Plastics contamination in archived biosolids from 1950 to 2016

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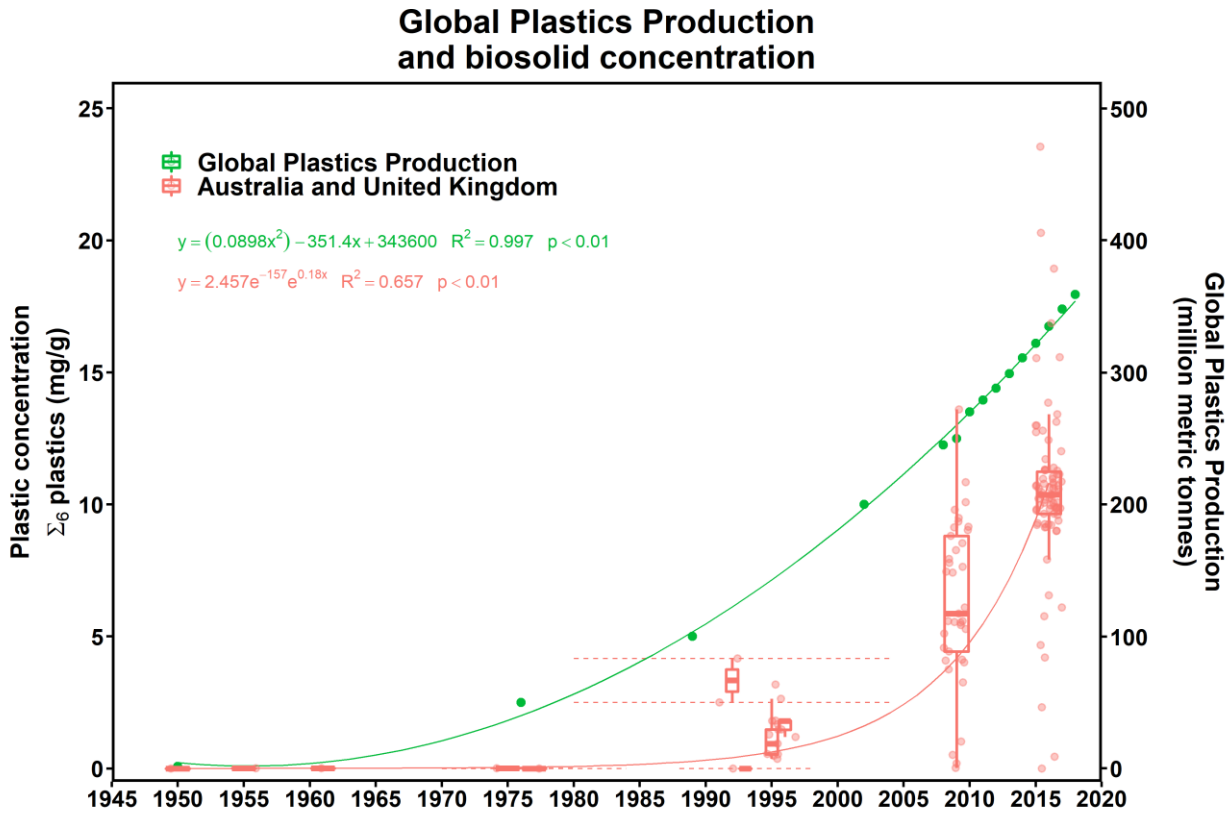
HIGHLIGHTS

- Archived biosolids from Australia and UK from 1950 to 2016 analyzed for 7 plastics
- Increasing concentrations over time of PP, PS, PET, PMMA, PVC and PE
- Prior to the 1990s, leakage of plastics into biosolids was limited except for PS
- Leakage from 1990s driven by increased production and consumption of PE, PET, PVC
- Concentrations of plastics closely correlate with production and consumption

46 GRAPHICAL ABSTRACT



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ABSTRACT

Plastics are ubiquitous contaminants that leak into the environment from multiple pathways including the use of treated sewage sludge (biosolids). Seven common plastics (polymers) were quantified in the solid fraction of archived biosolids samples from Australia and the United Kingdom from between 1950 and 2016. Six plastics were detected, with increasing concentrations observed over time for each plastic. Biosolids plastic concentrations correlated with plastic production estimates, implying a potential link between plastics production, consumption and leakage into the environment. Prior to the 1990s, the leakage of plastics into biosolids was limited except for polystyrene. Increased leakage was observed from the 1990s onwards; potentially driven by increased consumption of polyethylene, polyethylene terephthalate and polyvinyl chloride. We show that looking back in time along specific plastic pollution pathways may help unravel the potential sources of plastics leakage into the environment and provide quantitative evidence to support the development of source control interventions or regulations.

KEYWORDS: Plastics; Sewage sludge; Biosolids; WWTPs; Plastic production; Quantification; Pyr-GC/MS

1. INTRODUCTION

There has been a sustained increase in plastics production over the past 70 years, increasing from 1.5 million metric tons (Mt) in the 1950s to 359 million Mt in 2018 (PlasticsEurope. 2019, Statista. 2020). The availability of plastics-containing products has grown, with the commercial drivers being durability, cost-efficiency, versatility, elasticity, resilience and longevity (Brahney et al. 2020, MacArthur 2017). Plastics are used for many applications within a wide range of sectors including; building and construction, transport, packaging, electronics, automotive manufacture or agriculture (PlasticsEurope 2018, PlasticsEurope. 2019, Wang et al. 2019). Whilst the societal benefits from using plastics are extensive and in inexhaustible applications (Andrady and Neal 2009), plastics as a commodity have been the subject of growing environmental concern (Cole et al. 2011). Contamination of the environment with persistent plastics of all sizes (Li et al. 2020, Ribeiro et al. 2019, Rochman and Hoellein 2020) is recognized as one of the most widespread and long-lasting anthropogenic changes to the Earth´s biosphere. The presence of plastic particles has been reported in most environments including the marine (Andrady 2011, Cole et al. 2011, Gigault et al. 2016), freshwaters, such as lakes and rivers (Eerkes-Medrano et al. 2015), sediments (Jiang et al. 2018, Nuelle et al. 2014), soils (Chae and An 2018, Liu et al. 2018, Okoffo et al. 2021), dust and air (Allen et al. 2019, Gasperi et al. 2018, O'Brien et al. 2021).

Previous studies have shown that biosolids from the treatment of sewage are a sink for plastics and are a pathway of plastics release into the environment when applied to land (Corradini et al. 2019, Nizzetto et al. 2016a, Okoffo et al. 2020a, Okoffo et al. 2020b). As global plastics production and consumption continues to increase, without intervention, the release of plastics to wastewater treatment plants (WWTPs) will also likely increase; hence more plastic

will enter the environment via this pathway (Corradini et al. 2019, Okoffo et al. 2020b, Rillig 2020). Estimates suggest that annually 63,000–430,000 metric tons (Mt) and 44,000–300,000 Mt of plastics may be added to farmlands in Europe and North America, respectively, through the application of biosolids (Nizzetto et al. 2016a, Nizzetto et al. 2016b). Similarly, it is estimated that about 4,700 Mt of plastics are released into the Australian environment through biosolids end-use each year, equating to a release of approximately 200 g/person/year (Okoffo et al. 2020b).

There is potential for plastics released to land from biosolids end-use to persist and accumulate in soils due to slow degradation and microbial assimilation (Corradini et al. 2019, Rolsky et al. 2020). From here plastics may transfer to other environments such as rivers, lakes and oceans (Lusher et al. 2017, Nizzetto et al. 2016a). Plastic particles in soils have been shown to affect the health of soil organisms (Huerta Lwanga et al. 2016, Ju et al. 2019, Judy et al. 2019, Rodríguez-Seijo et al. 2018, Rodriguez-Seijo et al. 2017). Similarly, they can alter soil properties, impacting the growth and development of plants by negatively affecting the bulk density of soils, soil structure, nutrition contents, microbial activity and the water holding capacity (Bosker et al. 2019, de Souza Machado et al. 2019, de Souza Machado et al. 2018, Liu et al. 2017, Qi et al. 2018).

Whilst scientific research on plastics pollution is rapidly developing, quantitative measurement of plastics in biosolids has been extremely challenging, and as a result, only a few studies have successfully extracted and quantified plastics in biosolids (Campo et al. 2019, Edo et al. 2019, Ziajahromi et al. 2021). Using a number of different measurement techniques, including microscopy; Raman microscopy and Fourier Transform Infrared Spectrometry (FTIR), previous studies have provided particle count, size, shape, color and partly polymer type-related data

in biosolids which may not reflect the total mass concentration of plastics. In view of the limited mass-based concentrations data, and the recent concerns regarding the increasing consumption and release of plastics through biosolids, there is a need to fully understand the release pathway of plastics into the environment on a mass concentration basis. Such data are also required to understand the plastics cycle, from initial leakage from human activities into wastewater and subsequently into biosolids during treatment that are applied to soil (Narain 2018, Nizzetto et al. 2016a, Nizzetto et al. 2016b, Rillig and Lehmann 2020, WWT. 2018). How the contamination of biosolids with plastics has changed with time in the context of increasing global plastic production and consumption is currently unknown.

The aim of this study was to quantify the concentration of plastics in biosolids from between 1950 and 2016 to evaluate the historical trend in plastics release and evaluate the relationship between the concentration of plastics in biosolids and global plastic production and consumption. This was achieved through the analysis of archived and contemporary biosolids samples sourced from the United Kingdom (UK) and Australia from the 1950s to 2016 (Donner et al. 2015, Okoffo et al. 2020b). Polystyrene, polycarbonate, poly-(methyl methacrylate), polypropylene, polyethylene terephthalate, polyethylene and polyvinyl chloride plastics were quantified in the historical biosolids samples; constituting >70% of the plastics consumed worldwide (PlasticsEurope. 2019). The results of this study provide the first mass concentration-based quantitative data of plastics contamination in biosolids over time, thereby increasing our understanding of historical plastics leakage into wastewater.

2. MATERIALS AND METHODS

2.1 Materials and chemicals

Analytical standards of polyvinyl chloride, polystyrene and poly-(methyl methacrylate) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and low density polyethylene (referred to as Polyethylene) from Thermo Fischer Scientific. Polycarbonate and polyethylene terephthalate were provided by the Norwegian Institute for Water Research (NIVA, Oslo, Norway) and polypropylene was donated by a plastic manufacturer from Melbourne, Australia (LyondellBasell, VIC). Deuterated polystyrene (PS-d5) and polyethylene (PE-d4) were purchased from Polymer Source, Inc. (Quebec, Canada). Liquid chromatography grade acetone and liquid chromatography grade dichloromethane (DCM) were purchased from Merck (Darmstadt, Germany). Hydromatrix (a high purity, inert diatomaceous earth sorbent was purchased from Agilent, Santa Clara, CA, USA) was exhaustively pre-extracted with DCM using pressurized liquid extraction (PLE) before use. Pressurized liquid extraction (PLE) was performed using an Accelerated Solvent Extractor (ASE) 350 (Dionex, Sunnyvale, CA, USA).

2.2 Biosolids samples

A total of 59 biosolids samples were analyzed for plastics and were sourced from sample archives in the UK (23) and Australia (36) (Donner et al. 2015) (Table S1). The historical UK samples were acquired from a set of samples from the early 1950's to 1990's. These samples have been previously analyzed for metals and were archived following use (Riche 1968). The historical UK samples were dried and stored at room temperature and atmosphere in sealed glass jars from the time of production and initial use until they were sub-sampled for this study (Donner et al. 2015). The historical Australian biosolids from the 1970's to 2009 were collected from a biosolids storage facility containing stockpiled samples from a large wastewater

164 treatment plant (Donner et al. 2015). It should be noted that some details on the date of
165 production were not available from the historical Australian dataset where the production date
166 of n = 4 samples could only be identified as a range of years (see explanation in assumption
167 and limitations section) (Table S1). The biosolids at the facility were stored in open-air
168 stockpiles that were subjected to natural weathering processes from production to collection
169 in 2009 (Donner et al. 2015). For the contemporary 2009 and 2016 samples for the UK and
170 Australia, targeted sampling campaigns were undertaken to assess samples from a range of
171 wastewater treatment plant catchments (Donner et al. 2015, O'Brien et al. 2019, Okoffo et al.
172 2020b). It should be noted that all samples (from the 1950-2009) except the 2016 samples
173 have been previously analyzed for non-labile silver species and were archived following use
174 until they were sub-sampled for this study (Donner et al. 2015). The 2016 Australian biosolids
175 samples data from our previously published work was included in this study (Okoffo et al.
176 2020b) (Table S1). Those biosolids samples were sourced directly from wastewater treatment
177 plants in the UK and Australia in 2009 and 2016, dried and stored in sealed glass jars (Donner
178 et al. 2015, O'Brien et al. 2019, Okoffo et al. 2020b). Together, these historical and
179 contemporary samples provide a glimpse into the past that can help us understand historical
180 trends of plastics in biosolids.

181 2.3 Sample extraction and Pyr-GC/MS analysis

182 Biosolids samples were extracted and analyzed/processed following a validated method
183 previously reported (Okoffo et al. 2020a, Okoffo et al. 2020b). Briefly, samples (approximately
184 1 g each) were milled to a fine powder with a commercial grinder for 30 min (Extech equipment
185 Pty. Ltd, Victoria, Australia). Following this, each sample was weighed into a 5 ml pre-cleaned
186 PLE stainless steel extraction cell and filled with pre-cleaned hydromatrix. Cells were spiked

187 with deuterated internal standards (200 µg of polystyrene-d_5 and polyethylene-d_4; 1 mg/ml in
188 dichloromethane (DCM) and toluene, respectively) and extracted using DCM at 180 °C and
189 1500 psi with a static-time of 5 min using three extraction cycles. All plastic sizes in biosolids
190 samples were analyzed, as samples were not sieved or pretreated prior to extractions; hence
191 the results are obtained for the total mass and entire particle size spectrum of plastics
192 contamination in samples.

193 Immediately after extraction, 160 µl of each sample extract was transferred into pyrolysis cups
194 (Eco-Cup LF, Frontier Labs, Japan; solvent evaporated for 30 mins in laminar flow cabinet) for
195 double-shot Pyr-GC/MS analysis using a multi-shot micro-furnace pyrolyzer (EGA/PY-3030D)
196 equipped with an auto-shot sampler (AS-1020E) (both Frontier Labs, Japan) and attached to a
197 Shimadzu GC/MS - QP2010-Plus (Shimadzu Corporation, Japan) (Okoffo et al. 2020a, Okoffo et
198 al. 2020b). Detailed double-shot Pyr-GC/MS conditions are given in the Supporting Information
199 (Table S2). The first pyrolysis shot (ramped from 100-300°C) of the double-shot method was
200 used as a clean-up step to thermally desorb/remove the potentially interfering volatile and
201 semi-volatile organic materials co-extracted from biosolids samples with the second pyrolysis
202 shot (at 650 °C) used to quantitatively measure plastics identified in samples (Okoffo et al.
203 2020a, Okoffo et al. 2020b). To identify and quantify plastics in samples, plastics specific
204 indicator ions for polypropylene, polystyrene, polyethylene terephthalate, poly-(methyl
205 methacrylate), polyvinyl chloride, polycarbonate and polyethylene were selected as described
206 and identified previously (Okoffo et al. 2020a, Okoffo et al. 2020b) (Summarized in Table S3,
207 S4). The method used in this study was optimized to resolve indicator ion selectivity (i.e. against
208 a number of organic materials and biogenic polymers (natural materials)), thermal
209 degradation, solubility, dissolution and stability of PLE extracts, and matrix-related issues
210 identified for several of the plastics in our previous research (Okoffo et al. 2020a, Okoffo et al.

211 2020b). Details on these procedures can be found in our previous papers (Okoffo et al. 2020a,
212 Okoffo et al. 2020b, Ribeiro et al. 2020).

213 Instrumental calibration was performed for the seven plastics by PLE extracting plastic
214 standards and aliquoting into pyrolysis cups (10 calibration points ranging from 0.05 to 50
215 µg/cup, having $R^2 \geq 0.95$; Table S4). Calibration curves were made by plotting the peak area
216 ratio of indicator ions to internal standard ions, versus the concentration of each target plastic
217 and using the integration results for quantification. Polyethylene-d_4 was used as an internal
218 standard for polyethylene, polypropylene, and polyethylene terephthalate, while polystyrene-
219 d_5 was used for poly-(methyl methacrylate), polycarbonate, and polyvinyl chloride due to
220 similar extraction method recoveries (all values reported in the study were corrected for
221 recovery of the corresponding internal standard). Limits of detection (LOD) and quantification
222 (LOQ) for each plastic were calculated by multiplying the standard deviation of 7 replicate
223 injections of the lowest calibration standard with 3.3 and 10, having a signal-to-noise ratio
224 larger than 10 respectively (Table S4).

225 2.4 Quality assurance and Quality control (QA/QC)

226 Quality assurance and control steps were implemented to prevent contamination of samples.
227 All laboratory glassware and equipment were rinsed with liquid chromatography grade
228 acetone followed by liquid chromatography grade DCM prior to use. Cotton laboratory coats
229 were worn during all steps of analysis. Similarly, glass or metal equipment were used when
230 possible during laboratory procedures. The work was performed in a laminar flow cabinet to
231 minimize contamination by airborne plastics, with samples covered with aluminum foil when
232 not being processed. All working areas were wiped down with 70% ethanol prior to starting
233 experiments. Pressurized liquid extraction (PLE) cells were sonicated with acetone and DCM

234 prior to use to remove background plastic contamination. Prior to each PLE extraction batch,
235 PLE cells were conditioned to remove possible plastics contamination. Prior to Pyr-GC/MS
236 analysis, system cleans (no pyrolysis cups) and blank cups were analyzed to demonstrate the
237 absence of plastics contamination in the system. All pyrolysis cups used in the study were new
238 and washed in DCM before adding sample aliquots as a further cleaning step to avoid any
239 possible contamination. Procedural blanks (consisting of pre-washed hydromatrix, n = 10) were
240 treated as real samples and included in each batch of biosolids samples to undergo all
241 procedures to monitor processing and extraction contamination. Instrumental blanks (n = 10)
242 (e.g. pure DCM solvent, blank pyrolysis cups, no pyrolysis cups as a system clean) were included
243 and analyzed in each batch of samples (injected after every 10 samples) to demonstrate the
244 lack of cross contamination, carryover of target plastics from sample to sample, secondary
245 contamination, background response or potential instrument contamination. To evaluate the
246 risks of sample contamination during sample preparation and processing, glass fiber filters
247 (Whatman GF/D) (n = 10) were placed in the laminar flow cabinet and on the laboratory bench
248 where samples were prepared. These were treated, extracted and analyzed in the same batch
249 as biosolids samples. In all laboratory and procedure blank samples plastic was either not
250 detected or lower than the LOQs (Table S5). To assess the reproducibility of the extraction and
251 analysis methods over time, an aliquot of a composite biosolids sample was extracted and
252 analyzed with each batch of samples, as a QAQC sample. Similarly, ten duplicates of randomly
253 selected biosolids samples were analyzed in different batches to assess the repeatability of the
254 method, and the relative standard deviation (RSDs, %) of individual concentrations in QAQC
255 and duplicate samples were <20%. Instrumental drift in sensitivity was checked by injecting a
256 midpoint calibration standard after every 15 samples. Method recoveries of the individual
257 plastics were assessed through spiking five replicates of biosolids samples (plastics spiked into

biosolids before extraction) with between 20 to 100 µg of each plastic and 200 µg each of polystyrene-d_5 and polyethylene-d_4 internal standards and extracted following the above protocol. Average ± standard deviation absolute % recoveries (not internal standard recovery corrected) were: 107±16 (polyethylene), 103±18 (poly-(methyl methacrylate), 105±24 (polystyrene), 101±21 (polyethylene terephthalate), 98±18 (polycarbonate), 90±17 (polypropylene) and 102±25% (polyvinyl chloride) (Table S6). Recoveries were estimated by comparing concentrations of plastics obtained from spiked samples with those of an un-spiked sample, subtracting the concentrations found in the un-spiked sample (Okoffo et al. 2020a, Okoffo et al. 2020b). Internal standard recoveries ranged from 82 (polyethylene-d_4) to 96% (polystyrene-d_5).

2.5 Assumptions and Limitations

There are a number of assumptions and limitations that need to be considered when interpreting this study. UV irradiation and solar UV radiation are necessary to initiate photo-oxidation of most polymers (Chamas et al. 2020). UV radiation in sunlight causes oxidation of the polymer matrix resulting in chemical bond breakage (Napper and Thompson 2020). In environments lacking both sunlight and oxygen, degradation or weathering is unlikely to proceed naturally due to the high temperatures required (Ahmad et al. 2015, Chamas et al. 2020, Onwudili et al. 2009). The archived biosolids samples used in this study were freeze dried/air-dried biosolids that were stored under ambient conditions and atmosphere in sealed glass jars until sub-sampled; hence weathering or polymer degradation due to UV radiation, mechanical (abrasion), thermal, and chemical action were not considered a major issue during sample storage (as this was convenience sampling we could not take into account weathering of plastics before sampling but only after sampling and storage). It should be noted that

281 samples weren't available over the whole course of the 70-years' timeframe (1950s to 2016).
282 As these were obtained from archived samples, some year groups were not available, and
283 samples were not equally distributed over the years (Table S1). This study gathered available
284 samples by convenience, and we acknowledge the limitations in our study regarding sample
285 representativeness across the years. However, to the best of our knowledge no study has
286 evaluated plastics concentrations in biosolids before 2010 (Okoffo et al. 2019). Additionally, it
287 is possible that no other biosolid samples over this timeframe exist in a sample archive
288 elsewhere. One should also note the uncertainty around when 4 of the samples (1970s/early
289 1980s; late 1980s - late 1990s; 1980s - early 2000s; and 1990s - early 2000s (see Table S1))
290 were collected, where the exact year was not recorded in the archive, but was listed as a range
291 of years. We have plotted the data to the midpoint of the possible date range of the year
292 estimate (e.g. if late 1980s - late 1990s then it would be plotted as/at 1993 with a 5 year range)
293 and plotted dotted lines to indicate when the samples could have come from.

294 It should also be noted that over time more biosolids may have been retained from wastewater
295 as treatment processes have been improved, and that the recovery of the mass of biosolids
296 from wastewater, including sources such as industry might have likely changed. Likewise, a
297 significant shift in biosolids production might have occurred over this period, from minimal
298 treatment to maximum energy extraction. This will reduce overall solids and increase
299 concentration of recalcitrant components like plastics. Therefore, the continuously increasing
300 concentrations of plastics in the contemporary samples may be influenced by the treatment
301 processes being more effective in collecting plastics today than 1950s (i.e. assessing the
302 efficiency of the processes today compared to the 1950s). However, it was not possible to
303 account for any changes in wastewater treatment processes over the years and there has been

304 no analysis of change in processes over time during that time period in this study. Similarly, we
305 assume that the two countries (UK and Australia) might have similar increasing plastics
306 consumption trends to global plastic production rates, translating directly to plastics reaching
307 wastewater treatment plants biosolids over time. Nevertheless, we cannot assume that
308 wastewater treatment processes that generated biosolids have not changed since the 1950s
309 and is the same between the two countries. As such we do not seek to compare these samples
310 with each other or between the countries and only express plastic concentrations in these
311 samples as a function of global plastic production and consumption. We also do not take into
312 consideration or account for any specific polymer flocculating agents that might have been
313 used in the WWTPs or biosolids treatment processes over the years.

314 2.6 Statistical analysis

315 Statistical analysis was performed using GraphPad Prism 8 and R studio (4.0.2). The
316 concentration (mg/g dw biosolids) of plastics was summed in each sample for all plastics types
317 and the total plastics concentration was then fit with an exponential function for either the UK
318 and Australia (separately or combined). For the purposes of modelling, the plastics
319 concentration data below LOQ was substituted with LOQ/$\sqrt{2}$. Global plastic production
320 estimates were gathered from (Statista. 2020) and modelled with a second order polynomial
321 (as it had a better coefficient of variation than an exponential model). As the data was only
322 available for some years, the data were extrapolated to each year from 1950 to 2016 using a
323 linear spline function (Table S7). Spearman and Pearson correlations were calculated between
324 each combination of three variables: the available biosolids plastic concentrations, the
325 modelled global production data and the populations of the UK and Australia in the respective
326 years (e.g. Figure S1, S2 and S3). Population estimates were gathered from (Macrotrends.net.

2020a, b). There is some uncertainty for when some of the samples were collected (see explanation in assumptions and limitations section) and so the horizontal dotted lines of Figure 1, S4 and figure 2, S5 represent the range in years when the samples were collected. The boxplot has been placed at the mid-point of the year estimate (e.g. if late 1980s-late 1990s then it was placed at 1993 with a 5-year range).

3. RESULTS AND DISCUSSION

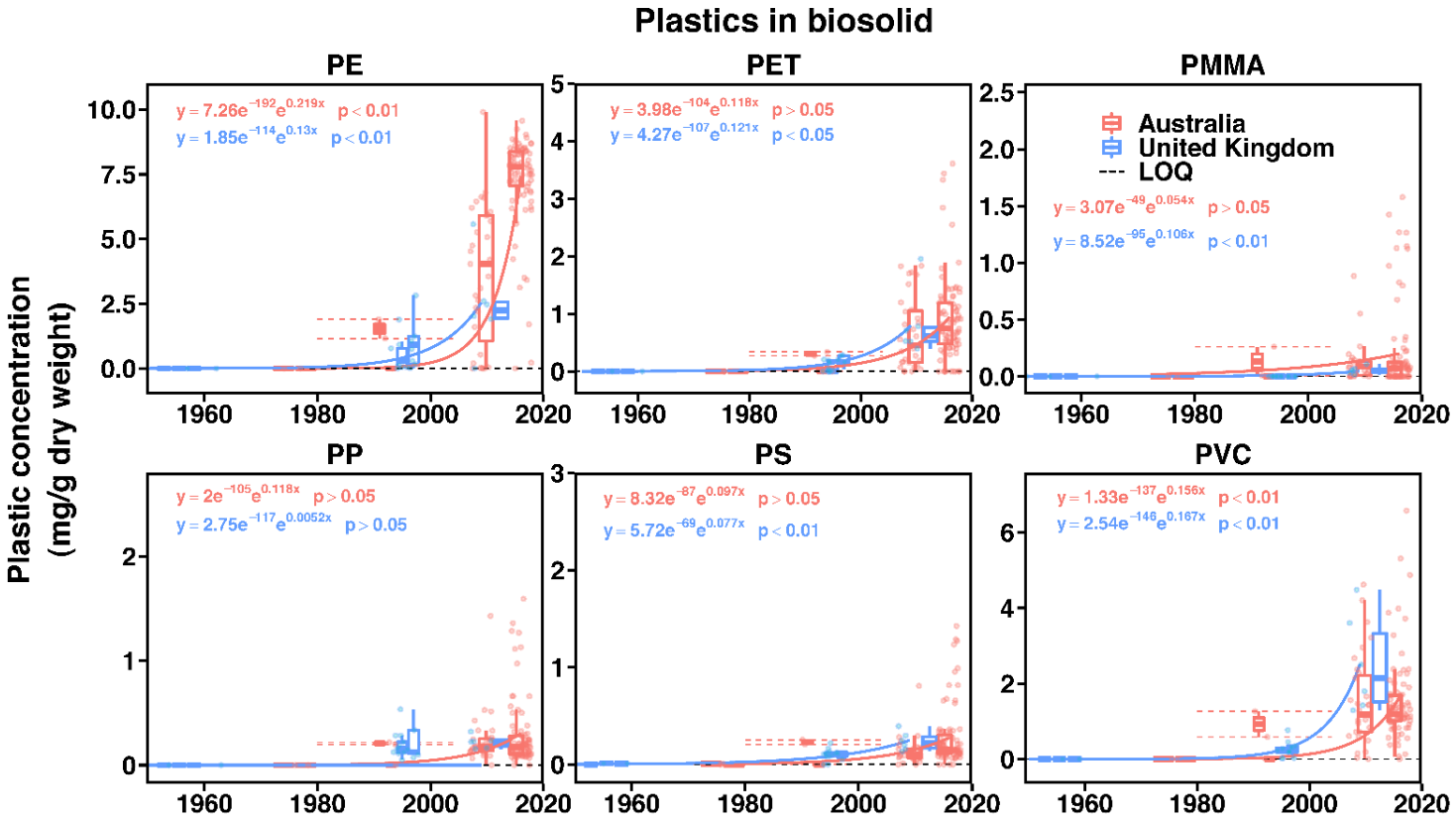
3.1. Concentration of Plastics in Biosolids

Six of the target plastics were detected in the samples analyzed (59 archived samples and the 82 samples included from our previous study (Okoffo et al. 2020b) (Table S1)), while polycarbonate was not detected in any sample (LOD; <0.07 μg/g). The concentrations of total plastics ($\sum_6$Plastics) ranged from 0.01 to 14 mg/g dry weight (dw) (median, 4.3 mg/g dw). Polyethylene (0.01-10 mg/g dw) and polyvinyl chloride (0.02-4.6 mg/g dw) were the most abundant plastics, followed by polyethylene terephthalate (0.02-2.0 mg/g dw). Polyethylene was the most prevalent plastic in the biosolids, contributing to 54% of the concentration of total plastics over the sampling period, followed by polyvinyl chloride (26%), polyethylene terephthalate (11%), polypropylene (5%), and polystyrene (3%), while poly-(methyl methacrylate) represented only 2% of the total. The profile of plastics in the analyzed biosolids agrees with previous studies (Li et al. 2018, Lusher et al. 2017, Okoffo et al. 2020a, Okoffo et al. 2020b). Polyethylene, polypropylene, polyethylene terephthalate, polyvinylchloride and polystyrene are all used as packaging materials (Andrady and Neal 2009, Geyer et al. 2017, PlasticsEurope. 2019). A large portion of these plastic products often have a relatively short service life, reaching WWTPs through their everyday use and via degradation and abrasion of

plastics packaging materials (Browne et al. 2011, Geyer et al. 2017, Mather and Wardman 2011).

There was little difference in the plastics profile identified in the biosolids between Australia and the UK with polyethylene > polyvinyl chloride > polyethylene terephthalate > polypropylene > polystyrene > poly-(methyl methacrylate) over the sampling period. Similarly, there was no significant difference between the concentrations of plastic types between the two countries ($p > 0.05$, unpaired t-test), except for polyethylene and $\sum_6$Plastics ($p < 0.05$); likely driven by higher concentrations in Australia in 2016, whereas the UK only had samples available up to 2009.

None of the measured plastics were detected above their respective limit of quantification (LOQs) in biosolids samples prior to the 1990s (Figure 1 & Figure S4), except for polystyrene in samples from 1955, 1961 and the 1970s. Polypropylene, polyvinyl chloride, polyethylene and polyethylene terephthalate were quantified in samples from the mid-1990s onwards, while poly-(methyl methacrylate) was only quantified in samples from the 2000s, with the concentration of plastics increasing over time for each plastic (Figure 1 & Figure S4, Table S1). The concentrations of polyethylene, polyethylene terephthalate and polyvinyl chloride were the highest and showed an increasing trend from mid 1990s (Figure 1 & Figure S4). During the study period (1950–2016), the mean detected yearly concentration of polyethylene ranged from 0.6 ± 0.6 to 7.4 ± 1.6, polyvinyl chloride from 0.2 ± 0.1 to 1.7 ± 1.2, polyethylene terephthalate from 0.2 ± 0.1 to 1.0 ± 0.7, poly-(methyl methacrylate) from 0.01 ± 0.01 to 0.3 ± 0.4, polypropylene from 0.2 ± 0.1 to 0.3 ± 0.3 and polystyrene from 0.01 to 0.3 ± 0.3 mg/g dw.



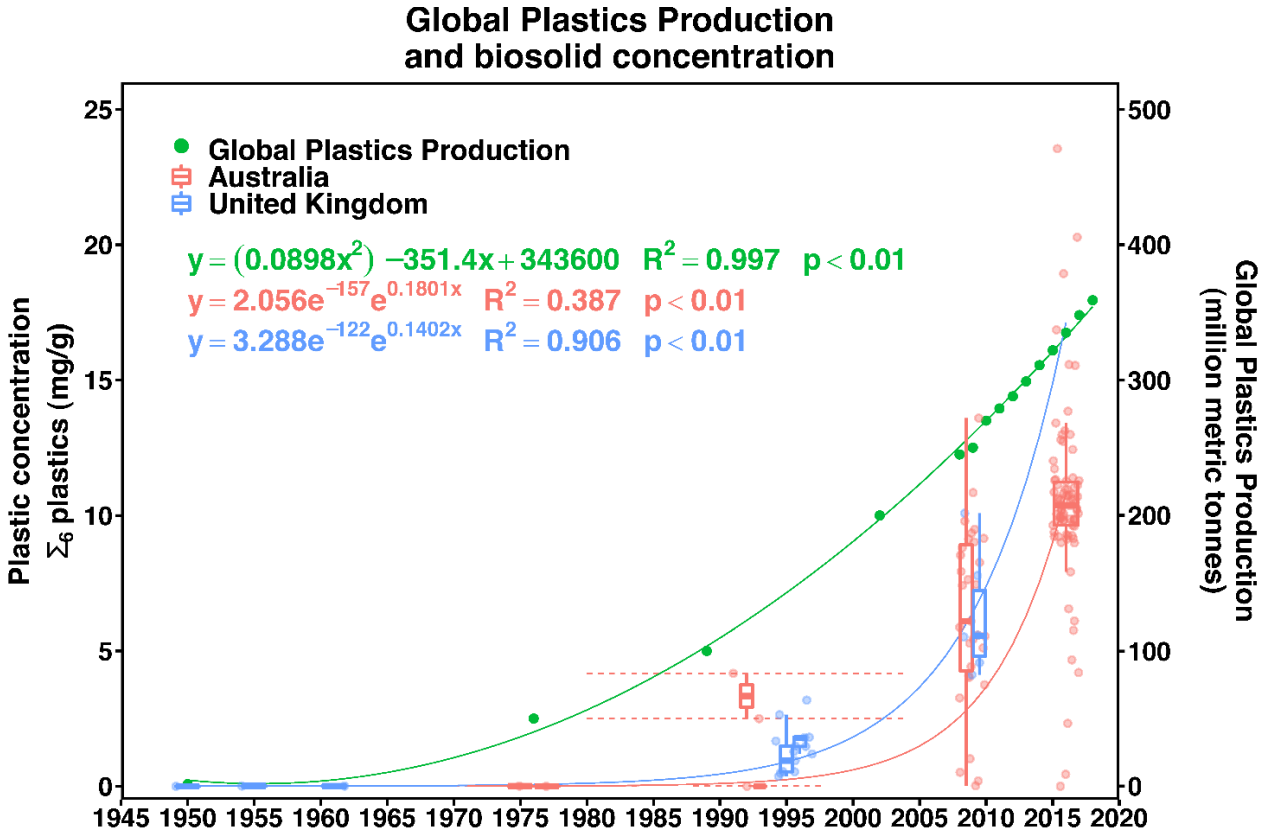
371

372 Figure 1. Concentrations (mg/g dw) of individual plastic types in biosolids from 1950 to 2016. The data are grouped as boxplot summary statistics,
373 with individual data points shown with an exponential trend line (Box = 25–75% interquartile range, crossbar = median, each box contains
374 concentration in each sample for the years of sampling). The points are slightly offset on the x-axis, to prevent overlap of the points. The dotted
375 red horizontal lines outline the uncertainty around when the samples could only be identified as a range of possible collection years (e.g. the
376 sample archive 1980s-1990s did not record the exact year; see explanation in assumption section). The points are plotted at the midpoint of the
377 range in possible dates. PP: polypropylene, PS: polystyrene, PET: polyethylene terephthalate, PMMA: poly-(methyl methacrylate), PVC: polyvinyl
378 chloride, PE: polyethylene.

3.2 Plastic Concentrations in Biosolids Compared with Global Production and Consumption

The total concentration of the six plastics ($\sum_6$Plastics) increased between the 1950s and 2016 (Figure 2 & Figure S5). The yearly sum of $\sum_6$Plastics ranged from 0.01 mg/g dw in 1955, where only polystyrene was detected, (*n=1*) to 860 ± 3 mg/g dw in 2016 (*n=82*) and continuously increased in the contemporary samples (Table S1). Comparison with global plastic production data from 1950 to 2016, (modelled data in Table S7 & Table S8 (Statista. 2020)) (Figure 2 & Figure S5), illustrates that increases in production volume occurred at a similar rate to the increasing concentrations of plastics in biosolids (Spearman rho = 0.995, Pearson r = 0.842, p <0.01 for UK and Australian data combined) (Table S9, Figure S1). Additionally, the concentration of plastics increased at a similar rate as population growth for Australia and the UK combined (Spearman rho = 0.998, Pearson r = 0.802, p < 0.01) (Table S9, Figure S4), with a significant correlation also observed between population and global production of plastics (Spearman rho = 0.995, Pearson r = 0.973, p <0.01) (Table S9, Figure S5) (Macrotrends.net. 2020a, b).

We show that global plastic production and consumption is closely correlated with concentrations in biosolids (Figure 2 & Figure S5). This implies a direct link between production, consumption and leakage into the environment, as has previously been observed for ocean plastic deposition (Brandon et al. 2019). Our data indicate that prior to the 1990s, the leakage of plastics into sewers and thereafter biosolids was not a major issue. From the 1990s plastics became detectable in biosolids, increasing at a similar rate to production and consumption. A large proportion of the increase in leakage is driven by polyethylene, polyethylene terephthalate and polyvinyl chloride (Figure 1 & Figure S4).



401

402 Figure 2. Plastic concentrations in biosolids increased over time along with worldwide plastic production, however concentration in biosolids
403 appeared to increase at a faster rate over the same time period (1950-2016). Total concentrations (mg/g) of all six plastic types measured in
404 biosolids ($\sum_6$Plastics 1950-2016) (graphed in red and blue to left y- axis, exponential trend lines) compared with worldwide plastic production data
405 (in million metric tons, graphed in green to right y-axis, second order polynomial trend line), 1950 to 2016 (Statista. 2020) (Table S7, S8) . The
406 figure uses the sum of total plastics showing all data points for each site, each data point represents the sum of the 6 plastics. The dotted red
407 horizontal lines outline the uncertainty around the sample production year (e.g. the sample archive 1980s-1990s did not record the exact year;
408 see explanation in assumption section).

409 Polyethylene (both high and low density) is the largest volume polymer used globally
410 (PlasticsEurope. 2019). Interestingly, the production volumes and use of polyethylene
411 increased rapidly in the 1990s, especially in applications such as food and general packaging,
412 carrier bags, consumer goods, electronics, and household goods, presumably leading to the
413 increased leakage into sewers. Since the mid-1990s synthetic polymers (largely driven by the
414 production of polyester) have dominated the textile market, surpassing cotton as the most
415 commonly used fiber type (Suaria et al. 2020). With effluents from laundering synthetic textiles
416 directly released to WWTPs through sewers, WWTPs have been identified as an important
417 point source for polyester-fibers (Salvador Cesa et al. 2017, Sillanpää and Sainio 2017).
418 Polyvinyl chloride production reached 61 Mt in 2016 (Allsopp and Vianello 2000, Plastics
419 Insight. 2020) from around 6 Mt in 1970 (Johnson 1990) and its use in wastewater pipes,
420 building materials and furniture, packaging, electronics, fiber for clothing etc., (Allsopp and
421 Vianello 2000, Plastics Insight. 2020) may have increased its leakage to the sewer (and hence
422 in biosolids) over the sampling period (Figure 1 & Figure S1).

423 Expanded polystyrene (EPS) was developed in 1954 and widely used as moldable packaging
424 material (e.g. cups and trays) and insulation for buildings (Andrady and Neal 2009). Polystyrene
425 was the only plastic type detected in samples prior to the 1990s (i.e. in the 1955, 1961 and
426 1970s samples) (Figure 1 & Figure S4) suggesting its use in consumer products and direct
427 releases into wastewater from the early 1950s. Poly-(methyl methacrylate), used in optical
428 lenses, acrylic nails, paint, laptops, smartphone displays screens, interior and exterior panels,
429 canopies, LCD screens, personal care products, furniture etc., (Ali et al. 2015, Creative Staff.
430 2020), was only detected in samples from the 2000s onwards (Figure 1 & Figure S4); possibly
431 implying that poly-(methyl methacrylate) leakage may only be a more recent issue. Although

polypropylene is one of the most versatile and extensively used polymers worldwide (Rogers 2020); second only to polyethylene in volume (PlasticsEurope. 2019); leakage into biosolids has only gradually increased over time in the samples analyzed (Figure 1 & Figure S4).

Given the lack of historical environmental pollution data for plastics, archived environmental samples can provide a historical perspective on plastic leakage pathways into the environment and how these have evolved with changing plastics production and consumption/use and populations. There is a clear association between leakage and population data for Australia and the UK (Figure S2 & Figure S3), suggesting that increasing population and a rise in the standard of living may have translated to increased plastic consumption and production.

Despite the pervasiveness of plastics pollution, we still lack a fundamental understanding of the extent and impacts of plastics leakage and the key pathways by which they enter the environment. This is a serious concern because even under the most ambitious contemporary waste reduction scenarios, contamination of the environment is predicted to continue to grow (Borrelle et al. 2020). In the context of historical plastics leakage presented in this paper, understanding is still needed on which products and uses resulted in the detected leakage. This will help identify urgently needed source control interventions to reduce leakage and slow down the trend of increasing plastics in biosolids. Suggested source control options could include filters on washing machines, eliminating, banning, substituting or reducing plastics in consumer products such as cosmetics, personal care products and textiles, and advocating reuse of plastic packaging products/single-use plastic bags or placing levies on single-use plastic products (Borrelle et al. 2020, Hopewell et al. 2020, Lv et al. 2019, Magni et al. 2019). Consequently, it is important to quantify the impacts of such practical interventions to validate their efficacy and design practical mitigation strategies for the future. The impact of effective

interventions also needs to be effectively communicated to facilitate the development of an evidence-based plastic pollution reduction strategy.

4. CONCLUSION

Understanding the historical leakage of plastics into the environment and how this relates to production and consumption will support developing evidence-based strategies to mitigate future plastics pollution. Here we explore archived biosolids from Australia and the UK from between 1950 and 2016, and for the first time provide quantitative mass-based concentration data for seven common plastics over a 70-year period. We show that concentrations of plastics in biosolids closely correlate with plastic production and consumption. We provide ground-breaking data that shows that prior to the 1990s, the leakage of plastics into sewers and thereafter biosolids was limited, except for polystyrene, with much of the increase in leakage from the 1990s onwards driven by increased production and consumption of polyethylene, polyethylene terephthalate and polyvinyl chloride. Understanding this timeline and the changes that took place in society at this time will facilitate an understanding of how we can change as a society to reduce future leakage of plastics into the environment via this pathway.

5. SUPPORTING INFORMATION

The following is the supplementary data related to this article: Additional information on instrumental parameters of the Pyr-GC/MS, blanks, recovery and spiked biosolids results and results of plastics in each individual sample, modelled data and a few explanatory schemes can be found in the Supporting Information.

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Data and materials availability: All data needed to evaluate the conclusions of this study (except identifiable information about the WWTPs involved) are freely available without restrictions as a data supplement to this article. Additional data related to this paper may be requested from the authors.

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