for the development of a Sampling and Analysis Plan (SAP) with specific requirements for the sampling of compounds related to Per- and Polyfluoroalkyl Substances (PFASs), including Perfluorooctanoic acid (PFOA) and Perfluorooctane sulfonate (PFOS).

Prior to conducting any investigative field work, routine monitoring, post closure sampling or any data gathering/sample collection project, a SAP will be developed that outlines the goals of the activity and methodology to achieve that goal. A well-developed SAP that is reviewed by all field team members will assure that the goals are obtainable, the methodology is consistent, and the data generated will meet the Data Quality Objectives (DQOs) for the project.

Given the ubiquitous nature of PFAS compounds, the low detection levels that are generally requested, and the different methodologies for which these compounds are tested, additional requirements regarding sampling methodology, equipment, and analysis for PFAS compounds should be included as part of the sampling plan and during the sampling event. This document outlines those specific requirements to be included in a PFAS sampling plan and during sampling.

3.0 GUIDELINES AND PROCEDURES

3.1 INTRODUCTION

A sampling and analysis plan, regardless of whether sampling for PFAS compounds or other potential contaminants, should include all the elements in SOP RWM-DR-014 – Development of a Sampling and Analysis Plan. Although not required to be included in the SAP, (as outlined in SOP RWM-DR-014), an assessment of the existing data should be conducted, a site reconnaissance completed, a conceptual site model developed, and data quality objectives determined as part of planning to assure the SAP will meet the goals of the sampling.

The SAP itself should include the goal of the sampling, end use of data, data quality objectives, schedule, sampling methodology, sampling locations, media to be sampled, analytical parameters, and QA/QC samples. Additionally, a site specific health and safety plan may be necessary (see SOP-DR-014) depending on the scope of the sampling event. For example, collection of samples in a large or moving water body, or as part of large sampling effort involving drilling rigs and/or excavation equipment would require a health and safety plan; residential well sampling would likely not.

3.2 SAMPLING METHODOLOGY/EQUIPMENT

A description of the sampling methodology will be included in the SAP. Generally, reference to an appropriate SOP for the sample methodology will be sufficient. The Division has developed multiple SOPs for sample collection of most media; please refer to the Division of Remediation's Quality Assurance Plan - Attachment B – Data Collection SOPs for a list of all data collection standard operating procedures.

3.2.1 Sampling Methodology

Sampling for PFAS will follow the standard procedures as outlined in the specific sampling method SOPs. In addition, the following task must be included in the SAP and field staff must perform the task as described below to prevent contamination of the sample:

> "Prior to sampling each location the sample handler must wash their hands and don nitrile gloves. PFAS contamination during sample collection can occur from several common sources, including food packaging and certain foods and beverages. Proper hand washing and wearing nitrile gloves will help to minimize this type of accidental contamination of the samples."

It should be noted that samples collected for PFAS analysis do not have to be headspace free.

3.2.2 Sampling Equipment/Supplies/Personal Protective Equipment (PPE)

The low detection limits required for PFAS water analysis and their common occurrence in frequently used items warrant attention to equipment and PPE used for sampling. A sampling equipment list for PFAS projects should follow the material guidelines in Table 1 of Attachment A, avoiding use of LDPE and any Teflon-lined equipment or tubing. If field decontamination of non-disposable equipment is necessary, washing with an approved soap solution, rinsing with DI water and then a rinse with laboratory-supplied PFAS-free water is recommended. New nitrile gloves should be used between locations and activities. Other recommended clothing and PPE requirements are noted in Table 1 of Attachment A.

3.3 Media Sampled/Analytical Parameters

A chart outlining the media collected and sample analysis methodology will be included in the SAP.

PFOA and PFOS are the typical potential contaminants of concern (COCs) at PFAS sites, although laboratory reporting lists may include 12 to 26 PFAS compounds depending upon method and laboratory. An additional analysis that may be warranted is the sum of all PFAS present, either by total extractable fluorinated compounds (TOP analysis) or evaluation of total fluorine by a method such as proton induced gamma-ray emission (PIGE). Both of these techniques can be followed by analysis of specific compounds, to assess the presence of precursors in environmental media that are not captured by the compound specific methods.

Parameters will be identified by either laboratory analysis methodology number, or generally accepted name of analysis. Given the different methods currently available for sampling PFAS, there must be a clear understanding between the project manager and the laboratory providing the analysis as to what the media sampled, test methodology, and detection levels will be.

Table 1 provides several current methods with their associated media:

TABLE 1
Media/Analytical Methodology

MEDIA	LABORATORY METHOD	HOLD TIME*/ PRESERVATION	ANALYSIS TIME	Reporting List
Drinking Water**	USEPA Method 537	14 days to extraction/Trizma***	28 days after extraction	Method specific
Groundwater	Modified Method 537	14 days to extraction/<6°C	28 days after extraction	DEP Minibid list ****
Surface Water	Modified Method 537	14 days to extraction/<6°C	28 days after extraction	DEP Minibid list ****
Soil/Sediment/sludge	Modified Method 537	14 days to extraction/<6°C	28 days after extraction	DEP Minibid list ****
Other (vegetation…)	Modified Method 537	Lab specific	Lab specific	DEP Minibid list ****
Water or Soil	TOP or other total fluorinated analysis	Lab specific/<6°C	Lab specific	Method specific

* Hold times may vary with contracted laboratory
** USEPA 537 is the only certified method for drinking water
*** Trizma needed for samples that may contain residual chlorine from treated water sources
*** Longer reporting lists may vary between laboratories, generally the DEP mini-bid list can be used for comparison to other selected laboratories

Other methods may be appropriate based on the data quality objectives of the sampling project.

The contracted analytical laboratory must be Maine certified to perform any method for which Maine provides certification. The contract lab must be able to accommodate the sample load and perform the analyses within holding times. The contract lab must be able to achieve PQLs, for all analyses, which are below the associated regulatory guideline value.

Deviations can be made from the laboratory method on a site or event specific basis, based on the goals of the sampling, end use of the data, and the data quality objectives. Rationale for deviations from these methods should be described in the SAP and/or the final report.

As with all parameters, containers, preservation, and holding times will be as recommended by the laboratory providing analytical services. Special or out of the ordinary containers or preservation should be noted in the SAP.

3.4 FIELD QC SAMPLES

Sample collection for PFAS analysis does not require specific field QC samples outside the normal requirements.

General recommendations for all sampling include one aqueous field blank, per field event, to be analyzed for PFASs to determine if water samples have been contaminated by sources unrelated to the project area, and to assess the overall field procedures. An equipment blank may be needed if non-dedicated equipment is used. The field blank is typically one bottle of PFAS-free water supplied by the laboratory, which is uncapped and poured to a second bottle. For multi-day events, one blank per day should be considered. If non-disposable equipment is used a PFAS-free water equipment blank is warranted to check field decontamination procedures.

4.0 PFAS SPECIFIC TEMPLATE

In the instances of a PFAS only sampling event, in which samples are being collected from a project which has a history of sampling for other analytes and a well-developed conceptual site model and/or an SAP already exists, a PFAS sampling specific template has been developed which provides the general requirements of a sampling plan. This template can be found in Attachment A of this Addendum.

5.0 REPORT GENERATION

As stated in SOP RWM-DR-014, A Sampling Event Trip Report (SETR) will be developed for every sampling event (see MEDEP/DR SOP# RWM-DR-013). The staff person responsible for developing the SETR will be stated in the SAP. Data obtained as part of the SAP will be assessed in the final report for which the data has been collected.

ATTACHMENT A
PFOA SAMPLING AND ANALYSIS PLAN FORM TEMPLATE

1.1 INTRODUCTION

The introduction will state the objectives of the sampling plan which include:

- Goals of the sampling plan;
- End use of data.

2.0 BACKGROUND INFORMATION

A BRIEF explanation of the background of the Site and/or conceptual site model (CSM) and reason for sampling for PFAS will be presented.

3.0 SITE SPECIFIC HEALTH AND SAFETY PLAN

If determined necessary, a Site Specific Health and Safety plan (HASP) will be developed and attached.

4.1 SAMPLING METHODOLOGY/ EQUIPMENT

A description of the sampling methodology will be included in the SAP. In instances where a MEDEP/DR SOP is available, reference to SOPs by either name or document number is sufficient.

Currently, the MEDEP/DR QAP has SOPs for the following sample collection tasks which may be pertinent to PFAS sampling:

- 001-Water-Sample-Colllection-From-Water-Supply-Wells;
- 002-Groundwater-for-Site-Investigation;
- 003-Low-Flow-Groundwater-Sampling;
- 004-surface-water-sediment;
- 006-soil-sampling;
- 010-Container-Sampling;
- 015-Incremental-sample-methodology;
- 023-Pore-Water-Sampling.

Other SOPs may be utilized on a project specific basis if MEDEP/DR does not have a current SOP for sampling a particular media or situation. Prior Department approval is necessary.

Prior to sampling each location the sample handler must wash their hands and don nitrile gloves. PFAS contamination during sample collection can occur from a number of common sources, including food packaging and certain foods and beverages. Proper hand washing and wearing nitrile gloves will help to minimize this type of accidental contamination of the samples.

Some sampling equipment, field supplies, field clothing and personal protective equipment are prohibited when sampling for PFAS. T able 1 outlines the prohibited items. This table must be included in the SOP and field staff informed as to what equipment is allowed.

Table 1: Summary of Prohibited and Acceptable Items for Use in PFAS Sampling

Prohibited Items	Acceptable Items
Field Equipment	
Teflon® containing materials. Aluminum foil.	High-density polyethylene (HDPE) and stainless steel materials
Storage of samples in containers made of LDPE materials	Acetate direct push liners
Teflon® tubing	Silicon or HDPE tubing
Waterproof field books. Water resistant sample bottle labels.	Loose paper (non-waterproof). Paper sample labels covered with clear packing tape.
Plastic clipboards, binders, or spiral hard cover notebooks	Aluminum or Masonite field clipboards
	Sharpies®, pens
Post-It Notes	
Chemical (blue) ice packs	Regular ice
Excel Purity Paste TFW Multipurpose Thread Sealant Vibra-Tite Thread Sealant	Gasoils NT Non-PTFE Thread Sealant Bentonite
Equipment with Viton Components (need to be evaluated on a case by case basis, Viton contains PTFE, but may be acceptable if used in gaskets or O - rings that are sealed away and will not come into contact with sample or sampling equipment.)	
Field Clothing and PPE	
New clothing or water resistant, waterproof, or stain treated clothing, clothing laundered with fabric softeners, clothing containing Gore-TexTM	Well-laundered clothing, defined as clothing that has been washed 6 or more times after purchase, made of synthetic or natural fibers (preferable cotton)
Clothing laundered using fabric softener	No fabric softener
Boots containing Gore-TexTM	Boots made with polyurethane and PVC
	Reflective safety vests, Tyvek®, Cotton Clothing, synthetic under clothing, body braces
No cosmetics, moisturizers, hand cream, or other related products as part of personal cleaning/showering routine on the morning of sampling	**Sunscreens** - Alba Organics Natural Sunscreen, Yes To Cucumbers, Aubrey Organics, Jason Natural Sun Block, Kiss my face, Baby sunscreens that are “free” or “natural” **Insect Repellents** - Jason Natural Quit Bugging Me, Repel Lemon Eucalyptus Insect repellant, Herbal Armor, California Baby Natural Bug Spray, BabyGanics

	Sunscreen and insect repellant - Avon Skin So Soft Bug Guard Plus – SPF 30 Lotion
Sample Containers	
LDPE, glass containers or passive diffusion bags.	HDPE (any media) or polypropylene (only for EPA Method 537 samples)
Teflon®-lined caps	Lined or unlined HDPE or polypropylene caps
Rain Events	
Waterproof or resistant rain gear	Polyurethane, vinyl, wax or rubber-coated rain gear. Gazebo tent that is only touched or moved prior to and following sampling activities
Equipment Decontamination	
Decon 90	Alconox® and/or Liquinox®
Water from an on-site well	Potable water from municipal drinking water supply (if tested as PFAS-free)
Food Considerations	
All food and drink, with exceptions noted on the right	Bottled water and hydration drinks (i.e. Gatorade® and Powerade®) to be brought and consumed only in the staging area

It is recommended that all water samples will be collected using dedicated or disposable sampling equipment where possible. Any re-usable equipment, such as plumbing fittings, that may be needed in certain cases to obtain a sample from the pressure tank tap, should be deconned using Alconox/Liquinox soap and rinsed with DI or PFAS-free water prior to use and between locations.

5.0 Sample Locations

A map showing planned sampling locations will be included in the sampling plan. If locations are not pre - determined, the method that samples will be chosen and collected (field observations, random, etc.) will be outlined in the SAP. Field or laboratory compositing procedures will also be described, if applicable.

This section should also indicate sampling collection priority and order, to assure that the most important samples are obtained, and that sampling is generally done from low areas of contamination to higher levels of contamination. It is recommended that critical samples be collected in duplicate.

6.0 Media Sampled

A chart outlining the media collected and sample analysis will be included in the SAP. Table 2 provides several current methods with their associated media:

TABLE 2
Media/Analytical Methodology

MEDIA	LABORATORY METHOD	HOLD TIME*/ PRESERVATION	ANALYSIS TIME	Reporting List
Drinking Water	USEPA Method 537	14 days to extraction/Trizma**	28 days after extraction	Method specific
Groundwater	Modified Method 537	14 days to extraction/<6°C	28 days after extraction	DEP Minibid list ***
Surface Water	Modified Method 537	14 days to extraction/<6°C	28 days after extraction	DEP Minibid list ***
Soil/Sediment/ Sludge	Modified Method 537	14 days to extraction/<6°C	28 days after extraction	DEP Minibid list ***
Other (vegetation…)	537 Modified	Lab specific	Lab specific	DEP Minibid list ***
Water or Soil	TOP or other total fluorinated analysis	Lab specific/<6°C	Lab specific	Method specific

* Hold times may vary with contracted laboratory, listed times from Vista Analytical Inc.

** Trizma needed for samples that may contain residual chlorine from treated water sources

*** Longer reporting lists may vary between laboratories, generally the DEP mini-bid list can be used for comparison to other selected laboratories

Other methods may be appropriate based on the data quality objectives of the sampling project.

The contracted analytical laboratory must be Maine certified to perform any method for which Maine provides certification. The contract lab must be able to accommodate the sample load and perform the analyses within holding times. The contract lab must be able to achieve PQLs, for all analyses, which are below the associated regulatory guideline value.

Containers, preservation, and holding times will be as recommended by the laboratory providing analytical services. Special or out of the ordinary containers or preservation should be noted in the SAP.

7.0 FIELD QC SAMPLES

The specific needs for QC samples for the project will be outlined. General requirements for PFAS sampling events include one aqueous field blank, per field event, to be tested for PFASs to determine if water samples have been contaminated by sources unrelated to the project area, and to assess the overall field procedures. The field blank is typically one bottle of PFAS-free water supplied by the laboratory, which is uncapped and poured to a second bottle. An equipment blank should be collected if non-dedicated equipment is used. For multi-day events, one blank per day should be considered, and for large events one blank per 10 or 20 samples is warranted, depending upon the project requirements. All blanks should be collected with laboratory supplied PFAS-free water. A source-water blank is handled like a trip blank, and assesses the laboratory supplied water and sample containers. This blank may be warranted depending on DEP experience with the laboratory or sensitivity of the project.

Additionally, any QC samples that will be collected in the field that are required as part of laboratory QC requirements and to allow data validation will be outlined.

4.9 REPORT GENERATION

A Sampling Event Trip Report (SETR) will be developed for every sampling event (See MEDEP/DR SOP# RWM-DR-013). Staff person responsible for developing the SETR will be stated.

ATTACHMENT 2

LABORATORIES APPROVED BY DEP FOR PFAS ANALYSIS

Alpha Analytical

72 Center Street, Suite 3, Brewer, ME 04412
Contact name: Stephen Knollmeyer
Email address: sknollmeyer@alphalab.com
Phone: (603) 498-7213
222 International Drive, Suite 155, Portsmouth, NH 03801
Contact name: Melissa Gulli
Email address: mgulli@alphalab.com
Phone: (603) 319-5010

ALS Environmental

1317 South 13th Avenue, Kelso, WA 98626
Contact name: Howard Boorse
Email address: Howard.Boorse@alsglobal.com
Phone: (360) 577-7222

Eurofins Lancaster

2425 New Holland Pike, Lancaster, PA 17601
Contact name: Jane Huber
Email address: JaneHuber@EurofinsUS.com
Phone: (717) 209-1438

Eurofins TestAmerica Laboratories, Inc

880 Riverside Parkway, West Sacramento, CA 95605
Contact name: Debby Wilson
Email name: Debby.Wilson@testamericainc.com
Phone: (949) 260-3228

SGS AXYS

2045 Mills Road West, Sidney, British Columbia, Canada V8L 5X2
Contact name: Nicholas Corso
Email address: nicholas.corso@sgs.com
Phone: (250) 655-5800

SGS North America, Inc

4405 Vineland Road, Orlando, FL 32811
Contact name: Geoffrey Pellechia
Email address: Geoffrey.pellechia@sgs.com
Phone: (508) 630-4940

Vista Analytical Laboratory, Inc

1104 Windfield Way, El Dorado Hills, CA 95762
Contact name: Jennifer Miller
Email address: jmiller@vista-analytical.com
Phone: (916) 673-1520

Science of the Total Environment 724 (2020) 138334

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Transfer and transport of microplastics from biosolids to agricultural soils and the wider environment

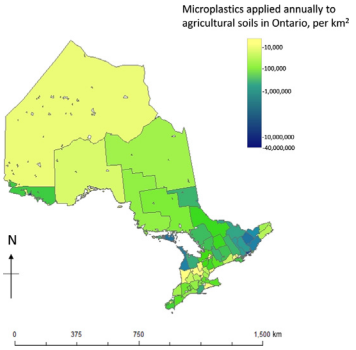
Jill Crossman [a,*,1], Rachel R. Hurley [b,1], Martyn Futter [c], Luca Nizzetto [b]

[a] School of the Environment, University of Windsor, Sunset Avenue, Windsor, Ontario N9B 3P4, Canada
[b] Norwegian Institute for Water Research (NIVA), Gaustadelléen 21, 0349 Oslo, Norway
[c] Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Science, Uppsala, Sweden

HIGHLIGHTS

- Microplastic (MP) concentrations of up to 1.4×10^4 MP kg^{-1} were found in biosolids.
- Storage of biosolids should be explored as a method for reducing biosolids' MP content.
- Some MP fibers are retained in soils, while fragments are predominantly exported.
- >99% of MPs applied from biosolids were likely exported to the aquatic environment.
- Biosolids application legislation may need revisions to incorporate MP management.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 January 2020
Received in revised form 28 March 2020
Accepted 29 March 2020
Available online 1 April 2020

Editor: Damia Barcelo

Keywords:
Microplastics
Soil
Agriculture
Biosolids
Management
Export
Aquatic

ABSTRACT

Between April to November of 2017, microplastics (MPs) were analysed in biosolids from two separate suppliers, and in the soils of three agricultural fields to which they were applied, in Ontario, Canada. Soils of a control site with no history of biosolid application were also examined. High MP concentrations of between 8.7×10^3 MP kg^{-1} and 1.4×10^4 MP kg^{-1} were found in biosolids samples. Lower MP concentrations observed in Provider 2 biosolids may be due to storage, settling and supernatant removal prior to applications. Annual MP additions to agricultural soils across Ontario were estimated at between 4.1×10^{11} and 1.3×10^{12} particles. All fields receiving biosolids had higher soil pre-treatment MP concentrations than the control. The field with the greatest number of previous biosolid treatments had the highest pre-treatment soil MP concentrations; suggesting some MP retention in soils between applications. Immediately following biosolids applications, two fields demonstrated significant increases in soil MP concentrations, with preferential retention of MP fibers over fragments observed, while a reduction in soil MP concentrations were observed in the third. Surprisingly, only one field demonstrated a net gain in soil MPs over the course of the study. At all three fields, >99% of MPs applied in biosolids in 2017 were unaccounted for. The study suggests that despite adhering to applicable legislation, biosolids applications at all sites likely result in high rates of MP export. This study is the first to track MP transport through soils following their application in biosolids, and contributes to filling current knowledge gaps regarding export of MPs to aquatic systems from the terrestrial environment.

---

* Corresponding author.
E-mail address: jhc@uwindsor.ca (J. Crossman).

[1] These authors contributed equally.

https://doi.org/10.1016/j.scitotenv.2020.138334

1. Introduction

Plastic items with a longest dimension smaller than 5 mm are defined as microplastics (MPs) and include both intentionally manufactured particles (primary MPs) and those originating from the breakdown of larger macroplastics (secondary MPs). Although secondary MPs are more common in the environment, primary MPs have gained the greatest public attention, and been the target of most legislation and management (Rochman et al., 2015; Xanthos and Walker, 2017). Due to their ubiquitous presence in environmental matrices and potential interaction with biota, MPs have emerged as a serious global concern.

While the generation of MPs is largely terrestrial, their transmission to the aquatic environment is believed to be driven primarily by urban surface runoff and wastewater discharge (Galafassi et al., 2019). Large volumes of MPs can be removed, however, when stormwater runoff, industrial effluent and household drainage pass through wastewater treatment plants (WWTP) (Carr et al., 2016). Despite this, MP concentrations in lakes and oceans continue to rise; there are an estimated 2.69×10^5 tons of MPs in the ocean (Xanthos and Walker, 2017), and an average of 4.30×10^4 MP km^{-2} in the surface waters of the Laurentian Great Lakes (Eriksen et al., 2013).

Once removed from wastewater, MPs culminate in biosolids; a nutrient-rich semi-solid waste product, created during the wastewater treatment process. In many countries, biosolids are applied to agricultural lands as a soil amending agent and fertilizer (Nizzetto et al., 2016a). It has been calculated that each year farmed soils in North America may receive to up to 300,000 tonnes of MPs through biosolid applications (Nizzetto et al., 2016a), however very little is known about their fate and transport through the terrestrial environment (Nizzetto et al., 2016a; Rocha-Santos and Duarte, 2015; Rillig, 2012; Ng et al., 2018; de Souza Machado et al., 2018). Specifically, no empirical information is available on whether subsequent to biosolids application, the soils act as an MP source to rivers and lakes, with MPs moving laterally towards watercourses; or whether soils act as a sink, with downward vertical movement dominating. Under repeated biosolids applications, some MPs may be retained in soils, which could result in significant MP accumulation over time (Brodhagen et al., 2017; Corradini et al., 2019), although MP retention has not yet been quantified. While the notion of a soil MP 'store' might be desirable for reducing transfer of MPs to aquatic systems, the permanence of such a store and its impacts on plant growth, soil biota and overall soil health are largely unknown.

Through the analysis of 1300 soil samples collected before, during and after biosolids applications from three cultivated fields and from one control site in 2017 (Fig. 1), in addition to samples of the biosolids applied, we aimed to quantify the spatial and temporal variability in MP fate and transport through agricultural soils in Ontario, Canada. Key objectives were to 1) identify MPs in biosolids applied to agricultural soils; 2) quantify impacts of biosolid applications on the MP content of agricultural soils; and 3) to identify biosolids management strategies to reduce MP inputs to agricultural soils.

2. Methods

2.1. Site description

Four agricultural fields in Ontario, Canada, were studied. Three active treatment sites were sampled (Field 1, Field 2 and Field 3) where biosolids had been previously applied between 2012 and 2016, and where applications were planned for 2017. A fourth control field with no history of biosolids use was selected within the same region. Proximity was important for minimizing between-site variability in exposure to airborne MP contamination. All sites were located proximal to tributaries which drained into large economically important waterbodies (Lake Simcoe and Lake Scugog) and were situated in sandy loam soils (Fig. 1).

Field 1 (10.24 ha) and Field 3 (34.4 ha) were treated with biosolids from the same supplier (Provider 1) whereas biosolids applied to Field 2 (26.1 ha) were supplied by a separate haulage company (Provider 2). Although the two providers obtained biosolids from different WWTPs, all treatment plants had separate stormwater and sanitary systems and served similar sized cities (≈140,000 people). There are, however, notable differences in biosolid treatment and storage methods between WWTPs. The WWTP supplying Provider 1 anaerobically digests solids in mixing tanks, whereas the WWTP supplying Provider 2 uses an additional aeration pre-treatment process to promote bacterial breakdown. Provider 1 transports biosolids directly from the WWTP to the fields on the day of application and incinerates waste from fall to spring when biosolids spreading is prohibited. Provider 2 collects biosolids from a centralized facility, used year-round by the WWTP for biosolid storage and settling (Albert, 2013), where the top liquid supernatant is syphoned off and returned to the WWTP for additional treatment. Thus, Provider 2 uses only the thicker portion of the settled biosolids for land applications.

In Ontario, biosolids may be either surface applied or injected into the soils, although restrictions exist as to time and conditions of use (Ontario Nutrient Management Act, 2002). Permitted application rates vary depending on soil saturation levels, season, proximity to watercourse and slope. Opportunities to apply biosolids were limited in early 2017 by heavy and frequent rainfall, resulting in soil saturation. Soil conditions improved sufficiently by April 27th for treatment to proceed at Field 3, where Provider 1 applied biosolids to the surface using precision methods with a tanker and hose, simultaneously applying and ploughing biosolids into the top soil layer. At the other two treatment sites, conditions were unfavorable for surface application until May 23rd (Field 2, Provider 2) and June 13th (Field 1, Provider 1), by which time crops had already been planted, precluding post-application ploughing. At all sites, heavy rainfall events combined with high runoff volumes were observed shortly after application. Application rates and total amounts of biosolids applied are summarized in Table 1.

2.2. Sample collection

A cylindrical stainless steel corer, 5x8cm was used to extract soil samples from three depths; 0–5 cm, 5–10 cm and 10–15 cm. Soil samples were not taken below 15 cm due to heavy soil compaction at all sites at this depth, making MP transport below this level unlikely. The 5 cm corer was chosen to minimize soil compaction during sampling. Samples from each profile depth were separately wrapped in aluminum foil on site, and frozen until analysis. Soil samples were taken before, during and after biosolid application (Table S1). Following biosolids application, soil samples were taken monthly and following heavy rainfall events. Coring locations were selected according to observed field characteristics. Fields 2 and 3 had relatively steep slopes and a clear ridge and furrow pattern. At these fields, on each collection date 11 cores were taken across a transect at each profile depth (between two ridges and furrows), and four additional cores collected at each profile depth across ridges and furrows at the highest and lowest points of the field. Field 1 and the control site were predominantly flat, with less variable microtopography (i.e., no ridge or furrow patterns). In these fields, 14 soil cores were taken at each depth on each collection date. Locations of soil cores in these fields were randomly selected, although the existence of dense alfalfa crops in Field 1 restricted sampling to the southern field perimeter. Biosolid samples were also collected directly from the trucks and hoses during application. Three to five liters of biosolids were collected during each event and stored in a fridge prior to analysis.

Due to highly localized precipitation patterns and biosolids application times, sampling dates did not necessarily coincide at all sites. Precipitation was monitored using electronic tipping bucket rain gauges

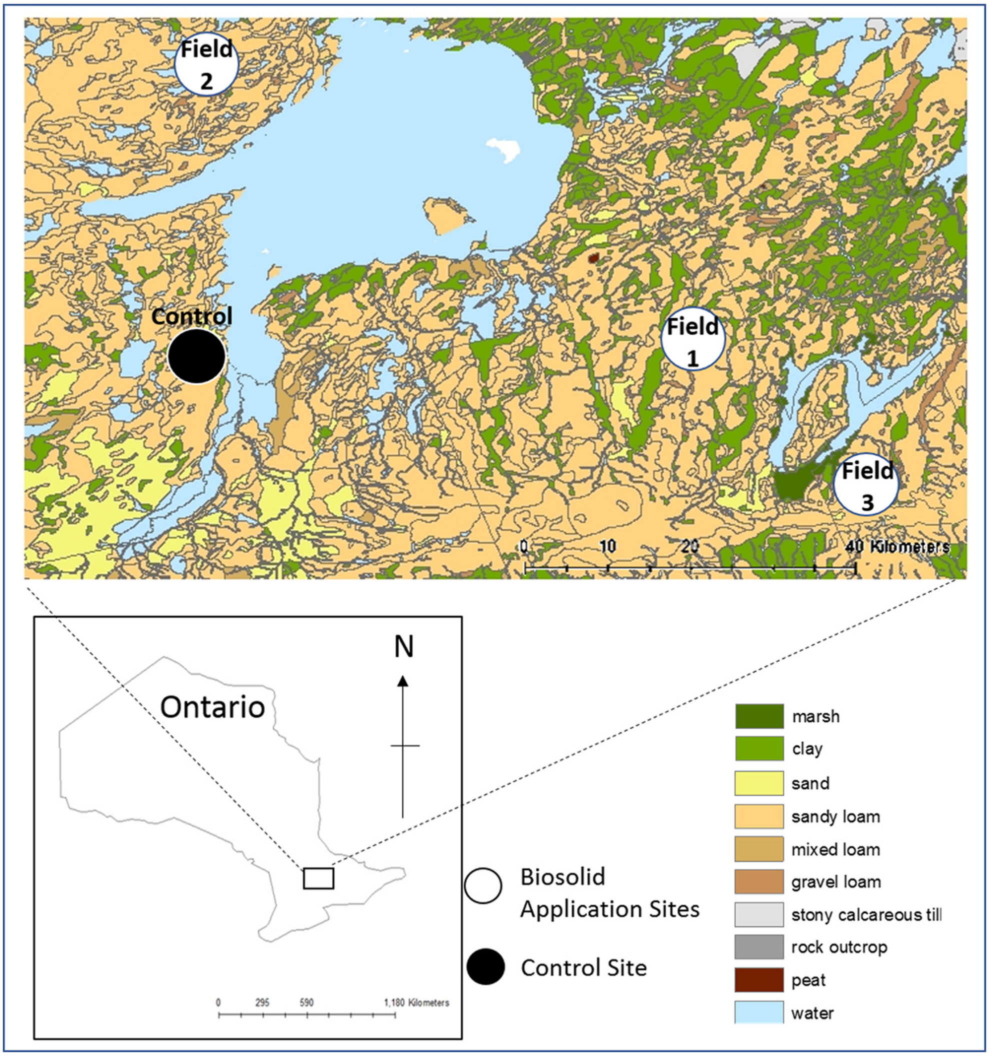


Fig. 1. Study sites, Ontario, Canada. Soils data derived from Soil Landscape of Canada Working Group (2010). Only approximate field locations are provided to ensure landowner anonymity.

installed in Fields 1 and 2. At the Control site and Field 3, established meteorological stations were used which were located within close proximity.

As with any field study, there remain limitations to the numbers of samples which can be collected. For example, fewer samples were taken from Field 3 due to limited site access. Every effort was made however to obtain a representative sample of the soil landscape, with over 1300 cores collected across the four fields. Through taking such a large number of samples, we incorporated variance in soil MP content across a range of soil depths, slope, ridges, furrows and general patchiness in soil matrices. This is the first MP study conducted within the soil environment at such a large spatial and temporal scale.

2.3. Analytical methods

At the University of Windsor, Ontario, soil samples were defrosted and 10 cm^3 selected for analysis from each core. This volume was weighed, and then placed in an oven at 65 °C until dry (with a minimum drying duration of 24 h). During drying, samples were covered with foil lids, with small holes inserted, to minimize likelihood of contamination.

Table 1
Biosolid application rates, and total amounts of MPs applied.

Site	Distance to water	Area (ha)	Biosolids provider	Biosolids application rate[a] (m^3 ha^{-1})	Application method	Total biosolids applied (m^3)	Biosolids dry weight MP concentration (MP kg^{-1})	Biosolids dry weight MP mass (mg kg^{-1})	Biosolids wet weight MP content (MP L^{-1})	Total number of MPs applied to field
Field 1	<150 m	10.24	1	78	Surface	799	11,469.4	Min: 1180	686	5.48×10^8
	>150 m	N/A	1	N/A				Max: 1276		
Field 2	<150 m	3.79	2	75	Surface	3183.2	8678	Min: 626	275	8.74×10^8
	>150 m	22.39	2	130				Max: 654		
Field 3	<150 m	3.67	1	74	Surface with post-application ploughing	4258.7	14,407	Min: 471	884	3.77×10^9
	>150 m	30.67	1	130				Max: 536		

[a] Biosolid application rates for Field 1 and 3 were supplied by Provider 1. Application rates for Field 2 were derived from regulatory guidelines (Ontario Nutrient Management Act, 2002).

Soil dry weights were calculated, and a composite sample for each field and sampling event created by combining dry samples from the same depth; resulting in 3 dried soil samples for each site sample date; vis, a 0–5 cm, 5–10 cm and 10–15 cm sample. Total volumes of biosolids sampled at each field were measured in a volumetric flask. Samples were poured into aluminum trays, covered, oven dried at 65 °C and then weighed. Temperatures were maintained ≤65 °C at all times to minimize plastic degradation. Finally, all dried samples were wrapped in aluminum foil, inserted in paper sampling bags, and shipped to the Norwegian Institute for Water Research (NIVA) for separation and identification of MPs.

As MPs in this study are encased in organic matrices (soils and biosolids), several processing steps are required for extraction including organic matter digestion, density separation, microscopic selection of MPs and identification of polymer types. All samples were first treated to remove organic matter using Fenton's reagent for digestion, following Hurley et al. (2018). MPs were then isolated from the sediment matrix through a series of density separations (SI). Following extraction, MPs were first visually identified using a Nikon SMZ 745T stereomicroscope at 20–40× magnification. Larger microplastics >300 μm, excluding fibers, were analysed on an Agilent Cary 630 single bounce ATR-FTIR. All smaller particles and fibers were analysed on a PerkinElmer Spotlight 400 μFT-IR. Spectra were compared to several libraries: including the Agilent Polymer and Elastomer, Oring and Seal ATR, PerkinElmer ATR Polymer, and BASEMAN libraries (Primpke et al., 2018). The a, b and c axis of each identified particle was recorded and used to establish particle volume, to facilitate a mass-based conversion between particle counts and particle masses. A detailed methodological description is provided in SI, including quality assurance and control (QA/QC) measures. Raw MP data are reported in Tables S5 and S6.

2.4. Contamination control

Throughout the study, care was taken to minimize MP contamination. During sample collection and drying, only glass or metal containers and instruments were used. Containers and instruments were prewashed with millipore water. Samples were covered where possible using aluminum foil or glass. At NIVA, sample processing and analysis was performed using a series of QA/QC measures, including measures to limit contamination, and the use of controls (SI), both positive (spiked matrix samples) and negative (blanks). The positive controls confirmed high extraction efficiencies for different particle types (PE beads: 97.3% ± 4.67%; PVC fragments: 92.7% ± 6.17%; Car tyre particles: 88.2% ± 5.75%; PET fibers: 80.0% ± 9.53%). For negative controls, only cellulosic particles were observed in biosolid samples, although viscose fibers were identified in soil samples. As viscose fibers represent <3% of MP types found within the soil samples, they were excluded from the dataset to account for a possible lab contamination source.

2.5. Data analysis

Three replicates of each composite soil sample were analysed, with dry weights between 19.3 and 30.8 g. The size, type (fragment/fiber), and polymer of each MP was recorded. Concentrations of MPs kg^{-1} in dried biosolid or soil were calculated by dividing the number of MPs in the replicate by the dried weight of the sample analysed. MP concentration L^{-1} of biosolid was calculated by dividing the number of MPs in the sample by the volume of sample analysed. Average MP concentrations and standard errors were calculated for the three replicates. Changes in MP distribution were calculated as the difference in MP soil concentrations at each soil depth between the baseline (before biosolid application) and date of sampling. MP accumulation was calculated as the sum of observed changes in MP distribution (positive and negative) over all soil depths, across the study period.

3. Results and discussion

3.1. Microplastics in biosolids

Microplastics were found in all biosolid samples (Fig. 2, Table 1). The highest dry and wet weight concentrations were found in biosolids supplied by Provider 1, applied to Field 1 (11,469 MP kg^{-1} or 686 MP l^{-1}) and Field 3 (14,407 MP kg^{-1} or 884 MP L^{-1}). The lowest concentrations were found in biosolids supplied by Provider 2, and applied to Field 2 (8678 MP kg-1 or 275 MP L^{-1}), and were significantly lower than those applied to Field 3 ($p < 0.01$). This range of concentrations is similar to those reported elsewhere (Primpke et al., 2018). Total numbers of microplastics applied to the fields ranged between 5.5×10^8 and 3.8×10^9 (Table 1).

The lower MP concentrations in biosolids from Provider 2 may be a result of several factors. First is the possibility of a difference in initial MP inputs to WWTPs; although treatment plants serve similar population sizes and have separate stormwater and sanitary systems. Second is the potential for differences in MP removal efficiency, i.e., the WWTP supplying Provider 2 may release more MPs in effluent and retain less in biosolids. High spatial and temporal variability in removal efficiency has been reported previously, e.g. between 54 and 91% MP removal efficiency was reported over 5 days in a Turkish WWTP (Gündoğdu et al., 2018) compared to a much more consistent 97–99% efficiency observed over a 13 day period in Canada (Gies et al., 2018). While this could partially explain the two-fold differences in biosolid MP concentrations measured in this study, short term variability in removal efficiency would likely have a minimal impact on biosolid MP concentrations, as biosolids are created from cumulative contributions from effluent flow over time. The third possibility is the difference in storage mechanisms; whereby Provider 2 used biosolids only after long-term storage and settling, and Provider 1 used materials directly from the WWTP. This settling process, in which the liquid fraction is syphoned off for re-treatment, equates to a form of density separation. As many plastic polymers are less dense than water (Nizzetto et al., 2016b), it is likely that MPs would be removed from biosolids during this process. The results indicate that long-term storage could be a possible mechanism for biosolid MP concentration reduction, and further research is therefore required to isolate the mechanisms causing variability in biosolids' MP concentrations between sources.

Several of the polymers identified in biosolids were found to be common between sources (Fig. 3, Table S2); polyethylene was found in similarly high concentrations in all samples from both providers, ranging from 4772 MP kg^{-1} (Provider 1) to 3926 MP kg^{-1} (Provider 2). Polypropylene, acrylics and polyesters were also found in high concentrations in all biosolids samples. Concentrations of other plastics common to all samples e.g. silicone, polyurethane, and ethyl-vinyl acetate were significantly lower in biosolids from Provider 2, at less than 30MP kg^{-1}, compared to up to 870MP kg^{-1} in biosolids from Provider 1. Furthermore, some plastic polymers found within Provider 1 biosolids samples at over 100MP kg^{-1} were entirely absent in biosolids from

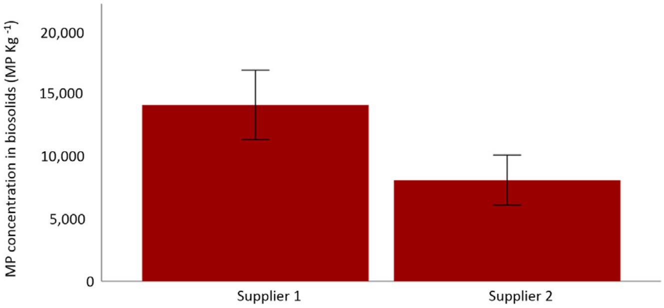


Fig. 2. MP concentrations in biosolids observed during 2017. Total samples analysed = 11. Error bars represent ± 1 Standard Error.

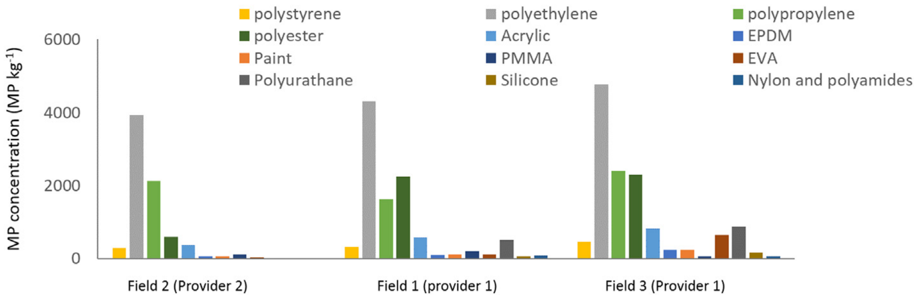


Fig. 3. Common types of plastics found in all biosolids from both providers applied to different fields.

Provider 2, including polycarbonate, polybutylene terephthalate, ethylene propylene rubber (EPR) and fluoroelastomers. These differences may again be due to the storage and density separation methods of Provider 2; since several of these polymers have a density less than or close to that of water, they are likely to have been preferentially removed during the settling process prior to application. Differences could also result from contrasting industrial inputs to the WWTPs, with Provider 1 receiving inputs from the automotive industry, and manufacturers of mining and railway equipment, steel fabrication and rubber products; and Provider 2 receiving inputs from manufacturers of motor vehicle parts, plastics, cement and concrete products.

All biosolids applied to Fields 1, 2 and 3 contained a similar dominance of fragments over fibers, with fragment content ranging from between 63% (Field 1) and 73% (Fields 2 and 3). This supports existing observations of preferential release of fibers in WWTP effluent waters (Sutton et al., 2016) and retention of fragments in biosolids (Weithmann et al., 2018).

3.2. Microplastics in soils

Soil MP concentrations prior to biosolid application were significantly different, both between depths and between sites (Fig. 4). Soils at Field 3 contained the highest number of MPs before application (average 541 MP kg^{-1}), with the control having the lowest (average 4 MP kg^{-1}). Biosolids were previously applied in 2013 and 2015 to Field 3, but only on one prior occasion on Fields 1 and 2; and there was no record of applications at the control site. High residual MP levels at Field 3, both in terms of MP numbers and MP mass (Table S3) may therefore represent accumulation of MPs from previous applications. Such accumulations have been hypothesized through laboratory experiments (Zubris and Richards, 2005) although not previously empirically observed in the environment.

Similar to the biosolids, high proportions and high concentrations of polypropylene, polyethylene, polyesters and acrylic were found in soils at all treated sites (Table S4). Soils also contained some of the polymers which were unique to individual biosolids providers. For example, poly butylene terephthalate (PBT) was found only in biosolids and soils from Provider 1, and polyvinyl chloride acetate (PVCA) was found only in biosolids and soils from Provider 2. The similarity in MP polymer types between individual biosolid sources and the soils to which they were applied indicates direct transfer and retention of plastic polymers between biosolids and agricultural soils. Much higher proportions of polyester MP fibers were found in soils (41–45%) (Fig. S1) than in original biosolid applications (8–21%). The higher dominance of polyester MP fibers in all soil sites, including the control, compared to biosolids, indicates that polyester MPs from an alternate source, e.g. atmospheric deposition, are preferentially retained in the soil profile.

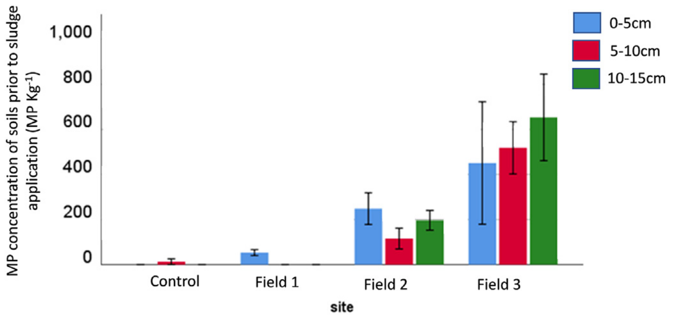


Fig. 4. Total MP concentrations in soils prior to 2017 biosolid application. Error Bars = ±1 standard error.

Following biosolids applications, an immediate increase in soil MP concentration was observed at both Field 1 and Field 2 (Fig. 5), whereas no increase was seen in Field 3, despite the higher MP concentration and quantity of biosolids applied at this site. At Field 1, elevated soil MP concentrations persisted throughout the study period, amounting to a net increase of 41% compared to pre-treatment concentrations (Table 2); although after 2 months the majority of the increase was limited to the bottom 10–15 cm, in contrast to the upper soil layer (0–5 cm) that displayed a partial loss of MPs during this period. Biosolids were applied to this field via surface spreading on established crops, with no subsequent ploughing; and the initial MP accumulation in upper soil layers, followed by its decline and sustained accumulation in deeper layers is consistent with a downward movement of MPs. Unique polymers found both in the biosolids and soil profile indicate that MPs found in Field 1 originate from Provider 1 (Table S4).

In Field 2 biosolids applications were also surface spread without ploughing, subsequent to crop planting. Initial MP enrichment in upper soil layers was also observed here for seven weeks. Beyond this timeframe, a net loss of MPs compared to the pre-application phase was observed from the top layer. Unlike Field 1, however, this loss was not matched by concomitant MP increases in lower layers, suggesting limited MP infiltration, followed by removal during runoff events. Throughout the study period, a net loss of 30% MPs was observed throughout the soil profile at this site (Table 2). In Field 3 the sustained MP losses of 45%, and absence of unique MPs matching Provider 1 biosolids, suggests that the majority of MPs from biosolids were removed during early surface flushing events following application. Field 3 was the only field where biosolids were applied with ploughing and prior to crop establishment. High rainfall following biosolids application may account for the lack of MP accumulation during 2017. Considering the high historical MP accumulation in soils in Field 3, however, it appears that such flushing is not a common occurrence at this site.

As between 5.5×10^8 and 3.8×10^9 MPs were applied through biosolids to each site during the study period, this small net increase, and large net reductions in soil MP concentrations indicate that between 99% (Field 1) and >102% (Fields 2 and 3) of the MPs applied in biosolids were unaccounted for during soil sampling, and were likely ultimately exported from the soils, where >100% indicates that both biosolids and existing baseline MPs were removed. Surprisingly, net soil MP accumulation was lowest where the highest biosolid MP concentrations and volumes were applied (Field 3; Table 2), indicating that the response of soil MP concentrations to applications through biosolids is not solely

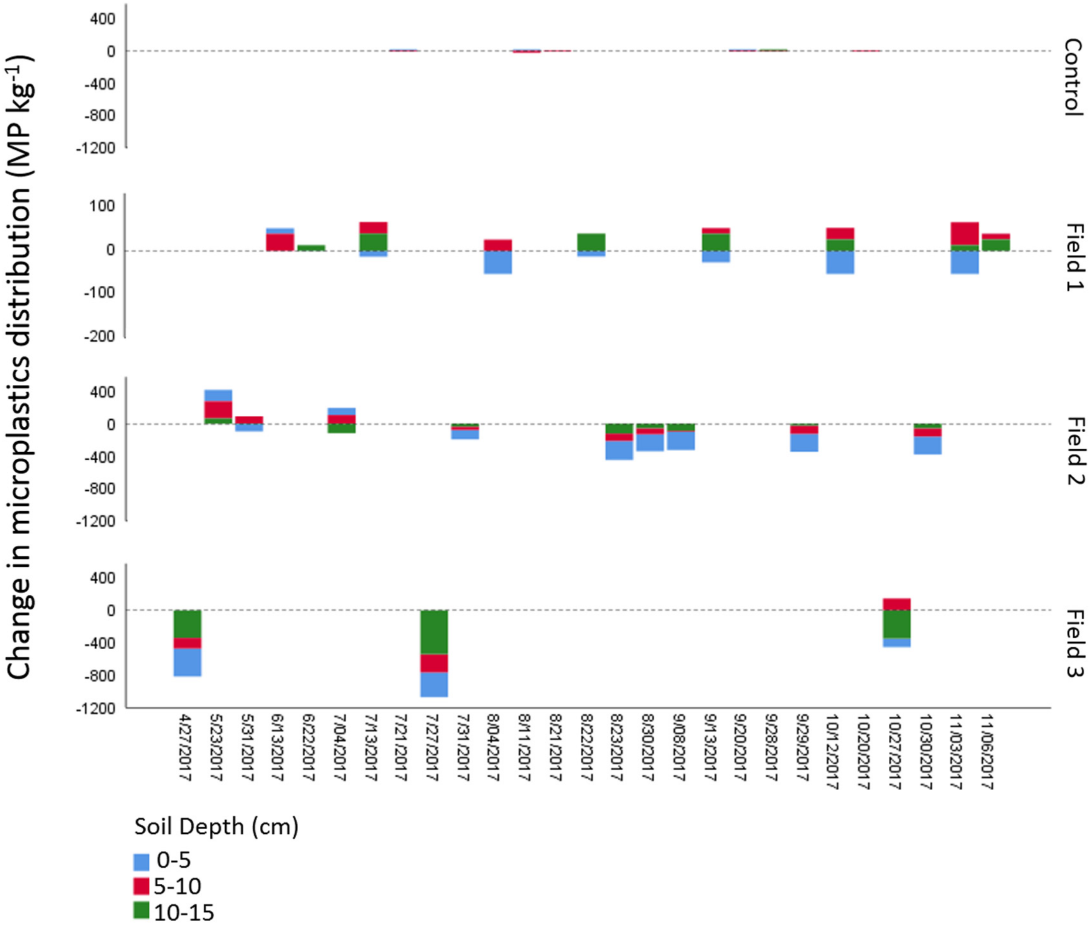


Fig. 5. Change in distribution of microplastics over time by soil depth. The change in distribution is calculated as MP numbers counted in soils prior to biosolids applications, subtracted from those identified after its application. Negative values indicate a reduction in MPs compared to the baseline; positive values indicate an increase. Note the larger scale axis for Field 1.

driven by the quantity of material used, but is influenced by a number of factors which affect subsequent MP mobilization within the soil. For instance, there is significant negative correlation between soil MP retention and soil wet density (Fig. 6). Fields 1 and 2 which retained MPs at deeper layers (Fig. 5), and which lost fewer MPs throughout the study period (Table 2) had significantly lower soil density than Field 3; which demonstrated no retention of MPs. The soil density is associated with its hydraulic properties. With higher density, and by association, fewer void spaces, MPs in Field 3 may have been subject to greater losses from surface runoff (Zemke et al., 2019) particularly during the unusually high rainfall events of 2017, with accumulation demonstrated in much drier years (Fig. 7). Applications of biosolids at Field 3 also occurred much earlier in the year (April) which likely increased the MPs exposure to these high rainfall amounts and saturated soils. Precipitation in April to June was more than double that in July; thus in Fields 1 and 2 where biosolids were applied later in the season, they were exposed to less rainfall, lower soil saturation, and were more easily able to move vertically through the soil profile. Pre-establishment of crops (Fields 1 and 2) could also facilitate vertical transport through bioturbation (Horton and Dixon, 2017) and preferential flow pathways enhanced by root growth; as it has been suggested that MP movement through soils could be impacted by soil macropores, strength of the soil matrix, accumulation within organic matter, and movement by soil biota (Rillig et al., 2017).

In all fields an increase in the proportion of MP fragments, a key characteristic of biosolids used, was noted either during or shortly following applications; although in Field 2 the increase was not observed until a full month after treatment (Fig. 8). Increases in fragments ranged

Table 2
Net change in average soil MP concentrations calculated between samples taken before and after spring applications of biosolids in 2017, including % relative error calculated across sample replicates and depth, measured as site average MP concentration divided by total range of MP concentrations.

Site	MP concentration (MP kg^{-1})		Net change	
	Before application	After	MP kg^{-1}	% increase
Field 1	18 ±22.2%	25 ±20.8%	7 ±43%	41 Min: 24% Max 59%
Field 2	187 ±53.1%	130 ±23.1%	−56 ±76%	−30 Min: −7% Max: −53%
Field 3	541 ±56.4%	298 ±39.1%	−244 ±95%	−45 Min: −2% Max: −88%

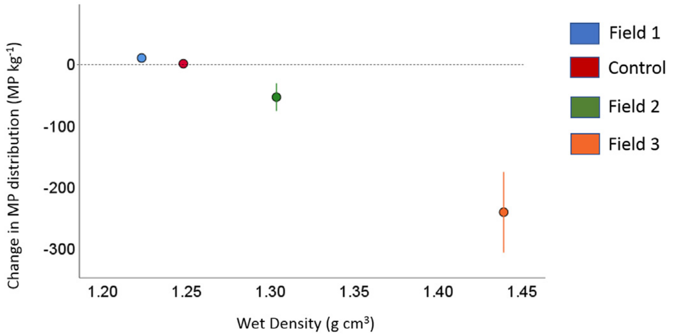


Fig. 6. Total change in microplastic distribution across all depths throughout the study period, by soil density. Error Bars = ±1 standard error.

from 4% (Fields 1 and 2) to 10% in Field 3. In Field 3 the increase was seen only during the application event itself, in comparison to Field 1 where the increase was sustained for several months. The eventual decline in proportion of fragments and increase in fibers in two of the three application sites might indicate that fragments from biosolids are preferentially transported out of the soil matrix, while fibers are retained. Previous studies on agricultural soils observed a high proportion of fibers, and suggested possible retention (e.g., Corradini et al., 2019; Zubris and Richards, 2005) due to entanglement within the matrix (Horton and Dixon, 2017).This study is the first empirical assessment of MP fragment and fiber transfer between biosolids and soils which is able to support this theory.

3.3. Wider implications

Total annual biosolid applications to agricultural land in Ontario, Canada (Central Lake Ontario Conservation Authority, 2007) have been estimated at 1.5 × 10^6 m^3. Using upper and lower biosolids MP concentrations from this study (Table 1), annual MP additions to agricultural soils in Ontario through biosolids use are between 4.1 × 10^{11} and 1.3 × 10^{12} particles (Fig. 9). Such high MP application rates, combined with the minimal capacity of soils to store MPs, as observed in this study, demonstrate the need for a targeted program for the protection of agricultural soils and the wider environment. For instance, results indicate that the long-term storage of biosolids and syphoning of supernatant liquid may be a relatively simple step which could reduce biosolid MP content and the quantities of MPs introduced to the environment.

4. Conclusion

This study reinforces the hypothesis that biosolids are a significant source of MPs to agrosystems, since up to 3.8 × 10^9 of MPs were applied to a single field in 2017. Different measures may need to be conceived to reduce MP inputs to agricultural soils treated with biosolids. Recently announced policies in many parts of the world, including Canada, to restrict single use plastics, along with existing regulations banning use of polymeric microbeads in cosmetics and personal care products will likely indirectly reduce the loads of MPs entering WWTPs, and thus reduce concentrations in sludge and biosolids. It is clear, however, that fibers, originating from laundry of synthetic clothes, will be unaffected by such legislation. In addition, revision of existing legislation surrounding biosolids management will be required to incorporate MP management, as results show that large numbers of MPs were lost from some sites following biosolid applications, despite adhering to all applicable regulations (e.g. use of Nutrient Management Plans). Meteorological conditions, soil characteristics, vegetative cover and timing of applications all impacted MP soil retention, and new legislation should be implemented to incorporate these factors and minimize transfer of MPs to watercourses.

Due to the current paucity of data on MP removal during different wastewater treatment steps and the near complete lack of MP measurements in agricultural soils, additional research is clearly needed to answer pressing questions. For instance, might heavy rainfall during spring alter agricultural soils from acting as an MP store, to an MP source? Can biosolid application subsequent to crop establishment reduce transmission of MPs into watercourses? What proportion of MPs are removed from biosolids through storage and filtering of surfactant

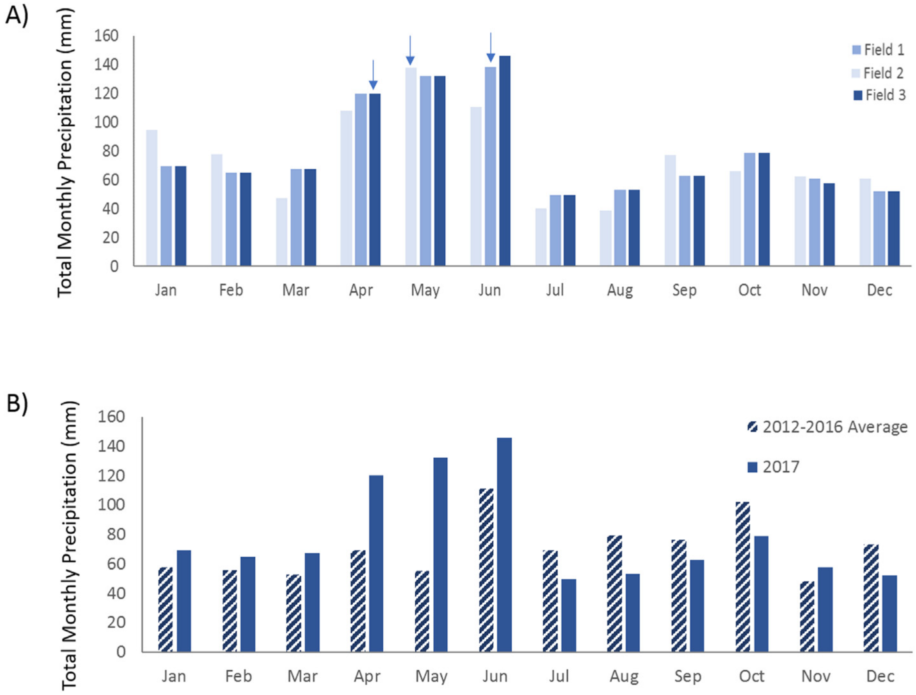


Fig. 7. A) total monthly precipitation (mm) at each field site during study period; arrows indicate locations and dates of biosolids application. B) Comparison of monthly precipitation amounts received at Site 3 between 2017 study period and average conditions over preceding 5 years (2012–2016) (ECCC, 2019).

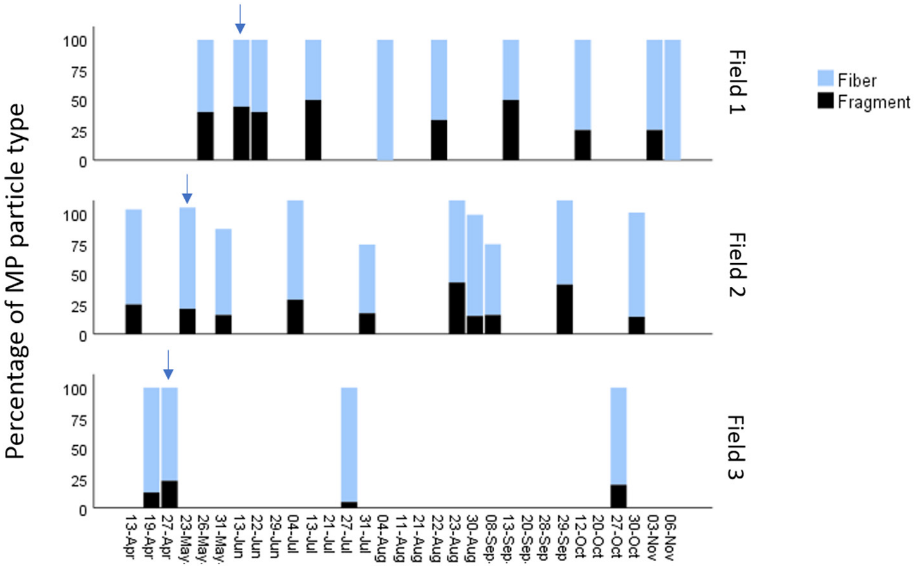


Fig. 8. Percentage of soil MP particles identified as fragments throughout the soil profile at active biosolid treatment sites (control site not included due to low numbers of particles). Arrows indicate dates of biosolid application.

liquids? Importantly, thresholds for ecological impact of MPs on soil biota have not yet been identified, meaning that currently an ecological risk assessment cannot be conducted on the results from this study. This study indicates that establishing a framework of estimating exposure to MPs in soil, a crucial step in any risk assessment, will require dealing with highly dynamic and complex processes. Additional research is therefore required as to whether the observed long-term accumulation of MP fibers in soils on plant growth and soil biota could pose a risk to

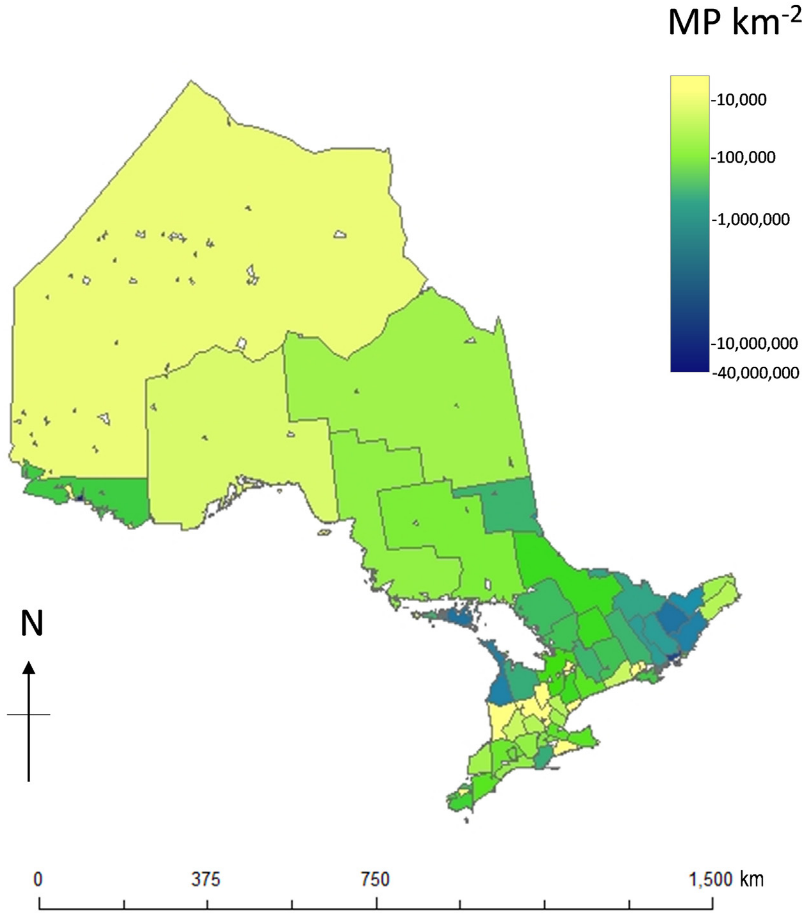


Fig. 9. Total number of microplastics applied to Ontario agricultural soils, calculated using annual biosolid application volumes (Central Lake Ontario Conservation Authority, 2007), farmland area (Ontario Ministry of Natural Resources, 2002) and observed average biosolid MP concentrations as quantified within this study.

agricultural sustainability. Researchers urgently need to address these uncertainties in order to enable effective management of terrestrial and aquatic MP pollution.

CRediT authorship contribution statement

Jill Crossman: Conceptualization, Funding acquisition, Methodology, Investigation, Formal analysis, Data curation, Visualization, Writing – original draft. **Rachel R. Hurley:** Methodology, Formal analysis, Data curation, Writing – original draft. **Martyn Futter:** Conceptualization, Funding acquisition, Investigation, Writing – original draft. **Luca Nizzetto:** Conceptualization, Funding acquisition, Methodology, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The study was funded under the frame of the collaborative international consortium (IMPASSE), financed under the ERA-NET WaterWorks 2015 co-funded call. The authors would like to thank the Canadian Research Council NSERC (WTWPJ506070-2016) the Swedish Research Council FORMAS (2017-00029) and the Research Council of Norway (271825) for funding parts of this study. ERA-NET is part of the Water Challenges for a Changing World Joint Programme Initiative (Water JPI), 2016. We would also like to thank field technician Mitch Hall for assistance with sample collection, and are extremely grateful to the anonymous stakeholders, landowners, WWTP managers and biosolids providers, who made this study possible. Thanks also to Dr. Jennifer Winter of the Ministry of Environment, Conservation and Parks for her initial stakeholder outreach help, and to Dr. Paul Helm for his valuable insights into methods of environmental microplastics sampling.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.138334.

References

Albert, M., 2013. City of Barrie secondary plan, background studies and infrastructure master plans–intensification and annexed lands. Final report. The City of Barrie. Available online at. https://www.barrie.ca/City%20Hall/Planning-and-Development/Engineering-Resources/Documents/Annexation%20PIC%203%20-%20Biosolids%20Management%20Class%20EA%20Report%20-%20Final.pdf.pdf.

Brodhagen, M., Goldberger, J.R., Hayes, D.G., Inglis, D.A., Marsh, T.L., Miles, C., 2017. Policy considerations for limiting unintended residual plastic in agricultural soils. Environ Sci Policy 69, 81–84.

Carr, S.A., Liu, J., Tesoro, A.G., 2016. Transport and fate of microplastic particles in wastewater treatment plants. Water Res. 91, 174–182.

Central Lake Ontario Conservation Authority, 2007. Source water protection plan program for the CTC CWP region. Available at. https://www.ctcswp.ca/app/uploads/2017/05/RPT_200703_WC_FNL.pdf.

Corradini, F., Mez, P., Equiliuz, R., Casado, F., Huerta-Lwanga, E., Geissen, V., 2019. Evidence of microplastics accumulation in agricultural soils from sewage sludge disposal. Sci. Total Environ. 671, 411–420.

de Souza Machado, A.A., Kloas, W., Zarfl, C., Hempel, S., Rillig, M.C., 2018. Microplastics as an emerging threat to terrestrial ecosystems. Glob. Chang. Biol. 24 (4), 1405–1416.

Environment and Climate Change Canada. 2019. Past Weather and Climate; Historical Data. Available at http://climate.weather.gc.ca/historical_data/search_historic_data_e.html Last Accessed August 2019.

Eriksen, M., Mason, S., Wilson, S., Box, C., Zellers, A., Edwards, W., Farley, H., Amato, S., 2013. Microplastic pollution in the surface waters of the Laurentian Great Lakes. Mar. Pollut. Bull. 77 (1–2), 177–182.

Galafassi, S., Nizzetto, L., Volta, P., 2019. Plastic sources: a survey across scientific and grey literature for their inventory and relative contribution to microplastics pollution in natural environments, with an emphasis on surface water. Sci. Total Environ. 693, 133499.

Gies, E.A., LeNoble, J.L., Noel, M., Etemadifar, A., Bishay, F., Hall, E.R., Ross, P.S., 2018. Retention of microplastics in a major secondary wastewater treatment plant in Vancouver, Canada. Mar. Pollut. Bull. 133, 553–561.

Gündoğdu, S., Çevik, C., Güzel, E., Kilercioľğu, S., 2018. Microplastics in municipal wastewater treatment plants in Turkey: a comparison of the influent and secondary effluent concentrations. Environ. Monit. Assess. 190, 626.

Horton, A.A., Dixon, S.J., 2017. Microplastics: an introduction to environmental transport processes. WIREs Water 5, e1268.

Hurley, R., Lusher, A.L., Olsen, M., Nizzetto, L., 2018. Validation of a method for extracting microplastics from complex, organic-rich, environmental matrices. Environ. Sci. Technol. 52 (13), 7409–7417.

Ng, E.L., Lwanga, E.H., Eldridge, S.M., Johnston, P., Hu, H.W., Geissen, V., Chen, D., 2018. An overview of microplastic and nanoplastic pollution in agroecosystems. Sci. Total Environ. 627, 1377–1388.

Nizzetto, L., Futter, M., Langaas, S., 2016a. Are agricultural soils dumps for microplastics of urban origin? Environ. Sci. Technol. 50, 10777–10779.

Nizzetto, L., Bussi, G., Futter, M.N., Butterfield, D., Whitehead, P.G., 2016b. A theoretical assessment of microplastic transport in river catchments and their retention by soils and river sediments. Environ. Sci.: Processes Impacts 18 (8), 1050–1059.

Ontario Ministry of Natural Resources, 2002. Ontario Land Cover Data Base. Second Edtion, 2000. -27 classes. PLC 2000. Reference date - revision: 2002-08-31 https://www.ontario.ca/page/open-government-licence-ontario.

Ontario Nutrient Management Act, 2002. Ontario regulation 267/03 S.O. 2002, c.4. Available at. https://www.ontario.ca/laws/regulation/030267#BK17.

Primpke, S., Wirth, M., Lorenz, C., Gerdts, G., 2018. Reference database design for the automated analysis of microplastic samples based on Fourier transform infrared (FTIR) spectroscopy. Anal. Bioanal. Chem. 410 (21), 5131–5141.

Rillig, M.C., 2012. Microplastic in terrestrial ecosystems and the soil. Environ. Sci. Technol. 6453–6454.

Rillig, M.C., Ingraffia, R., de Souza Machad, A.A., 2017. Microplastic incorporation into soil agroecosystems. Front. Plant Sci. 8, 1805.

Rocha-Santos, T., Duarte, A.C., 2015. A critical overview of the analytical approaches to the occurrence, the fate and the behavior of microplastics in the environment. Trends Anal. Chem. 65, 47–53.

Rochman, C.M., Kross, S.M., Armstrong, J.B., Bogan, M.T., Darling, E.S., Green, S.J., Smyth, A.R., Veríssimo, D., 2015. Scientific evidence supports a ban on microbeads. Environ. Sci. Technol. 49 (18), 10759.

Soil Landscapes of Canada Working Group, 2010. Soil Landscapes of Canada Version 3.2. Agriculture and Agri-Food Canada (Digital Map and Database at 1:1 Million Scale).

Sutton, R., Mason, S.A., Stanek, S.K., Willis-Norton, E., Wren, I.F., Box, C., 2016. Microplastic contamination in the San Francisco Bay. California. Marine Pollution Bulletin 109 (1), 230–235.

Weithmann, N., Moller, J.N., Loder, M.G., Piehl, S., Laforsch, C., Freitag, R., 2018. Organic fertilizer as a vehicle for the entry of microplastic into the environment. Sci. Adv. 4 (4), eaap8060.

Xanthos, D., Walker, T.R., 2017. International policies to reduce plastic marine pollution from single-use plastics (plastic bags and microbeads): a review. Mar. Pollut. Bull. 118 (1–2), 17–26.

Zemke, J.J., Enderling, M., Klein, A., Skubski, M., 2019. The influence of soil compaction on runoff formation. A case study focusing on skid trails at forested andosol sites. Geosciences 9 (204), 1–14.

Zubris, K.A.V., Richards, B.K., 2005. Synthetic fibers as an indicators of land application of sludge. Environ. Pollut. 138, 201–211.