



An Assessment of Contaminants in UK Road-Verge Biomass and the Implications for Use as Anaerobic Digestion Feedstock

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Abstract

Biomass from harvested road-verge herbage has potential value as a feedstock for anaerobic digestion (AD) energy plants. However, the proximity to road traffic related pollution sources introduces the possibility of contamination by potentially toxic elements and polycyclic aromatic hydrocarbons. Potential sources of pollution from road traffic emissions are identified and the consequent likelihood of certain contaminants being present at elevated levels is assessed. Samples of road verge biomass harvested from selected locations in Lincolnshire UK for use in AD plants were analysed to produce a set of measurements for the presence of the contaminants of interest. The measured levels of these contaminants are compared to reported background levels in UK herbage and soils to assess if there is significant increased concentration in road-verge biomass. Samples of digestate from an AD plant using the road-verge biomass as feedstock were also analysed to determine if there is notable risk of transfer and concentration of contaminants into agricultural land where the digestate may be used for fertilisation. While elevated levels of contaminants were detected, they were not found in concentrations on road verge biomass at high enough levels to cause adverse effects or concerns for its safe use as an AD feedstock.

Keywords Biomass feedstocks · Anaerobic digestion · Road verge · Potentially toxic elements · Polycyclic aromatic hydrocarbons

Statement of Novelty

This study was conducted as part of a wider investigation undertaken by Lincolnshire County Council for evaluation of potential harvesting road verge biomass. This included technological and economic analyses. The associated investigation described here was undertaken to assess the likely levels of key contaminants in the road verge biomass and possible risks associated with its use in anaerobic digestion (AD). The overall study was itself the first of its kind in terms of scale and scope. The data produced and presented in this article answers specific concerns about the viability

of the use of road verge biomass. The detail of the analysis are previously unpublished and are very useful reference for similar future projects.

Introduction

Anaerobic Digestion

A major advantage of AD as an energy conversion technology is the ability to use diverse feedstocks including sewage, food waste, industrial by-products (such as brewer's grains), residues from agricultural cultivation, conservation and land management as well as dedicated energy crops. Many of these feedstocks cannot be effectively used in other energy conversion systems while AD can also produce a digestate residue which can be utilised for agricultural fertiliser. Furthermore, the primary product, biogas, can be used for electricity generation (either locally or to grid), heat production or it can even be upgraded to high grade biomethane for injection into the national gas grid. Nevertheless, it is not

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necessarily economically attractive to businesses and farms to invest in AD without some certainty in the supply chains of low-cost feedstocks and in the price received for electricity, heat and biomethane. In the UK, as a result of policies to reduce carbon emissions and manage waste streams, the technology has been supported through renewable energy subsidy mechanisms including feed-in-tariffs and the renewable heat incentive [1]. AD applications cover a range of scales, a wide range of potential feedstock inputs and a range of product outputs. This has produced an interplay between food, water and energy sectors allowing optimisation of the sustainability of each [2]. The flexibility and sector cross-cutting aspects of AD have then allowed innovative applications and uses for materials as feedstocks where previously there were no economical or environmentally sustainable use for them. A good example of this is the potential use of herbage cuttings from the maintenance of green spaces such as road-verges by local authorities.

Road Verges Biomass for AD Feedstock

The potential for use of non-agricultural green ‘waste’ from municipal green spaces was investigated in Germany by Pick et al. [3]. This concluded that there is large potential for utilisation of such materials as feedstocks from biogas production but technical, legal and economic factors precluded the vast majority of biomass from being used. Studies into the feasibility of using road verge biomass specifically include the study by Meyer et al. in Denmark [4] and by Piepenschneider et al. in Kassel, Germany [5]. The Meyer study included an estimate that such a resource could account of up to 3% of Danish biogas production. The energy return on energy invested (the ratio of *useful energy produced* to the *total energy used* by the process) was estimated to be marginal (between 2 and 3) but with additional associated benefits accounted for, the practice can be considered economically viable. The additional benefits include the use of the digestate for fertiliser and soil improver [6, 7]. Furthermore, other studies have shown that removal of cuttings from verges can enhance biodiversity and ecological richness [8].

Road Verges Biomass in UK

AD plants have become increasingly common in the UK over the past decade with numbers of operational plants growing from around 30 in 2008 to over 600 in 2018. The majority of these plants are installed in rural areas and more than half on farms [9, 10].

There are nearly 400,000 km of roads in the UK, much of which are bordered by grass verges [11]. In certain areas, vegetation growth on road verges are managed by regular mowing for reasons of safety (driver visibility), road

maintenance and aesthetics. The cuttings from verge mowing are generally left to decompose or form mulch but, as established in previous studies, they can also be considered as a potential source of AD feedstock. Lincolnshire County Council, having responsibility for over 8750 km of mainly rural roads with grass verges, commissioned a feasibility study in 2015 on the use of road-verge biomass for use as an AD feedstock as a long-term practice. The resulting study [12] concluded that such proposals were feasible but would require innovative approaches and further evaluation including:

- Investigation on improved efficient and cost-effective means of harvesting and delivering to local AD operators;
- Field trials to assess actual harvest yields and biomethane potential;
- Analysis to establish the levels of contaminants in the harvested biomass.

The latter of these is the subject of this article and is thus effectively a continuation of the study undertaken for Lincolnshire County Council. The other aspects of the evaluation have been undertaken in a related work-package and reported in a separate study [13].

Potentially Toxic Elements (PTEs)

PTEs are a group of metals and metalloids that are known to be toxic to human and plant health if delivered in high doses. These elements are commonly called “heavy metals” but to be more precise, we refer to them here as PTEs [14].

In the context of AD, high concentrations of PTEs can adversely affect key biochemical processes. By binding to or displacing other metals from various biomolecules, PTEs can disrupt enzyme functions. In turn, this can inhibit both acidogenic and methanogenic microorganisms thus reducing the efficacy of biogas production [15]. While PTEs present more of a risk from feedstocks derived from sewage, they may also bioaccumulate in other feedstocks including grasses [16]. As a result, PTE toxicity is one of the main factors in reduced performance or failure of anaerobic digestors [15]. It is therefore important for AD operators to monitor and minimise levels of PTEs in their process water in order to sustain the effectiveness of the digestion process.

Additionally, operators must maintain acceptable levels of PTEs in their digestate. In the UK, the Environment Agency places strict legislative limits on the concentrations of PTEs that may be released into the environment through the use of digestate as fertiliser—as this could lead to the biomagnification of PTEs in the soil. An operator would have to pay significant disposal costs if their digestate did not meet the regulatory standards. In the UK, the key pieces

of environmental legislation that applies to PTEs in products from AD are:

- Environmental Permitting Regulations (EPR) - For an AD plant to operate it must hold environmental permits for the digestion of waste, use of a digester, the storage of digestate, biogas combustion and further permits for transport and other uses. The EPR legislation came into effect on 6th April 2010 and covers a wide range of industry and processes.
- End of Waste Criteria (EoW) - End of Waste criteria is composed of the Digestion Quality Protocol [17] and the applied publicly available specification PAS-110 [18]. These documents set out a framework for what type of biowaste can be digested, best practice and levels of contaminants in digestate—including PTEs. Once the EoW criteria have been met, the digestate and biogas are no longer classed as waste and can be used without obtaining an environmental permit.

A further consideration for AD operators to be aware of is the effect that some PTEs have as micronutrients and are required in low concentrations to maintain the complex biochemistry that occurs in AD plants. Although some (Cd, Pb, Hg) seem to offer nothing to bacterial processes, micronutrients such as zinc and manganese, stimulate biochemical processes that are vital for the production of biogas. In some cases, operators may add some of these elements to the feedstock to stimulate the AD process [19].

Sources of PTEs from traffic related emissions are likely to contribute to the contamination of road-verge biomass. The three main sources of PTE emissions from road vehicles are: (i) combustion engine exhaust; (ii) Particles from tyre

wear; (iii) particles from brake wear. In addition to this, particles from the road surface itself may contain PTE and PAH contaminant, particularly if the surfacing contains bitumen. Studies on the concentrations of PTEs from these sources are referenced to provide an indication of which are likely to be present in elevated levels [20, 21].

PTEs present in the wider environment of the UK were surveyed in 2007 by the Environment Agency [22]. The average levels reported in soils and on herbage from that survey can be used as references to assess if measured levels in feedstocks are unusually high. Published studies on the levels of PTEs in road dust can also be used as references for context and comparison with measured results [23, 24].

Table 1 presents data from published literature indicating the relative concentrations of the most prevalent PTEs as measured in various sources and in the road environment together with the PAS 110 limits where applicable.

Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a group of hundreds of compounds formed of multi-fused aromatic rings. They generally have high boiling points and low vapour pressures and are therefore solid in standard conditions. They are non-polar so tend to have very low aqueous solubility although they are also lipophilic so tend to be very soluble in organic solvents.

PAH compounds are ubiquitous and persist throughout the environment in soil, air and water, many having a half-life of 2 years. High concentrations are a concern owing to their potential to be harmful to organisms and human health. Exposure can be by ingestion from contamination of food or by inhalation of PAH particulates (from smoke for

Table 1 PTE contamination: traffic related sources; levels measured in environment; PAS 110 limits

PTE	Traffic related pollution sources			Levels measured in environment			PAS 110 Limit in digestate µg/g
	Brake wear particles	Tyre wear particles	Transport fuel emissions	Road dust	UK rural soil average	UK rural herbage average	
	µg/g	µg/g	µg/kg	µg/g	µg/g	µg/g	
Arsenic (As)	<2–11	–	0.26–0.34	–	10.9	0.56	–
Manganese (Mn)	62–5640	0.8–2.5	–	486	612	243	–
Nickel (Ni)	80–730	<1–3	0.79–1.1	–	21.1	1.76	50
Copper (Cu)	70–39 k	<2–3	3.4–8.7	75–87	20.6	7.26	200
Zinc (Zn)	120–27 k	5650–9640	16–44	122–175	81.3	35.90	400
Selenium (Se)	4.5–115	–	0.18–0.2	–	–	–	–
Cadmium (Cd)	<0.1–2.6	<0.05–0.34	0.24–0.34	1.4	0.39	0.14	1.5
Lead (Pb)	4–1290	1–5.7	1.3–1.8	39–233	52.6	2.12	200
Mercury (Hg)	<0.1–0.3	<0.01–0.03	2.3–9.2	–	0.13	0.07	1.0
Chromium (Cr)	135–1320	<1–2	5.6–13	56	34.4	1.76	100
Source reference	[20, 25]	[20, 25]	[21]	[23, 24]	[22]	[22]	[18]

example). In humans, they can cause adverse health effects such as depressed immune function, internal organ damage and pulmonary disease as well as being carcinogenic [26].

In the AD process, PAHs can be concentrated in the digestate so use of this as fertilizer risks increasing PAH concentration in agricultural soils and bioaccumulation in crops [27]. This is clearly undesirable where food crops are cultivated owing to the health risks of PAH ingestion described previously.

Sources of PAH contamination include pyrogenic processes (from pyrolysis or incomplete combustion of organic fuels), petrogenic (from crude oil or coal) or biological (from degradation of vegetation) [26]. In the context of road verge contamination, the sources of PAH contamination that are likely to contribute to elevated levels are from road vehicles. The three main sources of PAH emissions from road vehicles are the same as with PTEs: (i) combustion engine exhaust; (ii) Particles from tyre wear; (iii) particles from brake wear.

Particles formed of or containing PAH compounds can be deposited on herbage directly as dry particulate precipitation. Rainfall may also contain PAH from the atmosphere which is then deposited on leaves. However, rainfall will also wash extraneous material off herbage and into the soil. Concentrations of PAH in soils are therefore likely to be much higher than those on the herbage itself.

The presence of PAH in the wider environment of the UK were surveyed in 2007 by the Environment Agency [28]. The average levels reported in soils and on herbage from that survey can be used as references to assess if measured levels in feedstocks are unusually high.

The United States Environmental Protection Agency (US EPA) established a list of 16 priority PAHs based on their high levels of toxicity and concentrations in the environment as well as standardised methods for analysis of PAHs in environmental samples [29]. The 16 ‘priority PAHs’ are listed in Table 2 with data from literature indicating the relative concentrations of PAHs as measured in various sources and in the road environment.

The environmental legislation that applies to PTEs in products from AD do not cover PAH contamination. However, the use of AD digestate as a soil improver/fertiliser is comparable to similar use of sewage sludge for which there is a proposed EU limit of 6 mg/kg [33].

Scope of Study

This study addresses one of the issues identified in the feasibility study on use of road-verge biomass for AD prepared for Lincolnshire County Council [12], namely: to establish the levels of contaminants in the harvested biomass. From a review of key pollutants associated

Table 2 PAH contamination: traffic related sources and levels measured in environment

PAH	Traffic related pollution sources			Levels measured in environment		
	Brake wear particles	Tyre wear particles	Diesel fuel emissions	Road dust	UK rural soil average	UK rural herbage average
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Napthalene			1.83			
Acenaphthylene		8.2–20	0.46		0.03	0.030
Acenaphthene			0.26		0.01	0.010
Fluorene			0.41		0.12	0.013
Phenanthrene	0.97	6.2–18	0.54	3.9	0.13	0.047
Anthracene		0–1.6	0.21	0.84	0.12	0.011
Flouranthene	0.69	9.4–29	0.31	6.9	0.23	0.017
Pyrene	1.1	11–70	0.30	9.4	0.19	0.015
Benz(a)anthracene	1.5	0–3.8	0.21		0.12	0.007
Chrysene	1.7	8.2–14	0.21		0.15	0.011
Benzo(b)fluoranthene	0.42		0.15		0.22	0.012
Benzo(k)fluoranthene	0.62		0.18		0.09	0.013
Benzo(a)pyrene	0.74	3.9–6.4	0.18		0.22	0.009
Indeno(1,2,3,cd)pyrene	2.6		0.03		0.14	0.007
Dibenzo(a,h)anthracene			0.03		0.032	0.005
Benzo(g,h,i)perylene	0.34	0–34	0.62		0.12	0.011
∑16 PAH					1.92	0.22
Source reference	[30, 31]	[31]	[32]	[31]	[28]	[28]

with road vehicles, a selection of PTEs and PAHs have been identified as contaminants likely to be in elevated concentrations in road-verge biomass. The concentrations of these contaminants in samples from road-verge biomass harvesting trails in Lincolnshire are evaluated in this study. This allows assessment to establish if the observed levels are significantly higher than background levels. In addition, samples of digestate resulting from use of the road-verge biomass in AD are analysed to assess the levels of the same contaminants. While this covers a limited geographical and temporal scope, evidence regarding the risks associated with feedstock contamination is provided and the study provides a useful body of data on this subject.

Methodology

Harvesting Sites and Sampling

Trials for harvesting road verge biomass for evaluating the feasibility of its use in AD were undertaken by Lincolnshire County Council in 2016. Fig. 1 shows the location of the sites chosen for these trails with further details provided in Table 3. The sites vary from main trunk-roads (UK ‘A’ roads) and smaller rural lanes.

The sample designations are given by a reference in the form Sx.Hy.z where: Sx indicates the site reference: where x = 1,2,6,9,10,11 as listed in Table 3 and shown on map in Fig. 1.

Hy.z indicates the harvesting reference: There may be 2 or more harvests in a season: y = 1 indicates first harvest

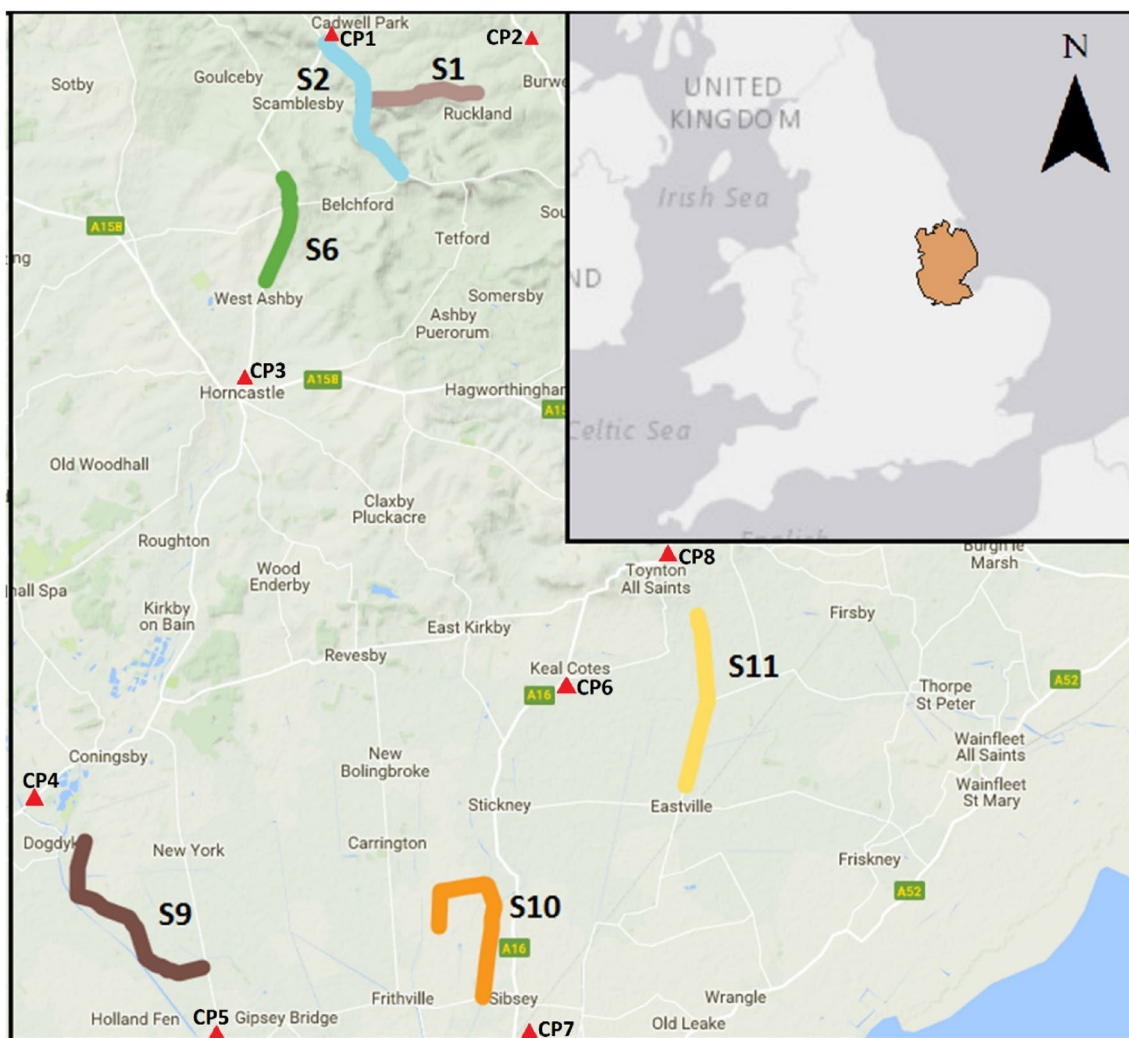


Fig. 1 Map of part of Lincolnshire in eastern England showing the sites (S1/S2/S6/S9/S10/S11) of road verge biomass harvesting for AD trials in 2016 (filled triangle indicates traffic count point)

Table 3 Sampling site details

Site	Road	Nearest main road(s)	Distance to nearest main road (km)	Distance to nearest count point (km)	Average daily traffic count ^a	Traffic count point reference (see Fig. 1)
S1	Oslear's lane (unclassified)	A153	3	3	3583	CP1
		A16	1	4	8316	CP2
S2	Bluestone heath road (A1028)	A153	1	1	3583	CP1
		A16	6	6	8316	CP2
S6	Foxendale hill (A153)	A153	0	4	3583	CP1
		A153	0	5	10,547	CP3
S9	Hurnbridge lane (unclassified)	A153	3	3	8405	CP4
		A1121	7	7	7535	CP5
S10	Trader bank lane (unclassified)	A16	1	9	6198	CP6
		A16	1	6	21,219	CP7
S11	Spilsby road (unclassified)	A16	3	5	6198	CP6
		A16	3	3	10,712	CP8

^aData for all motor vehicles from nearest monitoring points—average daily traffic flow 2014–2016 [34]

of season. In some cases, the cutting machinery may be required to run along the verge twice to cover a wider width or higher growth of verge during the same harvest. $z = 1$ indicates the first swath of cutting during the harvest; $z = 2$ indicates a second swath of cutting on same stretch of road.

In addition to the road-verge biomass samples, other samples were obtained of feedstocks currently used in an on-farm AD plant at Scrivelsby, located near to the sampling sites. These feedstocks were taken from farm storage systems (vertical-wall concrete storage clamps) and included maize, rye grass and grass silage. Samples of digestate resulting from AD with the road-verge biomass were also collected from this AD plant. Details of the AD plant of this site can be found in a public database of operational AD plants [35].

Samples (1–2 kg) were taken from the mixed bulk material on site and transported in air-tight containers to the lab where they were then stored at $-20\text{ }^{\circ}\text{C}$ prior to the analysis. Sub-samples for analysis were obtained by coning and quartering (in accordance with ISO 14,780). Moisture content of the 'as-received' samples was measured (in accordance with ISO 18134-3:2015). The measured moisture content of each feedstock was as follows: road-verge biomass 76%; rye grass 84%; maize 53%; grass silage 73%.

PTE Analysis

The samples were initially reduced to $< 100\text{ }\mu\text{m}$ particle size using a Retsch SM300 cutting mill. The first part of the sample to be passed through the mill was disposed of to reduce the risk of inclusion of contamination from mill surfaces. While there is also a possibility that contamination from abrasion of the steel cutting blades may have occurred, since the samples were all soft materials, this is considered

low risk. The milled samples were digested in nitric acid ($\text{HNO}_3 > 70\%$) according to the method set out in EN-ISO-16,968:2015. Duplicate aliquots were each prepared from 500 mg of each sample and made up as an aqueous solution for analysis. A reagent blank sample and a sample using a standard reference material were also prepared. Each of these was analysed using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) to quantify the trace quantities of PTEs in accordance with EN-ISO-17294-1:2006. The instrument was externally calibrated using standard solutions (50 ppb, 1000 ppb). The ICP-MS spectral data were analysed using methods developed at The University of Leeds accounting for errors from matrix effects. Analysis results for mercury and chromium were not reliably quantified in this process so a subset of the samples were subsequently analysed in an external laboratory to determine levels of these elements.

PAH Analysis

PAH analysis was conducted by following a multi-step procedure: extraction; evaporation-concentration; determination. Materials for analysis were kept intact 'as received' as much as possible (without milling) to avoid loss of surface contaminants. The extraction step was carried out using an accelerated solvent extractor (ASE®) with the conditions as summarised in Table 4 and following a procedure adapted from the methodology as presented in reference [36]. The evaporation/concentration step was carried out using an automated evaporator (SP Scientific *Genevac Rocket*). This step removes the solvent (toluene) and concentrates the residue through heating ($40\text{ }^{\circ}\text{C}$) and centrifuging (1500 rpm) of the samples in evaporation flasks.

Table 4 Accelerated solvent extraction conditions

System pressure	11 MPa
Oven temperature	120 °C
Sample size	10 g
Oven heat-up time	5 min
Static time	10 min
Static cycles	2
Rinse volume	40 mL
Solvent	Toluene
Nitrogen purge	300 s
Extraction time	30 min
Cell size	100 mL

PAH content in the processed samples was determined by measurement in accordance with standard methods [37] using a GC-MS instrument (Perkin Elmer Clarus 600C) coupled with SIM (Single Ion Monitoring) at 70 eV. The GC oven was set at 60 °C for 4 min, then increased at 5 °C/min to 300 °C, held for 10 min, then cooled to 290 °C. The GC injection port was heated at 300 °C and the transfer line from the GC to MS was heated at 290 °C. Target compounds were separated with a Perkin Elmer Elite 5 ms 5% phenylmethyl silicone column 30 m×0.25 mm with 1 µm film thickness (J&W Scientific Folsom). A sample volume of 1 µl was injected for each sample at split-less mode by supplying helium as carrier gas at a constant column flow rate of 1.4 ml/min. A deuterated internal standard (PAH Mix 31) and EPA 16 PAH calibration mixture (PAH Mix 25) were used for calibration [29].

Results and Discussion

Measured Levels of PTE Contamination

The measured levels of PTEs in the harvested road-verge biomass samples, the farm feedstocks and the digestate are presented in Table 5. The average concentrations of PTE in the road-verge biomass, the farm feedstocks and in the digestate are presented in Fig. 2 (on a log scale) for comparison.

There are a few individual samples of road-verge biomass which show levels of PTEs notably higher than other samples. For example, the concentrations of Pb and Mn at site one (S1) are statistically significantly higher than other samples and higher than the farm feedstocks. In general, the levels of PTEs in the road-verge biomass are broadly in line with the levels observed in the farm feedstock. While the comparison shows that average levels of arsenic and manganese are slightly elevated and that for lead is considerably higher, most of the measured values were commensurate with the background average levels in UK herbage (see Table 1). Sample S1/H1.1 was the only sample to show

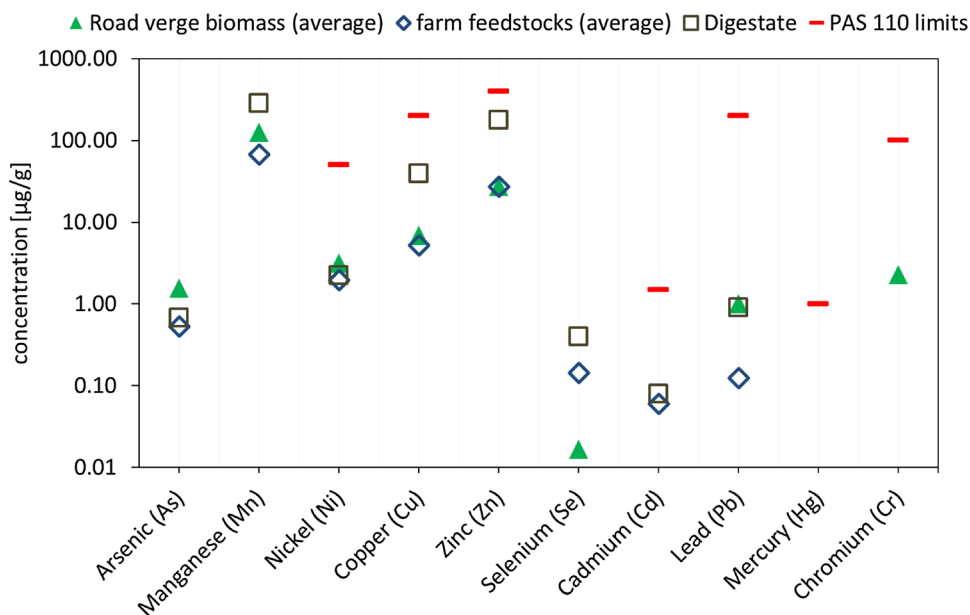
Table 5 Measured concentrations of PTEs in feedstock samples and digestate

PTE concentration [µg/g]	S1/H1.1	S1/H1.2	S2/H1.1	S2/H1.2	S6/H1.1	S9/H1.1	S9/H1.2	S10/H1.1	S10/H1.2	S11/H1.1	Maize	Rye	Silage	Digestate
Arsenic (As)	3.6	2.0	0.63	0.63	0.96	1.7	1.7	1.0	1.4	1.0	0.22	0.38	0.98	0.67
Manganese (Mn)	330	170	81	81	88	140	83	89	69	91	28	54	120	290
Nickel (Ni)	5.6	2.8	1.9	1.9	1.4	3.8	2.0	3.8	4.0	3.4	1.9	1.3	2.6	2.2
Copper (Cu)	10	6.9	11	11	6.3	5.8	5.4	4.7	5.9	5.7	2.8	6.0	6.8	39
Zinc (Zn)	50	32	33	33	31	23	19	18	20	21	29	30	22	180
Selenium (Se)	0.04	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.11	<0.1	0.14	0.09	0.2	0.4
Cadmium (Cd)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.02	<0.1	<0.1	0.13	0.04	0.01	0.08
Lead (Pb)	3.0	0.25	<0.1	<0.1	1.7	1.1	2.0	<0.1	<0.1	1.2	0	0.37	0	0.9
Mercury (Hg) ^a	<0.1	<0.1	-	-	-	<0.1	<0.1	-	-	<0.1	-	-	-	-
Chromium (Cr) ^a	3.9	2.7	-	-	-	1.5	1.1	-	-	2.3	-	-	-	-

Estimated measurement error ±20%

^aMercury and chromium results from external laboratory analysis

Fig. 2 Comparison of PTE concentrations in feedstocks and digestate (logarithmic scale)



levels consistently higher than the average background. It is noted that a study of metals content of urban road-verge grass in Germany [38] reported levels of Mn, Zn, Cu, Pb, Cr and Cd which were all similar or, at least, in the same order of magnitude as those reported here.

In all cases for the farm feedstocks and in most cases for the road verge biomass, the levels of PTEs were similar or lower than in the output digestate. The levels in the digestate were well within the limits set out in PAS 110. It is noted that levels of Mn, Cu, Zn and Se in the digestate were increased by a higher proportion compared to the other PTEs. These elements are present in the additives used as AD stimulants. Other possible sources of some of these metals include contamination from wear of metal parts in the AD plant itself. AD stimulant additives were used at the Scrivelsby plant so it is likely that this is the main source of the increased levels in the digestate.

Measured Levels of PAH Contamination

The measured levels of 16-priority US EPA PAH as well as the total $\sum 16$ PAH in the harvested road-verge biomass samples, the farm feedstocks and the digestate are presented in Table 6. The average concentrations of PAH in the road-verge biomass, the farm feedstocks and in the digestate is presented in Fig. 3 (on a log scale) for comparison.

Sample S10/H1.1 showed the highest concentrations of benzo(a)pyrene (BaP) and $\sum 16$ PAH at 370 and 3400 $\mu\text{g}/\text{kg}$ respectively. These two PAH metrics are commonly used as markers for overall PAH contamination. These values are considerably higher than the mean levels reported in UK rural herbage which are 9 and 220 $\mu\text{g}/\text{kg}$ for BaP and $\sum 16$ PAH respectively (see Table 2). This suggests that the

pollution from road vehicles is indeed a significant contributor to the contamination of the verge. It is noted that normal background concentrations (NBCs) for BaP soil contamination in rural areas are advised as 500 $\mu\text{g}/\text{kg}$ [39]. Despite contamination in many samples being above the expected levels for rural areas, all samples contained concentrations of benzo(a)pyrene and $\sum 16$ PAH below the recommended limits for agriculture soils (1.5 and 40 mg/kg respectively) [40].

PAH concentrations varied greatly between sites but they are comparable to other values reported in the literature for herbage [41].

While the traffic monitoring data (see Table 3) does not, in some cases, present the actual traffic flow at the precise location of the site, a qualitative analysis shows a crude correlation between proximity to main roads and PAH concentrations in samples. The sites in proximity to the higher traffic levels (S6 and S10) presented the highest PAH concentrations. Sites adjoining main roads with lower traffic levels (S1 and S2) presented lower contamination.

The farm feedstocks (maize, rye grass and grass silage) showed, on average, a lower degree of contamination by PAH than the road verge biomass. The maize sample did show a level of contamination in a similar order to the road-verge samples although this appears to be almost entirely owing to a very high concentration of indeno(1,2,3-cd)pyrene. The provenance of this contamination is not clear and the datum appears to be an outlier.

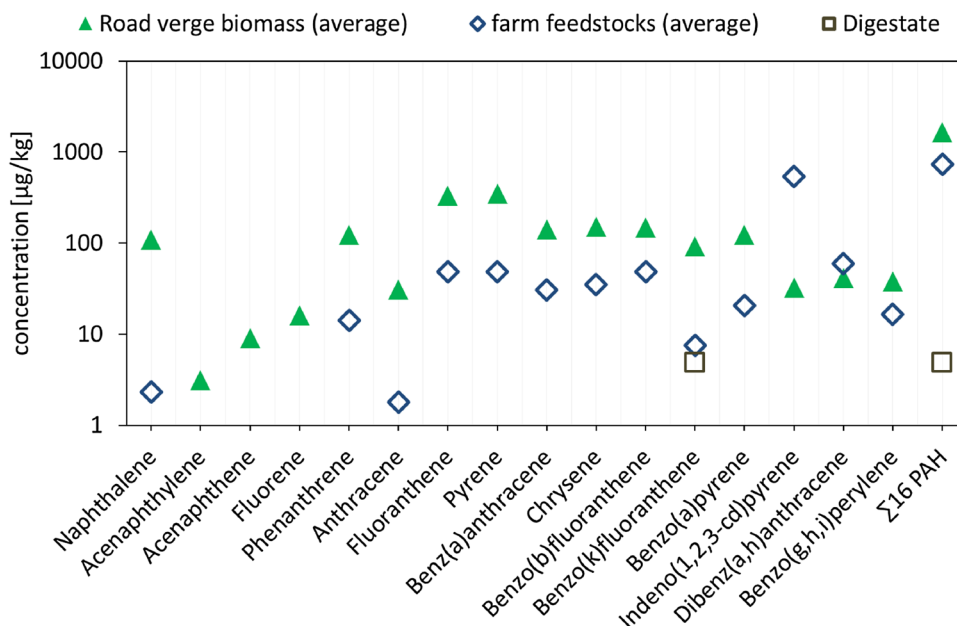
The digestate contained very low levels of PAH with just 4.8 $\mu\text{g}/\text{kg}$ of benzo(k)fluoranthene detected and other PAHs indicated below the reliable measurement limit of the method. The implication of this observation is that the AD process may have either degraded the PAH compounds or they are partitioned away from the digestate in the process. If

Table 6 Measured concentrations of PAHs in feedstock samples and digestate

PAH concentration [$\mu\text{g}/\text{kg}$]	S1/H1.1	S1/H1.2	S2/H1.1	S6/H1.1	S9/H1.1	S9/H1.2	S10/H1.1	S10/H1.2	S11/H1.1	Maize	Rye	Silage	Digestate
Naphthalene	66	6.5	18	190	–	180	200	120	95	2.3	Trace	2.3	Trace
Acenaphthylene	–	–	–	1.0	–	–	6.1	4.0	1.5	–	–	–	–
Acenaphthene	–	19	0.4	4.6	–	7.3	13	17	2.2	–	–	–	–
Fluorene	–	16	–	–	–	–	–	–	–	–	–	–	–
Phenanthrene	19	150	20	230	–	110	190	190	74	9.1	32	1.5	–
Anthracene	5.9	34	1.1	40	–	38	58	55	14	1.5	2.1	–	–
Fluoranthene	62	280	41	530	–	300	610	630	220	9.9	87	–	Trace
Pyrene	61	320	38	480	–	220	720	700	270	1.5	96	–	Trace
Benz(a)anthracene	27	110	17	200	–	110	270	290	110	–	31	–	Trace
Chrysene	28	110	20	220	–	120	320	300	110	–	35	–	Trace
Benzo(b)fluoranthene	44	130	26	27	–	160	370	290	130	–	49	–	–
Benzo(k)fluoranthene	–	35	12	110	–	–	140	170	–	–	13	2.3	4.8
Benzo(a)pyrene	28	92	18	140	–	100	370	–	–	–	34	7.7	–
Indeno(1,2,3-cd)pyrene	26	17	16	63	–	63	38	28	12	1600	6.3	1.5	–
Dibenz(a,h)anthracene	40	78	20	25	–	44	72	–	9.6	–	86	33	–
Benzo(g,h,i)perylene	22	–	14	52	–	71	45	–	22	–	18	15	–
Σ 16 PAH	430	1400	260	2300	–	1500	3400	2800	1100	1600	490	63	4.8

Estimated measurement error \pm 25%

Fig. 3 Comparison of PAH concentrations in feedstocks and digestate (logarithmic scale)



the former is the case, AD could be a useful means for PAH biodegradation to reduce contamination in soils. However, it is possible that the PAHs are mainly removed from the solid digestate as the liquid fraction is separated. A more detailed and focussed study would be useful to investigate this aspect of the process.

Conclusions

This study analysed a series of samples of road-verge biomass to assess the levels of contamination by both PTEs and PAHs. For comparison, three different farm-feedstocks used for AD were also analysed. The digestate from an AD plant using both the road-verge biomass and the farm-feedstocks was also analysed.

The results showed that the PTE levels in the road verge biomass are broadly comparable to the levels measured in the farm-feedstocks and also in-line with the background levels reported in UK rural areas. The AD digestate had some increased levels of contaminants compared to the feedstocks but this is likely due to the addition of zinc, copper, manganese and selenium, all of which are used in AD stimulant additives. In any case, the levels of all PTEs in the digestate were well within statutory limits for use of the material as agricultural fertilizer.

PAH contamination was observed to be somewhat higher in the road verge biomass compared to the farm feedstocks and higher than the expected background levels reported in UK rural areas. This is not unexpected since emissions from road vehicles is a known source of PAH pollution. Despite the noted contamination levels, the resulting digestate showed

no significant contamination suggesting that the AD process either effectively degrades the PAH or the PAHs are partitioned in the AD process and separated from the solid digestate.

From this study, it is shown that known sources of PTE and PAH contamination from road traffic are not found in concentrations on road verge biomass at high enough levels to cause adverse effects or concerns for its safe use as an AD feedstock.

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