Environmental Pollution 330 (2023) 121786

Contents lists available at ScienceDirect

Environmental Pollution

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

Occurrence of emerging contaminants in biosolids in northern Queensland, Australia☆

Ravinder Kumar[a], Anna Whelan[a,b], Patrick Cannon[c], Madoc Sheehan[a], Louise Reeves[d], Elsa Antunes[a,*]

[a] College of Science & Engineering, James Cook University, Townsville, QLD 4811, Australia
[b] Townsville City Council, Wastewater Operations, Townsville, QLD, 4810, Australia
[c] Mackay Regional Council, Mackay, QLD, 4740, Australia
[d] Queensland Water Directorate, Brisbane, QLD, 4009, Australia

ARTICLE INFO

Keywords:
Emerging contaminants
Biosolids
Pharmaceuticals and personal care products
PFAS
Heavy metals
Polycyclic musks
Environmental risk

ABSTRACT

This study aims to identify and quantify different classes of emerging contaminants (ECs), such as pharmaceutical and personal care products (PPCPs), per-and polyfluoroalkyl substances (PFAS), heavy metals (HMs), polycyclic musks (PMs) in biosolids from different sewage treatment plants (STPs) from regional councils across Northern Queensland, Australia. Biosolids samples were named BS1 to BS7 for each council. The results revealed significant variations in the concentrations of different ECs in biosolids which could be explained in some instances by the characteristics of the upstream sewage network. For instance, BS4-biosolids from a small agricultural shire (largely sugarcane) showed the highest concentration of zinc and copper, which were 2430 and 1050 mg/kg, respectively. Among PPCPs, the concentration of ciprofloxacin was found to be the highest in BS3 and BS5, two large regional council areas which are a mix of domestic and industrial (predominantly domestic) biosolids of 1010 and 1590 ng/g, respectively. In addition, the quantity of sertraline was consistently high in all biosolids except from BS7, one of the smaller regional councils, which is indicative of the domestic catchments attached. PFAS compounds were detected in all biosolids samples except in BS6, one of the small (agricultural and tourist) catchments. Two PFAS compounds emerged as the most common pollutants that were perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). The largest industrial catchment biosolids, BS2 showed the highest concentration of PFOS at 253 ng/g, while the smallest regional council, BS7 showed the maximum concentration of 7.90 ng/g of PFOA. Overall, this study concludes that certain ECs such as HMs, antibiotics, PFOS and PFOA in biosolids may pose high environmental risks.

1. Introduction

Biosolids are the mixture of water and organic matter generated as a by-product of sewage treatment processes. Typically, biosolids contain nearly 80% water and 12% of organic matter, and the remaining content comprises macronutrients, micronutrients, and traces of other compounds (Clarke & Smith, 2011). Approximately 349,000 tonnes of dry biosolids (contains 25% solids content) were produced in the year 2021 across Australia (ANZBP, 2021). The three most populated states of Australia produce the major quantity of biosolids. Notably, 29% of the biosolids are produced in Victoria, 26% from New South Wales and Australian Capital Territory, 19% from Queensland and 26% are produced in the remaining states (ANZBP, 2021). Since biosolids contain macronutrients like nitrogen, potassium, and phosphorus, and micronutrients such as copper, zinc and calcium, they serve as a high-quality fertiliser, soil conditioner, or soil replacement product (Clarke & Smith, 2011). Biosolids have a great potential to replace inorganic fertilisers in agriculture, and for every tonne of dry biosolids used, it can avoid nearly 6 tonnes of CO_2eq from the production of inorganic fertilisers (Darvodelsky, 2012). It was estimated that if all biosolids replace inorganic fertilisers in Australia, the release of approximately 2 million tonnes of CO_2eq can be avoided per year (Darvodelsky, 2012).

Though biosolids are considered a low-cost, eco-friendly and sustainable material for soil amendment, with increasing pollutants

☆ This paper has been recommended for acceptance by Eddy Y. Zeng.

* Corresponding author.
E-mail address: elsa.antunes1@jcu.edu.au (E. Antunes).

https://doi.org/10.1016/j.envpol.2023.121786
Received 4 February 2023; Received in revised form 4 May 2023; Accepted 6 May 2023
Available online 6 May 2023
0269-7491/

reaching wastewater treatment plants, biosolids are often contaminated with various types of pollutants that might restrict the use of biosolids for certain agricultural applications (Coggan et al., 2019; Kumar et al., 2023; Martínez-Alcalá et al., 2021; Petrie et al., 2015). A number of emerging contaminants (ECs) have been found in biosolids worldwide (Kumar et al., 2022). ECs are of great concern due to their potentially detrimental effects on the surrounding environment since they have great potential to leach from biosolids and translocate to the surrounding water sources, soil and plants. For instance, Johnson (2022) demonstrated per-and polyfluoroalkyl substances (PFAS) contamination in soil and groundwater after biosolids agricultural applications. The results suggested that after biosolids application for six years (57 MTD ha^{-1}), the total PFAS concentration in the surface soil was in a range of 73.0–196 ng/g, exhibiting the highest concentration for perfluorooctanesulfonic acid (PFOS), in the range of 36.0–100 ng/g (Johnson, 2022). On the other hand, the concentrations of perfluorooctanoic acid (PFOA) and PFOS in groundwater were substantially low compared to the soil, which were reported <29.0 and 2.00 ng/L, respectively (Johnson, 2022).

There is a high tendency that PFAS or other ECs from contaminated soil or groundwater can leach out to the surrounding flora and fauna and could lead to detrimental effects. Exposure to PFAS in humans has shown adverse effects on cell membrane disruption, liver cell hypertrophy, carcinogenicity and developmental toxicity (Mhadhbi et al., 2012). Accumulation of PFAS (translocated from biosolids-amended soils) in corn plants and earthworms has also been reported (Navarro et al., 2016). On the other hand, the presence of antibiotics in biosolids can promote the development of antibiotic-resistance genes (ARGs) in soils (Kimbell et al., 2018). Therefore, it is pivotal to identify and quantify the ECs in biosolids and carry out the necessary measures to mitigate their potential negative influence on the environment.

In this study, biosolids from STPs from North Queensland, Australia, were collected, and the concentrations of ECs were analysed. Selected STPs range from different treatment capacities and sources of wastewater and might contain various contaminants of emerging concerns whose concentrations are unknown to date. The sources of catchments and treatment techniques employed in the STP can have a significant effect on the final concentration of a contaminant in biosolids. Therefore, efforts were made to compare the results based on the size of STPs, sources of catchments and treatment techniques (wherever the information was available). The results were also compared with previous studies and possible adsorption mechanisms of contaminants were discussed. The risk assessment of ECs identified in biosolids was examined by calculating Risk Quotient.

2. Experimental section

The study examines the presence of different classes of emerging contaminants in biosolids from wastewater treatment plants located in North Queensland, Australia. Table S1 shows the nomenclature of biosolids samples, participation of STPs, their treatment capacities and sources of wastewater. STPs were selected assuming each STP receives wastewater from specific catchments and different population sizes, thus could show interesting trends in the variety and quantities of ECs in biosolids.

Biosolids samples were collected from all treatment plants in specific and sealed containers (glass containers for PBDEs and PPCPs, and polypropylene containers were used for PFAS). The biosolid samples were collected from the final stage of the treatment at STPs (ready for translocation for further applications). All STPs used powered polymer, mixed with the sludge before getting fed into the centrifuges. The polymer concentration was around 0.500 mg/L. The moisture content in biosolids samples was between 81 and 89%. The samples were stored in a refrigerator at 4 °C for a maximum period of 36 h to slow down the microbial activity. Biosolids samples were collected from all STPs, and a final composite from each council was prepared and analysed except for the largest council A, where biosolids from the two largest STPs were studied separately, please see supplementary information (SI) file for detail. The biosolids samples were sent to Eurofins on the same day of the sample preparation. The samples were sent to Eurofins in an esky (filled with ice bricks) with overnight freight service, delivering the samples within 24 h. The mass ratio used for preparing the composite samples was determined considering the annual biosolids production of each STP. Table S2 shows the percentage share of biosolids quantity to prepare the composite sample for the council and Table S3 shows the average annual biosolids production in individual STPs (BS1 and BS2) and collective for other biosolids samples. A minimum of three biosolids samples were collected from each STP of the councils. Table S4 shows the total number of biosolids samples and dates of collection. Average concentrations of contaminants with standard deviation were reported. One-way ANOVA (analysis of variance) was used as the statistical tool to determine if there is a significant difference between them. Table S5 presents the list of target contaminants analysed in biosolids; however, PBDEs and clandestine drugs were below the detection limit in all samples and, thus, are not discussed in the results. Previous studies suggest that PBDEs are not very common in Australian biosolids. Mainly BDE 47, BDE 99 and BDE 209 have been found in noticeable concentrations, from 13.0 to 190 ng/g, while other BDEs are either present in very low concentrations (lower than 9.60 ng/g) or below the detection limit (Clarke et al., 2010).

The flux of each contaminant was also calculated by multiplying its concentration with annual biosolids production per year, the results are shown in Table S6. All biosolids samples were tested at Eurofins laboratory for target compounds. All the results reported were the dry basis, biosolids used for the analysis as received without any treatment. The complete information related to the analysis of ECs is provided in the SI file.

3. Results and discussion

Quantities of all ECs are shown in Table S7 which contains the mean value, maximum value, minimum value, median and standard deviations. Results for each classified contaminant such as heavy metals, PPCPs and PFAS are discussed in detail in further sections.

3.1. Heavy metals

Fig. 1 shows the concentration of heavy metals (HMs) detected in biosolids samples collected from the six councils. At a glance, it can be observed that the concentration of HMs in biosolids has a similar trend across all samples. For instance, the concentration of zinc, copper and manganese was high in all biosolids samples, while the concentration of beryllium was below the detection limit. Similarly, the concentrations of cadmium, arsenic and mercury were less than 7.00 mg/kg in all biosolids samples. Among all councils, BS4-biosolids showed the highest concentrations for the majority of HMs. Noticeably, zinc, copper, cobalt, manganese, chromium, and mercury were significantly higher compared to biosolids collected from the other councils. The high concentration of heavy metals in biosolids from BS4 can be mainly attributed to the sewerage catchment characteristics (being largely agricultural and industrial with a small domestic population) and comparatively inefficient techniques for heavy metal removal employed in STPs. BS1, BS2 and BS3 generating STPs employed advanced treatment techniques such as biological nutrient removal (BNR), ultraviolet treatment and membrane filtration, while in the BS4, wastewater treatment is carried out using biological trickling filters and clarifiers for removal of suspended solids and organic matter. On the other hand, BS6 and BS7 use a combination of treatment techniques including trickling filter, single batch reactor membrane bioreactor aeration and membrane bioreactors, and aerobic and anaerobic digesters. A noticeable variation (standard deviation) can be seen in the concentration of zinc and copper for BS4 and BS2, respectively. This is because biosolids samples were

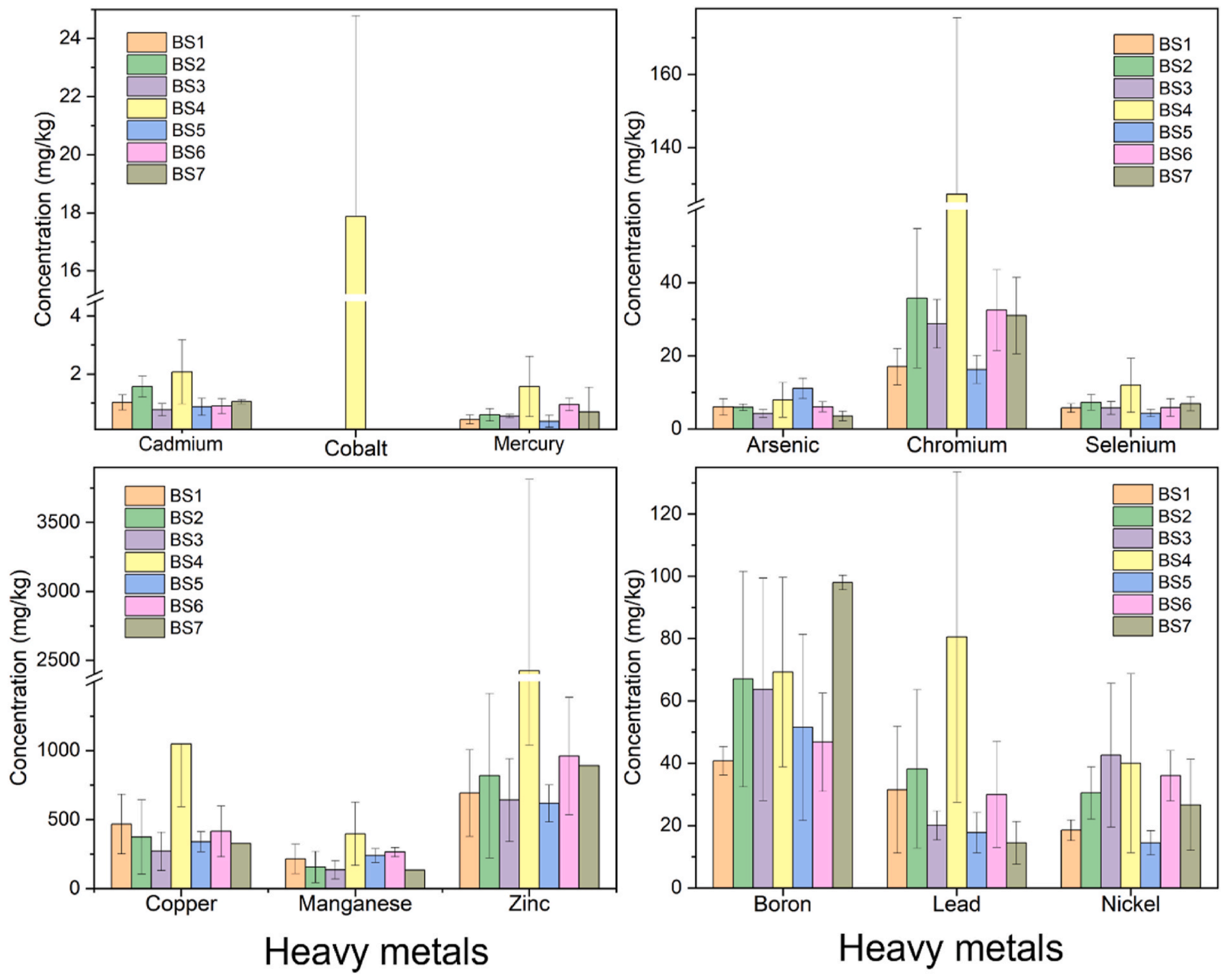

Fig. 1. Quantification of heavy metals in biosolids from six northern councils of Queensland. The whisker on each column represents the standard deviation. Note: A minimum of three samples of biosolids were analysed, and their average concentrations were reported.

collected at different time intervals with a difference of 30–45 days and thus STPs can receive wastewater from different catchments that might bring varying levels of contaminants, largely depending on activities in industry, households, and agriculture.

BS7 biosolids also showed high concentrations of zinc and copper, which were found to be 890 ± 626, and 328 ± 271 mg/kg, respectively. In rival to all councils, BS7-biosolids reported the highest concentration of 98.0 mg/kg of boron, which can be ascribed to the natural weathering of rocks and soils, and the use of boron-containing pesticides and fertilizers. STPs producing BS7 biosolids mainly receive wastewater from domestic and agricultural activities, therefore, the source of zinc and copper can be attributed to these HMs-containing pesticides and fertilizers, and domestic contamination from personal care and pharmaceutical products. On the other hand, high concentrations of zinc in biosolids can be ascribed to the translocation of zinc from mining and mineral processing, landfill and dumpsite spills, and household wastewater, including leaching from brass materials (Kimbrough, 2009). The presence of copper in biosolids can be associated with agricultural activities such as the dissolution of copper minerals in algicides and insecticides and the corrosion of copper alloy pipes used for water distribution (Latosińska et al., 2021). Alternative sources of copper may include fuels and lubricants, fungicides and larvicides, paints and PPCPs (Agoro et al., 2020). The sorption of heavy metals like zinc and copper on biosolids also depends on the occurrence of organic and inorganic constituents (minerals like manganese, sulfide, and iron oxide) (Donner et al., 2012). In addition to the hydrophobic nature of the contaminants, electrostatic interactions, proportions of total organic carbon, extracellular polymeric products and pH affect the sorption capacities of HMs and ultimately are responsible for their accumulation in biosolids (Semblante et al., 2015). Table S8 compares our results for HM contamination in biosolids with previous studies, to show that these HMs are frequently observed in biosolids. For instance, high concentrations of zinc and copper have been reported in biosolids in most of the studies.

Overall, the study provides important insights into the concentration of HMs in biosolids samples collected from different councils and highlights the need for efficient techniques for heavy metal removal in STPs to reduce the concentration of these contaminants in biosolids. In terms of Australian standard guidelines of HMs in biosolids, the majority of biosolids analysed in this study fall in Grade B, mainly due to the presence of high concentrations of zinc and copper (End of Waste Code Biosolids), which indicates restricted agricultural applications of studied biosolids.

3.2. Pharmaceuticals and personal care products

Fig. 2 presents the concentrations of targeted PPCPs in biosolids from six councils, categorised into four main classes: beta-blockers, antihistamines and antidepressants, antibiotics, and other PPCPs. The results demonstrated that the concentration of PPCPs varies significantly across the biosolids samples. The concentrations of certain antibiotics, antidepressants, and pharmaceuticals used for heart diseases were found to be comparatively high among other PPCPs in biosolids. In the category of beta-blockers, BS4 showed the maximum concentration of atenolol

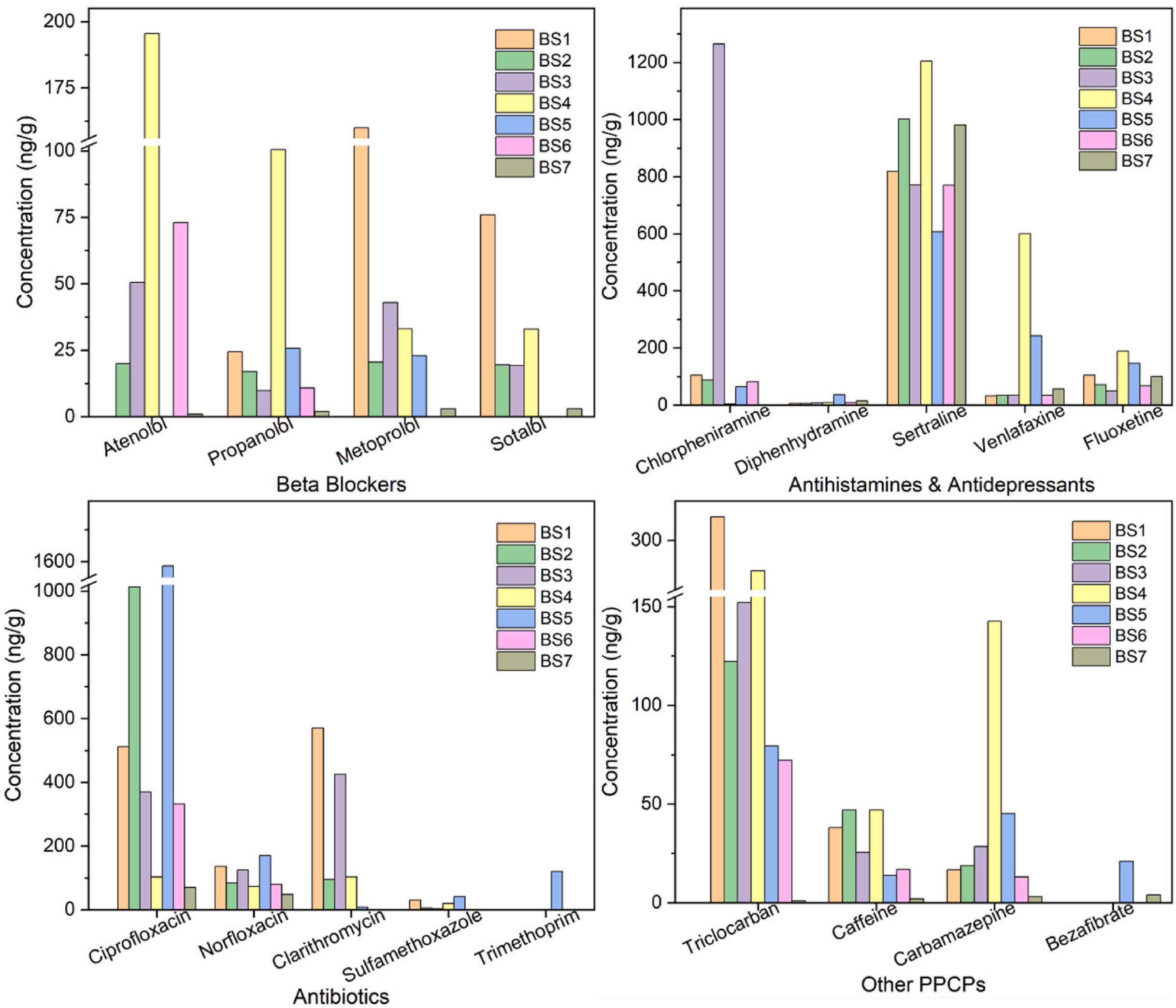

Fig. 2. Quantification of different classes of PPCPs in biosolids such as beta-blockers, antihistamines and antidepressants, antibiotics, and other PPCPs. Note: A minimum of three samples of biosolids were analysed, and their average concentrations were reported.

(196 ± 176 ng/g) and propranolol (101 ± 41.7 ng/g), while BS1 achieved the highest quantities of metoprolol (160 ng/g) and sotalol (76.0 ± 32.0 ng/g). The high concentration of metoprolol in BS1 can be attributed to the fact that STP receives wastewater from hospital catchments and domestic households. In contrast, BS7 showed the lowest concentrations of these beta-blockers; only propranolol was detected with a concentration of 21.3 ng/g, while others were below the detection limit. This is mainly because BS7 does not receive wastewater from hospital catchments and mainly depends on domestic and agricultural activities. The concentration of metoprolol found in this study was similar to Mercl et al. (2021) which also detected metoprolol in biosolids with a concentration of 160 ng/g. The concentration of chlorpheniramine was significantly higher in BS3 compared to other councils. This can be attributed to the fact that BS3-STPs serve comparatively a large population and subsequently, receive a high volume of human waste sludge-containing pharmaceutical products. Antidepressants like sertraline were found consistently high in all biosolids, BS4 showing the highest concentration of 1200 ± 1690 ng/g. A study by Mercl et al. (2021) from the Czech Republic reported 1040 ng/g of sertraline in biosolids, indicating their occurrence in biosolids worldwide.

Antibiotics like ciprofloxacin were considerably high in all biosolids except for BS4 and BS7; BS5 contained the highest concentration of 1590 ± 1200 ng/g. The results are similar to a previous study that also showed high concentrations of ciprofloxacin in biosolids in the range of 2560–3760 ng/g (Riva et al., 2021). However, the quantity of clarithromycin was high in BS1 (570 ng/g) and BS3 (425 ± 718 ng/g), while it was below the detection limit in BS6 and BS7. The high concentrations of antibiotics in BS1 and BS3 can mainly be attributed to the point that STPs serve a large population and receive wastewater heavily from industries (pharmaceutical manufacturing facilities and other industrial sites that use pharmaceuticals), hospitals (hospitals, clinics, and other healthcare facilities use pharmaceuticals extensively) and domestic households.

Antibiotics have also been dominant in wastewater and significant quantities have been reported in previous studies, which might lead to the development of antibiotic-resistant bacteria (ARB) and antibiotic-resistant genes (ARGs) in wastewater. Alternatively, the concentration of antibiotics may vary in wastewater depending on the season, winter or summer. Tahrani et al. (2017) investigated the concentrations of several antibiotics in wastewater in winter and summer and found interesting trends in their occurrence. For instance, in winter, 17.4 ng/mL of sulfamethoxazole was found in the effluent whereas its concentration in summer was found to be 4.10 ng/mL, however, the concentration of trimethoprim was found almost similar in both seasons (Tahrani et al., 2017).

Caffeine and carbamazepine were also noticed in nominal quantities (from 8.15 to 143 ng/g) in all biosolids. Caffeine can be found in various chemical compounds, including beverages like coffee, tea, energy drinks and medicines to improve mental alertness, while carbamazepine is an anticonvulsant medication used mainly in the treatment of epilepsy and neuropathic pain. Therefore, it can be predicted that caffeine and carbamazepine were primarily derived from human and animal waste, pharmaceuticals manufacturing or chemical production, and consumer beverages such as coffee, tea, and energy drinks. These products can enter wastewater and ultimately accumulate in biosolids. Carbamazepine is considered a highly stable chemical compound and not easily degraded by current STP processes, which leads to its presence in effluents and ultimately accumulation in biosolids (Sim et al., 2010). It requires additional advanced technologies to degrade carbamazepine in wastewater. For instance, Yao et al. demonstrated the application of an osmotic membrane bioreactor and achieved 88–94% removal efficiencies of carbamazepine (Yao et al., 2020). Significant concentrations of caffeine and carbamazepine in biosolids have been reported in previous studies. For instance, a study in Portugal showed the occurrence of 1140 ng/g of caffeine and 22.0 ng/g of carbamazepine in biosolids (Silva et al., 2021). In addition, a study in Italy reported a concentration of 23.7 ng/g of carbamazepine in biosolids (Riva et al., 2021). The presence of carbamazepine and caffeine compounds in biosolids indicates their stability, ability to sorb to solids, and the incompetency of treatment technologies to break them down in the biological treatment process, consequently accumulating in biosolids.

Triclocarban was also found in noteworthy concentrations in the biosolids from all councils. Triclocarban is an antibacterial agent commonly used in body wash, hand wash, soaps and lotions. BS1 contained the highest triclocarban concentration of 312 ± 609 ng/g, and BS7 showed the minimum concentration of 46.7 ± 27.8 ng/g. These results can be explained by the fact that BS1-STP receives wastewater mainly from domestic and hospital catchments, while BS7-STPs mainly receive wastewater from domestic and agricultural activities. Hence, the high concentration of triclocarban in biosolids from BS1 could be attributed to the primary wastewater sources. In literature, a similar concentration of BS1 has been reported by Mercl et al. (2021) which detected 323 ng/g of triclocarban in biosolids.

The primary sources of PPCPs in biosolids could be industrial wastewater, hospital and household-generated wastewater. Other factors that affect the sorption of PPCPs comprise the physicochemical properties of PPCPs, pH and the nature of dissolved organic matter (DOM) in biosolids (Langdon et al., 2010; Wang et al.). The major interactions that might help in the sorption of PPCPs on biosolids include hydrophobic interactions, hydrogen bonding and electrostatic interactions (Stevens-Garmon et al., 2011). The literature suggests that PPCPs with more positively charged functional groups such as atenolol and clozapine exhibit high sorption potential compared to PPCPs with neutral (like caffeine and acetaminophen) or negatively charged functional groups (like naproxen and ibuprofen) (Maoz & Chefetz, 2010; Stevens-Garmon et al., 2011). In addition, the treatment methods used for sewage sludge such as lime treatment has shown to generate a number of hydroxyl ions and increase biosolids pH, affecting the physicochemical properties of PPCPs and DOM and consequently, playing a decisive role in their interactions and mobility of PPCPs into the soluble phase (Nascimento et al., 2020). A study showed that lime treatment of biosolids increased the mobility of erythromycin and naproxen by 21.7% and 33.8%, respectively, while the mobility of other PPCPs studied (like carbamazepine, fluoxetine, gemfibrozil and triclosan) was suppressed, suggesting lime treatment can help to retain some PPCPs in biosolids but may also enhance the mobility of some PPCPs in biosolids soluble phases (Wang et al., 2018). In addition, variability in drug presence can also be influenced by network hydraulics (long detention times, hot sewers, septicity and low pH conditions etc.) and sewage treatment activity such as level of treatment, biological process, and type of filtration employed in the treatment plant (Nascimento et al., 2020; Ren et al., 2021).

3.3. Polycyclic musks

In this study, high concentrations of tonalide and galaxolide were found in the biosolids samples, indicating their ability to sorb to solids and be removed from the waste stream in the biosolids process. Fig. 3 shows the average concentration of PMs in biosolids from six regional councils. Among all the biosolids samples collected, BS4 exhibited the highest concentration of these compounds with a total of 3770 ± 1200 ng/g. All STPs receive wastewater from domestic catchments, therefore, concentrations of PMs in biosolids can be mainly attributed to household activities. The lowest concentration of PMs in BS7 can be ascribed to the small size of STPs that receives wastewater from a low number of dwellers in the town. In contrast, the highest concentration in BS4 biosolids can be primarily related to the inefficient treatment technologies to remove PMs since the size of STPs was medium-small and can be assumed to receive a low amount of wastewater from households. Generally, PMs show low biodegradability and are likely adsorbed on biosolids through adsorption mechanisms, such as hydrophobic interactions, electrostatic, hydrogen bond, and pore interception effects (Liu et al., 2021).

High concentrations of tonalide and galaxolide have been reported in sewage sludge in previous studies. For example, Košnář et al. (2021) reported 4320 ng/g of galaxolide and 1130 ng/g of tonalide in sewage sludge samples. Another study showed the concentration of galaxolide of 1290 μg/L and tonalide of 450 μg/L in the digested sludge (Carballa et al., 2007). Since polycyclic musks are widely used in personal care products and detergents, their major sources in biosolids are households, whereas industrial sources play an insignificant role in their discharge into the wastewater.

3.4. Per- and poly-fluoroalkyl substances

Fig. 4 shows the average concentrations of PFAS compounds detected in biosolids. The results revealed four categories of PFAS in biosolids that are perfluoroalkyl carboxylic acids (PFCA), perfluoroalkyl sulfonic acids (PFSA), perfluoroalkyl sulfonamido substances (PFSAS), and n:2 Fluorotelomer sulfonic acids (n:2 FTSAs). No PFAS compounds were found in BS7. In contrast, BS2 showed the presence of various PFAS compounds, including PFCA, PFSA and n:2 FTSAs. Major sources of PFAS in BS2 have been identified (which could be discharged from aqueous film-forming foam (AFFF)-contaminated sites, industrial discharges, and consumer products like non-stick cookware, stain-resistant carpets, and waterproof clothing) and are explained in the next section in detail. Similarly, BS3 and BS4 contained small quantities of all four categories of PFAS compounds. The major sources of PFAS in these biosolids (BS3 and BS4) have been linked with landfills and industrial discharges. PFAS-containing products that are disposed of in landfills and released from manufacturing facilities can leach into groundwater and ultimately enter STPs.

In the PFCA category, long-chain PFCA such as perfluorooctanoic acid (PFOA), perfluorodecanoic acid (PFDA), Perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), and Perfluoroundecanoic acid (PFUnDA) were found in noticeable quantities in BS2 and BS7 (4.20–13.0 ng/g), whereas other PFCA compounds were present in negligible concentrations in all biosolids (0.100–7.90 ng/g). These results support previous demonstrations that also showed high concentrations of PFOA in biosolids, in the range of 8.30–8.63 ng/g (Kundu et al., 2021; Moodie et al., 2021).

On the other hand, in the PFSA category, perfluorooctanesulfonic acid (PFOS) was found in biosolids from five councils in significant concentrations (4.60–253 ng/g), and perfluoroheptanesulfonic acid (PFHpS) was only observed in BS2. The concentration of PFOS was the highest in BS2 (253 ± 187 ng/g). As mentioned before, high concentrations of PFOS in BS2 can mainly be attributed to AFFF-contaminated sites and industrial discharges, while in other biosolids, additional sources of PFOS like landfills, consumer products (like carpets, textiles,

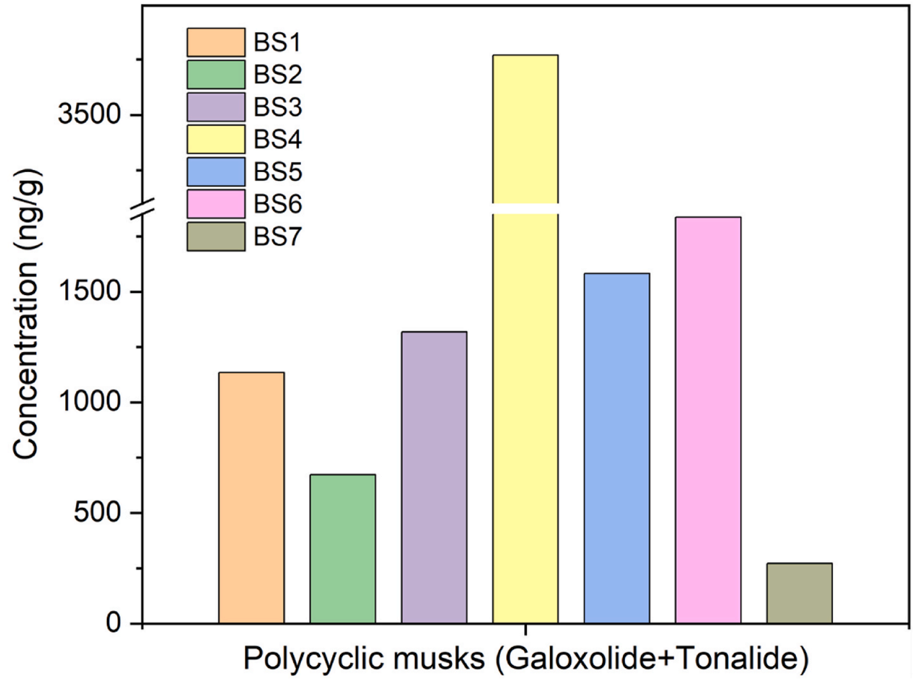

Fig. 3. Quantification of polycyclic musks (Galoxolide + Tonalide) in biosolids from northern councils of Queensland. Note: A minimum of three samples of biosolids were analysed, and their average concentrations were reported.

and leather products), contaminated biosolids reuse in agriculture or soil amendment can influence their concentration in biosolids.

Perfluoroalkyl sulfonamido (PFSAS) substances were found in low concentrations (<5.20 ng/g) in BS4 and BS3 biosolids samples. Some n:2 Fluorotelomer sulfonic acids (n:2 FTSA) were also observed in minor quantities in BS3 and BS4. However, a noticeable amount of 8.10 ± 9.76 ng/g of 6:2 FTSA was found in BS2. Table S9 compares our results for PFAS quantification with previous studies. The main purpose to compare our results with the literature was to show that these contaminants are ubiquitous and are frequently observed in biosolids. The most pervasive PFAS compounds, PFOA and PFOS, have been detected in noticeable concentrations in biosolids worldwide. For example, in Australia, Moodie et al. (2021) analysed PFAS contamination in biosolids and showed that PFOS had a maximum concentration of 23.0 ng/g in biosolids. Other PFAS present in high concentrations were PFDA (14.0 ng/g) and PFOA (8.30 ng/g).

The accumulation of PFAS in biosolids can be mainly attributed to the translocation of PFAS compounds from primary sources (such as industries involved in manufacturing and processing, leachate from landfills) into wastewater and the formation of intermediate PFAS compounds during the wastewater treatment process (Abunada et al., 2020; Schultz et al., 2006). The accumulation of PFAS in biosolids is further influenced by the physicochemical characteristics of PFAS and biosolids, as well as the interaction forces between them (Semerad et al., 2020). A PFAS contains a hydrophobic tail made up of carbon-fluorine atoms and a hydrophilic head with polar groups like carboxylate and sulfonate groups. The sorption capacity of PFAS on biosolids has been directly correlated to their hydrophobic nature (Cai et al., 2022). The hydrophobic tail is responsible for its sorption capacity on biosolids, and a longer hydrophobic tail increases the sorption capacity of PFAS on biosolids. Polar head groups impact the electrostatic interactions with chemical species of biosolids (Arvaniti et al., 2014). PFAS compounds with sulphonate group are more hydrophobic compared with PFAS with carboxylate groups (Semblante et al., 2015). Moreover, PFAS having electron donating groups like hydroxyl and amine groups possess high biodegradability and thus show less accumulation in biosolids (Semblante et al., 2015). In addition, characteristics of biosolids such as pH, and the presence of metals and minerals play a pivotal role in the adsorption of PFAS. Low pH provides an overall positive surface charge that is conducive for cationic species to interact with anionic species of PFAS, and divalent cations such as Mg^{2+} and Ca^{2+} reduce electrostatic repulsions by acting as ion bridges between anionic groups of PFAS and negatively charged groups of biosolids (Ebrahimi et al., 2021). Therefore, high concentrations of long-chain PFAS found in our study and previous studies can be partially credited to the high sorption capacity achieved by the long hydrophobic tail and reduction in electrostatic repulsions by hydrophilic head groups.

Overall, the majority of PFAS compounds were found in low quantities in biosolids samples (except for BS2). Recently, the Government of Australia released a draft for PFAS National Environmental Management Plan 3.0 which suggests PFAS limit value for biosolids application. Considering the minimum margin for safety, the draft suggests concentrations of PFOS + PFHxS and PFOA should not be over 6.20 and 25.0 ng/g, respectively for biosolids threshold restricted use, while the concentrations of 0.220 and 1.00 ng/g are suggested for the unrestricted use (PFAS NEMP 3.0). In our study, we found two samples, BS4 contains concentrations of PFOS + PFHxS and PFOA below the restricted use limits, while BS7 did not show any PFAS and thus can be considered for unrestricted use. Whereas all other biosolids samples contained PFAS concentrations above the restricted and unrestricted use limits.

4. A case study of council A

Biosolids from STP1 (named BS1) and STP2 (named BS2) showed the presence of contaminants with emerging concern; however, the most striking difference was in the quantities of PFAS (one-way ANOVA). Where in STP1, the mean concentration of PFOS was 29.3 ng/g, it was 253 ng/g in biosolids from STP2. In addition, other PFAS such as PFPeA, PFHxA, PFOA, PFNA PFBS, PFHxS, PFHpS were also present in minor quantities (0.300–7.67 ng/g) in biosolids from STP2, which otherwise were absent in STP1 biosolids. There could be a few reasons for the occurrence of significant PFAS in STP2 biosolids. STP2 receives heavy industrial and domestic wastewater from suburbs like Garbutt, Mount Louisa, and Cranbrook. Garbutt suburb in Townsville contains a RAAF

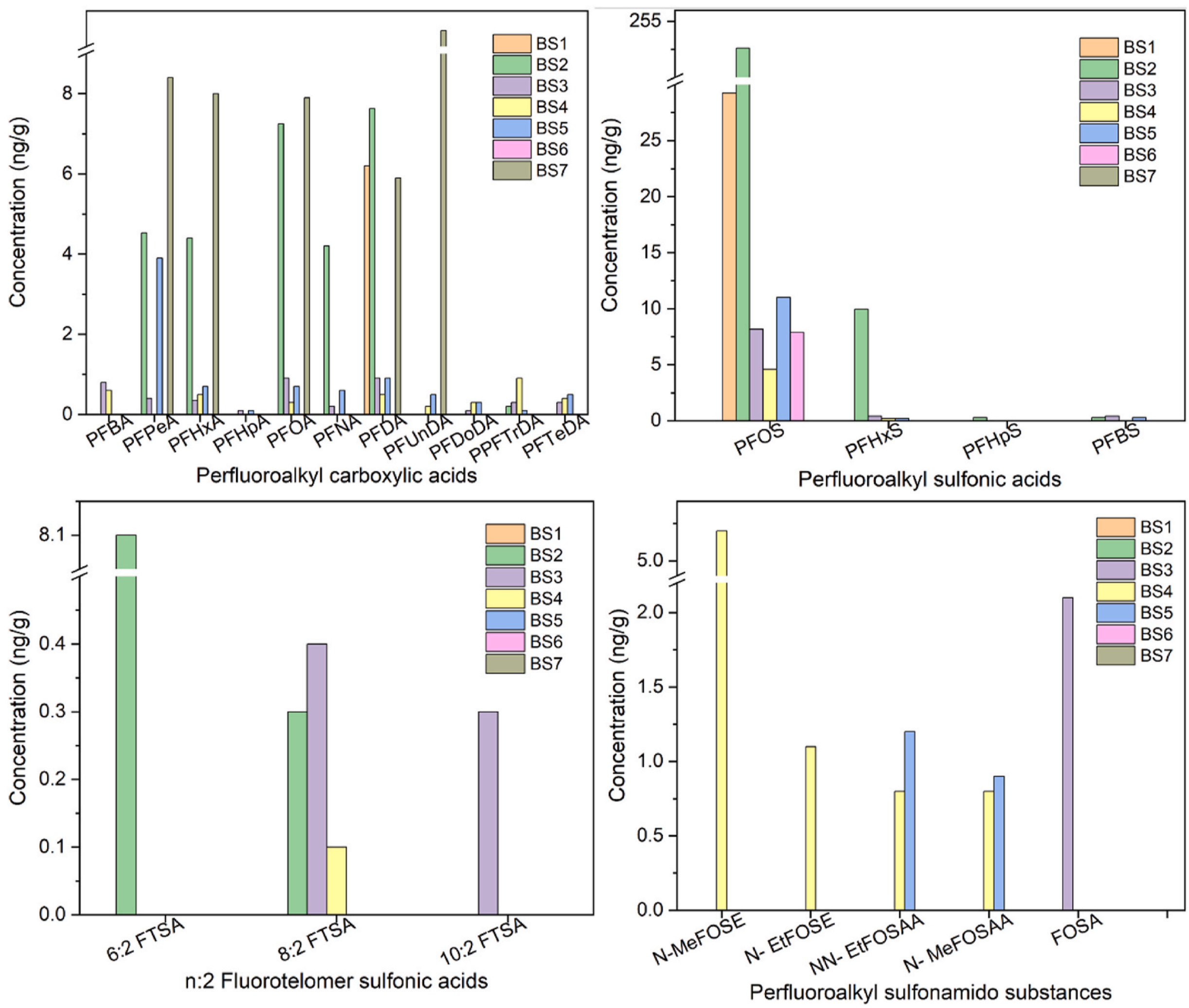

Fig. 4. PFAS compounds detected in biosolids, such as perfluoroalkyl carboxylic acids, perfluoroalkyl sulfonic acids, n:2 fluorotelomer sulfonic acids, and perfluoroalkyl sulfonamido substances. Note: A minimum of three samples of biosolids were analysed, and their average concentrations are reported. For abbreviations, please check Table S5 in the SI file.

base. The Department of Defence (Australian Government) have a longstanding and publicly acknowledged PFAS contamination legacy issue associated with firefighting foams. In 2018, a thorough investigation was carried out by the Department of Defence to examine the surrounding area of RAAF, and the results confirmed PFAS contamination in soil and groundwater (Harris, 2018). The primary PFAS detected was PFOS, and its quantity in soil samples was reported up to 73.2 mg/kg, and in groundwater, up to 2310 ng/L of PFOS and 4050 ng/L of PFHxS were reported (Harris, 2018). The report further suggested that PFAS contamination in soil and groundwater was linked to historical fire training, equipment testing and sparging of fire truck tanks, accidental discharges and spills from AFFF-containing fire deluge systems in hangars, and historical production of foam (Harris, 2018). Garbutt and Mount Louisa also accommodate industries that are involved in the production of lubricants, hydraulic oils, automotive, paints, and safety equipment. These types of products are known to contain PFAS compounds and could be one of the reasons for high concentrations of PFOS in STP2 biosolids. In addition to this, the majority of automobile repair centres and wreckers are present in Garbutt and Mount Louisa. These automobile repair centres utilize heavy amounts of grease, lubricants and automobile oils that might be another potential source of PFAS. Wastes from construction industry materials such as paint, adhesives, sealants, flooring materials and roof coating also contribute to PFAS contamination, which might reach the STP and accumulate in biosolids.

Compared to STP2, biosolids from STP1 showed higher concentrations of the majority of PPCPs analysed in this study except for a few PPCPs like ciprofloxacin and sertraline. For example, the concentrations of clarithromycin, fluoxetine, metoprolol, norfloxacin, sulfamethoxazole, sotalol, and triclocarban in STP1 biosolids were significantly higher than STP2 biosolids (suggested by one-way ANOVA). This could be mainly because, in addition to domestic wastewater, STP1 also receives wastewater from hospitals like Townsville University Hospital (Douglas), Mater Private Hospital Townsville (Hyde Park and Pimlico), and Weststate Private Hospital (West End), which might contribute to additional concentrations of PPCPs since medical centres utilize these drugs more frequently. STP2 applies aerobic digestion for sludge treatment while STP1 applies two steps of anaerobic digestion; however, noticeable quantities in biosolids suggest inefficient capabilities to remove PPCPs entirely through current biological digestion methods.

For HMs, both STPs showed a similar trend and high concentrations for the majority of HMs were found in biosolids, no significant differences were observed as suggested by one-way ANOVA. The high concentration of HMs in biosolids can mainly be attributed to their primary sources. For example, zinc can be derived from zinc oxide, automobiles, anti-corrosion coatings, die castings, construction materials, fertilizers, pharmaceuticals, and cosmetics. Secondly, these metals can also be formed from their primary products (for example, zinc oxide is commonly used in sunscreens and shampoos) during the wastewater treatment process (Mitroshkov et al., 2019). Since STP2 receives industrial wastewater, various heavy metals released from manufacturing processes can end up in wastewater and reach the STP and finally in biosolids. On the other hand, high HM contamination in STP1 can be ascribed to the formation of their primary household products and pharmaceutical products.

5. Risk assessment of emerging contaminants

Risk assessment for all contaminants found in biosolids was estimated by calculating Risk Quotient by dividing the exposure value of the contaminant by the Toxicity Reference Value suggested by the Australian guidelines. The results revealed that Risk Quotient was >1 for HMs in all biosolids samples, indicating significant risks for human health and the environment. The presence of high concentrations of HMs in biosolids may increase their concentrations in the soil and could be detrimental to crops when biosolids are used for agricultural applications. Further, heavy metals in soil have the potential to enter the food chain through plants (Latosińska et al., 2021). The exposure of HMs to humans could be from agricultural products or drinking water and may pose adverse health effects. For example, high concentrations of copper and zinc can cause mental diseases such as Alzheimer's and sideroblastic anemia, respectively (Hosseini Koupaie & Eskicioglu, 2015). Cadmium can cause kidney dysfunction, bone fracture, hypertension, and damage to the lungs and liver and is also carcinogenic (Chaharlang et al., 2012). Arsenic and lead can cause damage to the brain and the nervous system. They can also accumulate in soils and plants, leading to contamination of the food chain. Whereas nickel, magnesium and selenium can cause respiratory problems and other health issues (Hosseini Koupaie & Eskicioglu, 2015).

For PPCPs, interesting trends were observed for Risk Quotient values. For example, Risk Quotient values for ciprofloxacin, fluoxetine, norfloxacin, sertraline, and triclocarban in all biosolids samples were >1, suggesting considerable risks for human health and the environment. In addition, the Risk Quotient values for carbamazepine (for BS4 and BS5), chlorpheniramine (for BS3), clarithromycin (for BS1 and BS3), trimethoprim (for BS5) and venlafaxine (for BS4 and BS5) were also found >1, suggesting substantial risks for human health and environment, while the Risk Quotient values of these PPCPs in other biosolids samples were <1. The presence of high concentrations of antibiotics, such as ciprofloxacin, norfloxacin in biosolids may increase their concentrations in the soil and can promote the generation of antibiotic resistance genes (ARGs) to develop in soil, subsequently could have detrimental effects on human health (Kimbell et al., 2018). For all other PPCPs including acetaminophen, atenolol, bezafibrate, caffeine, diphenhydramine, metoprolol, propranolol, sotalol, and sulfamethoxazole, Risk Quotient values were <1, which indicates no potential risks for human health and environment.

For PMs (galaxolide and tonalide), Risk Quotient values for all biosolids samples were >1, suggesting high potential risks for human health and the environment. Galaxolide and tonalide are well known to possess alarming environmental concerns in aquatic and terrestrial environments. They have shown neurotoxic and endocrine-disrupting properties because they can mimic natural hormones and have the potential to interfere with neurotransmitter pathways (Ehiguese et al., 2021; Yamauchi et al., 2008). Galaxolide and tonalide can induce irreparable deoxyribonucleic acid (DNA) damage and oxidative stress in aquatic organisms (Parolini et al., 2015).

Risk Quotient values of PFOS and PFHxS for all biosolids samples, PFOA (for BS2 and BS7), and PFNA (for BS2 and BS5) were >1, suggesting significant risks for human health and the environment. On the other hand, Risk Quotient values of PFOA (for BS3, BS4 and BS5) and PFNA (for BS3) were <1, indicating no potential risks for human health and the environment. PFOS and PFOA have shown a considerable impact on the growth and reproduction of aquatic organisms (Karnjanapiboonwong et al., 2018; Marziali et al., 2019). There is a high probability that PFAS compounds presented in biosolids can leach into the soil and ultimately bio-accumulate into terrestrial organisms and plants (Marziali et al., 2019; Semerad et al., 2020). PFAS exposure is often linked to human health problems. These compounds generally enter the human body through food such as fish and crustaceans, soy products and drinking water (Pizzurro et al., 2019). Traces of PFAS compounds have been found in human blood, and exposure to high concentrations has shown adverse effects on human health such as carcinogenicity, cell membrane disruption, developmental toxicity, liver cell hypertrophy, changes in hormone levels, and decreased reproductive outcomes (Mhadhbi et al., 2012).

6. Conclusion

This study identified and quantified selected emerging pollutants like PPCPs, PFAS, HMs, PMs in biosolids from sewage treatment plants located in North Queensland, Australia. The results revealed that the majority of biosolids contained high levels of HMs like zinc, manganese, copper and nickel; PPCPs such as ciprofloxacin, caffeine, and sertraline; PFAS compounds like PFOS and PFOA. Among all the biosolids, BS4 contained high concentrations of HMs, while BS2 showed concerning concentrations of PFOS in biosolids. Ciprofloxacin quantities were relatively high in BS5, whereas BS4 contained the highest amount of sertraline (1200 ng/g) and PMs (3770 ng/g). The presence of these ECs is likely symptomatic of the types and hydraulics of wastewater networks connected to those STPs, the presence/proportion of the industry, agriculture, domestic and commercial contributions to sewer and, the type of technology employed to treat the wastewater at the STP. Risk assessment analysis suggests that HMs in all biosolids, some PPCPs like ciprofloxacin, norfloxacin, sertraline and PFAS such as PFOS and PFHxS possess a significant risk to human health and the environment. The removal of ECs before the application of biosolids to land through various emerging technologies such as gasification and pyrolysis could be considered environmental best practices and are certainly ahead of current legislative requirements currently in place in Queensland.

Authorship statement

All authors read the manuscript and approved it for publication in the journal **Environmental Pollution**. Author's contribution for this manuscript is: **Conception and design of study:** Elsa Antunes, Ravinder Kumar, and Anna Whelan. **Acquisition of data:** Elsa Antunes and Ravinder Kumar. **Analysis and/or interpretation of data:** Elsa Antunes and Ravinder Kumar. **Drafting the manuscript:** Ravinder Kumar. **Revising the manuscript critically for important intellectual content:** Elsa Antunes, Anna Whelan, Patrick Cannon, Madoc Sheehan, and Louise Reeves.

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.

Data availability

Data will be made available on request.

Acknowledgement

The authors thank the Queensland Water Regional Alliance Program, Queensland Water, the regional councils of Northern Queensland, and the Queensland Government, Australia for funding this research.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2023.121786.

References

Abunada, Z., Alazaiza, M.Y.D., Bashir, M.J.K., 2020. An overview of per- and polyfluoroalkyl substances (PFAS) in the environment: source, fate, risk and regulations. Water 12, 3590.

Agoro, M.A., Adeniji, A.O., Adefisoye, M.A., Okoh, O.O., 2020. Heavy metals in wastewater and sewage sludge from selected municipal treatment plants in eastern cape province, South Africa. Water 12, 2746.

ANZBP, 2021. Australian Biosolids Statistics.

Arvaniti, O.S., Andersen, H.R., Thomaidis, N.S., Stasinakis, A.S., 2014. Sorption of Perfluorinated Compounds onto different types of sewage sludge and assessment of its importance during wastewater treatment. Chemosphere 111, 405–411.

Cai, W., Navarro, D.A., Du, J., Ying, G., Yang, B., McLaughlin, M.J., Kookana, R.S., 2022. Increasing ionic strength and valency of cations enhance sorption through hydrophobic interactions of PFAS with soil surfaces. Sci. Total Environ. 817, 152975.

Carballa, M., Omil, F., Ternes, T., Lema, J.M., 2007. Fate of pharmaceutical and personal care products (PPCPs) during anaerobic digestion of sewage sludge. Water Res. 41, 2139–2150.

Chaharlang, B.H., Bakhtiari, A.R., Yavari, V., 2012. Assessment of cadmium, copper, lead and zinc contamination using oysters (Saccostrea cucullata) as biomonitors on the coast of the Persian gulf, Iran. Bull. Environ. Contam. Toxicol. 88, 956–961.

Clarke, B.O., Porter, N.A., Symons, R.K., Marriott, P.J., Stevenson, G.J., Blackbeard, J.R., 2010. Investigating the distribution of polybrominated diphenyl ethers through an Australian wastewater treatment plant. Sci. Total Environ. 408, 1604–1611.

Clarke, B.O., Smith, S.R., 2011. Review of 'emerging' organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids. Environ. Int. 37, 226–247.

Coggan, T.L., Moodie, D., Kolobaric, A., Szabo, D., Shimeta, J., Crosbie, N.D., Lee, E., Fernandes, M., Clarke, B.O., 2019. An investigation into per- and polyfluoroalkyl substances (PFAS) in nineteen Australian wastewater treatment plants (WWTPs). Heliyon 5, e02316.

Darvodelsky, P., 2012. Biosolids Snapshot, 01/06/2012 Ed, pp. 1–38.

Donner, E., Ryan, C.G., Howard, D.L., Zarcinas, B., Scheckel, K.G., McGrath, S.P., de Jonge, M.D., Paterson, D., Naidu, R., Lombi, E., 2012. A multi-technique investigation of copper and zinc distribution, speciation and potential bioavailability in biosolids. Environ. Pollut. 166, 57–64.

Ebrahimi, F., Lewis, A.J., Sales, C.M., Suri, R., McKenzie, E.R., 2021. Linking PFAS partitioning behavior in sewage solids to the solid characteristics, solution chemistry, and treatment processes. Chemosphere 271, 129530.

Ehiguese, F.O., Rodgers, M.L., Araujo, C.V.M., Griffitt, R.J., Martin-Diaz, M.L., 2021. Galaxolide and tonalide modulate neuroendocrine activity in marine species from two taxonomic groups. Environ. Res. 196, 110960.

Harris, D., 2018. RAAF Base Townsville Detailed Site Investigation. PFAS, Brisbane.

Hosseini Koupaie, E., Eskicioglu, C., 2015. Health risk assessment of heavy metals through the consumption of food crops fertilized by biosolids: a probabilistic-based analysis. J. Hazard Mater. 300, 855–865.

Johnson, G.R., 2022. PFAS in soil and groundwater following historical land application of biosolids. Water Res. 211, 118035.

Karnjanapiboonwong, A., Deb, S.K., Subbiah, S., Wang, D., Anderson, T.A., 2018. Perfluoroalkylsulfonic and carboxylic acids in earthworms (Eisenia fetida): accumulation and effects results from spiked soils at PFAS concentrations bracketing environmental relevance. Chemosphere 199, 168–173.

Kimbell, L.K., Kappell, A.D., McNamara, P.J., 2018. Effect of pyrolysis on the removal of antibiotic resistance genes and class I integrons from municipal wastewater biosolids. Environ. Sci. Water Res. Technol. 4, 1807–1818.

Kimbrough, D.E., 2009. Source identification of copper, lead, nickel, and zinc loading in wastewater reclamation plant influents from corrosion of brass in plumbing fixtures. Environ. Pollut. 157, 1310–1316.

Košnář, Z., Mercl, F., Chane, A.D., Pierdonà, L., Míchal, P., Tlustoš, P., 2021. Occurrence of synthetic polycyclic and nitro musk compounds in sewage sludge from municipal wastewater treatment plants. Sci. Total Environ. 801, 149777.

Kumar, R., Dada, T.K., Whelan, A., Cannon, P., Sheehan, M., Reeves, L., Antunes, E., 2023. Microbial and thermal treatment techniques for degradation of PFAS in biosolids: a focus on degradation mechanisms and pathways. J. Hazard Mater. 452, 131212.

Kumar, R., Vuppaladadiyam, A.K., Antunes, E., Whelan, A., Fearon, R., Sheehan, M., Reeves, L., 2022. Emerging contaminants in biosolids: presence, fate and analytical techniques. Emerg. Contam. 8, 162–194.

Kundu, S., Patel, S., Halder, P., Patel, T., Hedayati Marzbali, M., Pramanik, B.K., Paz-Ferreiro, J., de Figueiredo, C.C., Bergmann, D., Surapaneni, A., Megharaj, M., Shah, K., 2021. Removal of PFASs from biosolids using a semi-pilot scale pyrolysis reactor and the application of biosolids derived biochar for the removal of PFASs from contaminated water. Environ. Sci. Water Res. Technol. 7, 638–649.

Langdon, K., Warne, M., Kookana, R., 2010. Aquatic hazard assessment for pharmaceuticals, personal care products, and endocrine-disrupting compounds from biosolids-amended land. Integrated Environ. Assess. Manag. 6, 663–676.

Latosińska, J., Kowalik, R., Gawdzik, J., 2021. Risk assessment of soil contamination with heavy metals from municipal sewage sludge. Appl. Sci. 11.

Liu, J., Zhang, W., Zhou, Q., Zhou, Q., Zhang, Y., Zhu, L., 2021. Polycyclic musks in the environment: a review of their concentrations and distribution, ecological effects and behavior, current concerns and future prospects. Crit. Rev. Environ. Sci. 51, 323–377.

Maoz, A., Chefetz, B., 2010. Sorption of the pharmaceuticals carbamazepine and naproxen to dissolved organic matter: role of structural fractions. Water Res. 44, 981–989.

Martínez-Alcalá, I., Guillén-Navarro, J.M., Lahora, A., 2021. Occurrence and fate of pharmaceuticals in a wastewater treatment plant from southeast of Spain and risk assessment. J. Environ. Manag. 279, 111565.

Marziali, L., Rosignoli, F., Valsecchi, S., Polesello, S., Stefani, F., 2019. Effects of perfluoralkyl substances on a multigenerational scale: a case study with Chironomus riparius (Diptera, chironomidae). Environ. Toxicol. Chem. 38, 988–999.

Mercl, F., Kosnar, Z., Marsik, P., Vojtisek, M., Dusek, J., Szakova, J., Tlustos, P., 2021. Pyrolysis of biosolids as an effective tool to reduce the uptake of pharmaceuticals by plants. J. Hazard Mater. 405, 124278.

Mhadhbi, L., Rial, D., Perez, S., Beiras, R., 2012. Ecological risk assessment of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in marine environment using Isochrysis galbana, Paracentrotus lividus, Siriella armata and Psetta maxima. J. Environ. Monit. 14, 1375–1382.

Mitroshkov, A.V., Zhong, L., Thomas, L.M.P., 2019. Analysis of Perfluorinated, Pharmaceutical, Personal Care Compounds and Heavy Metals in Waste Water Sludge Using GC-MS/MS and Multicollector ICP-MS, 1494304. PNNL-28216.

Moodie, D., Coggan, T., Berry, K., Kolobaric, A., Fernandes, M., Lee, E., Reichman, S., Nugegoda, D., Clarke, B.O., 2021. Legacy and emerging per- and polyfluoroalkyl substances (PFASs) in Australian biosolids. Chemosphere 270, 129143.

Nascimento, A.L., de Souza, A.J., Oliveira, F.C., Coscione, A.R., Viana, D.G., Regitano, J. B., 2020. Chemical attributes of sewage sludges: relationships to sources and treatments, and implications for sludge usage in agriculture. J. Clean. Prod. 258, 120746.

Navarro, I., de la Torre, A., Sanz, P., Pro, J., Carbonell, G., Martínez, M.d.l.Á., 2016. Bioaccumulation of emerging organic compounds (perfluoroalkyl substances and halogenated flame retardants) by earthworm in biosolid amended soils. Environ. Res. 149, 32–39.

Parolini, M., Magni, S., Traversi, I., Villa, S., Finizio, A., Binelli, A., 2015. Environmentally relevant concentrations of galaxolide (HHCB) and tonalide (AHTN) induced oxidative and genetic damage in Dreissena polymorpha. J. Hazard Mater. 285, 1–10.

Petrie, B., Barden, R., Kasprzyk-Hordern, B., 2015. A review on emerging contaminants in wastewaters and the environment: current knowledge, understudied areas and recommendations for future monitoring. Water Res. 72, 3–27.

Pizzurro, D.M., Seeley, M., Kerper, L.E., Beck, B.D., 2019. Interspecies differences in perfluoroalkyl substances (PFAS) toxicokinetics and application to health-based criteria. Regul. Toxicol. Pharmacol. 106, 239–250.

Ren, B., Shi, X., Jin, X., Wang, X.C., Jin, P., 2021. Comprehensive evaluation of pharmaceuticals and personal care products (PPCPs) in urban sewers: degradation, intermediate products and environmental risk. Chem. Eng. J. 404.

Riva, F., Zuccato, E., Pacciani, C., Colombo, A., Castiglioni, S., 2021. A multi-residue analytical method for extraction and analysis of pharmaceuticals and other selected emerging contaminants in sewage sludge. Anal. Methods 13, 526–535.

Schultz, M.M., Higgins, C.P., Huset, C.A., Luthy, R.G., Barofsky, D.F., Field, J.A., 2006. Fluorochemical mass flows in a municipal wastewater treatment facility. Environ. Sci. Technol. 40, 7350–7357.

Semblante, G.U., Hai, F.I., Huang, X., Ball, A.S., Price, W.E., Nghiem, L.D., 2015. Trace organic contaminants in biosolids: impact of conventional wastewater and sludge processing technologies and emerging alternatives. J. Hazard Mater. 300, 1–17.

Semerad, J., Hatasova, N., Grasserova, A., Cerna, T., Filipova, A., Hanc, A., Innemanova, P., Pivokonsky, M., Cajthaml, T., 2020. Screening for 32 per- and polyfluoroalkyl substances (PFAS) including GenX in sludges from 43 WWTPs located in the Czech Republic - evaluation of potential accumulation in vegetables after application of biosolids. Chemosphere 261, 128018.

Silva, S., Cardoso, V.V., Duarte, L., Carneiro, R.N., Almeida, C.M.M., 2021. Characterization of five Portuguese wastewater treatment plants: removal efficiency of pharmaceutical active compounds through conventional treatment processes and environmental risk. Appl. Sci. 11, 7388.

Sim, W.-J., Lee, J.-W., Oh, J.-E., 2010. Occurrence and fate of pharmaceuticals in wastewater treatment plants and rivers in Korea. Environ. Pollut. 158, 1938–1947.

Stevens-Garmon, J., Drewes, J.E., Khan, S.J., McDonald, J.A., Dickenson, E.R.V., 2011. Sorption of emerging trace organic compounds onto wastewater sludge solids. Water Res. 45, 3417–3426.

Tahrani, L., Van Loco, J., Anthonissen, R., Verschaeve, L., Ben Mansour, H., Reyns, T., 2017. Identification and risk assessment of human and veterinary antibiotics in the wastewater treatment plants and the adjacent sea in Tunisia. Water Sci. Technol. 76, 3000–3021.

Wang, K., Larkin, T., Singhal, N., Song, Y., 2018. Mobility of pharmaceutical and personal care products in lime amended wastewater biosolids. Sci. Total Environ. 624, 1263–1273.

Yamauchi, R., Ishibashi, H., Hirano, M., Mori, T., Kim, J.W., Arizono, K., 2008. Effects of synthetic polycyclic musks on estrogen receptor, vitellogenin, pregnane X receptor, and cytochrome P450 3A gene expression in the livers of male medaka (*Oryzias latipes*). Aquat. Toxicol. 90, 261–268.

Yao, M., Duan, L., Wei, J., Qian, F., Hermanowicz, S.W., 2020. Carbamazepine removal from wastewater and the degradation mechanism in a submerged forward osmotic membrane bioreactor. Bioresour. Technol. 314, 123732.