EFFECT OF REPEATED BIOSOLIDS APPLICATIONS ON SOIL POLYCYCLIC AROMATIC HYDROCARBON (PAH) CONCENTRATIONS

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Abstract

As a result of the relatively long persistence of polycyclic aromatic hydrocarbons (PAHs) in the environment, concerns have been expressed that repeated biosolids additions to agricultural soils could lead to the accumulation of elevated PAH levels. Notably, proposed revisions to the EU Sludge Directive have included maximum permissible concentration limits for PAHs in biosolids. In order to assess the potential for long-term accumulation in agricultural soils, PAH concentrations in untreated control treatments were compared with biosolids amended treatments at seven of the "Long-term Sludge Experiment" (LtSE) sites following eleven years of annual biosolids additions.

At the seven LtSE sites, there were no significant increases (P>0.05) in soil PAH concentrations (sum of the 9 EU congeners of concern) above the untreated control. In summary, the added risk from eleven years of annual biosolids applications was un-measurable in the soil.

Keywords

Biosolids, organic materials, polycyclic aromatic hydrocarbons.

Introduction

The recycling of organic materials to land is regarded as the best practicable environmental option in most circumstances, completing both natural nutrient and carbon cycles. Organic materials are valuable sources of major plant nutrients (*i.e.* nitrogen – N, phosphate – P_2O_5, potash – K_2O and sulphur – SO_3), which are essential for plant growth and therefore sustainable crop production. Organic materials also provide a valuable source of organic matter, which improves soil water holding capacity, workability and structural stability *etc*.

Treated sludges (commonly called biosolids) and other organic materials (e.g. livestock manures, compost, digestate) are widely used by farmers and growers to meet crop nutrient requirements and to maintain soil fertility. Biosolids (e.g. digested cake, lime stabilised cake) and green compost (i.e. composted plant and vegetable material) are the most common non-farm organic materials that are applied to agricultural land. On a fresh weight basis, 3-4 million tonnes of biosolids (Water UK, 2010) and 1.9 million tonnes of compost (WRAP, 2012) are recycled to agricultural land on an annual basis.

The application of organic materials to land, as well as conferring benefits to the receiving soil, must not cause harm to either the receiving land or the wider environment (*i.e.* soil, water and air quality, or human health). The risks posed by nutrient enrichment have been documented and researched (Shepherd, 1996; Withers, 2011), and as a result, legislation governing the recycling of organic resources to land is aimed at limiting the impact of nutrients (e.g. Defra/EA, 2008) on the wider environment. Similarly, research has focused on the impact of heavy metals in biosolids on soil quality and fertility (Gibbs *et al.*, 2006; McGrath, 1994; McGrath *et al.*, 1995) and as a result legislation (i.e. SI, 1989) and the Code of Practice for the Agricultural Use of Sewage Sludge (DoE, 1996) limit heavy metal loading rates to soils.

In contrast, there are no guideline or limit values controlling Organic Compound Contaminant (OCC) loading rates to agricultural land. However, the 3rd Working Document of the EU Commission on Sludge Management (EU, 2000) and the Second Draft Working Document on the Biological Treatment of Biowaste (EU, 2001) contained proposed limit values for polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins/dibenzofurans (PCDD/Fs) and polycyclic aromatic hydrocarbons (PAHs), amongst others (Table 1).

Table 1: Proposed limit values for concentrations of organic compound contaminants in sewage sludge and biowaste (EU, 2000; EU, 2001)

Organic Compound Contaminants	Limit values (mg/kg dry matter)
Polycyclic Aromatic Hydrocarbons (PAHs)[1]	6[4]/3[5]
Polychlorinated Biphenyls (PCBs)[2]	0.8[4]/0.4[5]
Absorbable Organic Halogens (AOXs)	500[4]
Linear Alkylbenzene Sulphonates (LASs)	2,600[4]
Di(2-ethylhexyl)phthalate (DEHP)	100[4]
Nonylphenol and Nonylphenolethoxylates (NPEs)	50[4]
	Limit value (ng TE[3]/kg dry matter)
Polychlorinated dibenzodioxins/ dibenzofurans (PCDD/Fs)	100[4]

[1] Sum of acenapthene, phenanthrene, fluorene, pyrene, benzo(b+j+k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene indeno(1,2,3,c,d)pyrene
[2] sum of PCB numbers 28, 52, 101, 118, 138, 153, 180
[3] TE = Toxic equivalent
[4] EU (2000)
[5] EU (2001)

More recently, the 3rd Working Document on Proposed End-of-Waste Criteria for "Biodegradable Waste Subject to Biological Treatment" (IPTS, 2012) contained proposed standards for various OCCs including some previously proposed and some new OCCs (i.e. Perfluorinated compounds – PFC), Table 2. As a result, it is likely that OCCs will receive ongoing attention and limit values may be put in place, which organic resources will have to meet, in order to be considered 'suitable' for recycling to land.

Table 2: Proposed limit values for concentrations of organic compound contaminants in biodegradable waste (IPTS, 2012)

Organic Compound Contaminants	Limit values (mg/kg dry matter)
Polycyclic Aromatic Hydrocarbons (PAHs)[2]	6.0
Polychlorinated Biphenyls (PCBs)[1]	0.2
Perfluorinated compounds (PFCs)[3]	0.1
	Limit value (ng TE[4]/kg dry matter)
Polychlorinated dibenzodioxins/ dibenzofurans (PCDD/Fs)	30

[1] sum of PCB numbers 28, 52, 101, 118, 138, 153 and 180
[2] sum of naphthalene, acenaphthylene, acenapthene, fluorene, phenanthrene, anthracene, , fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3,c,d)pyrene, dibenzo(a,h)anthracene, benzo(ghi)perylene.
[3] sum of Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS)
[4] TE = Toxic equivalent

Notably, there is little consensus between the three determinands (i.e. EU, 2000; EU, 2001; IPTS, 2012) in terms of the OCCs proposed, congeners selected (particularly for PAHs) and the level at which proposed limit values are set.

PAHs are of particular concern to regulators and stakeholders because of their relatively long persistence in the environment. They are produced when organic matter containing carbon and hydrogen is exposed to temperatures exceeding 700°C i.e. during pyrolytic processes and incomplete combustion. Most direct PAH releases are to the air, both from natural (e.g. forest fires and volcanoes) and anthropogenic (e.g. power generation, domestic burning of wood, vehicle engines) sources. PAHs typically reach soils as a result of atmospheric deposition, with metropolitan areas generally have higher concentrations than rural areas, due to their proximity to emission sources. Numerous studies have identified the presence of and reported PAH concentrations in feedstuffs, drinking water, stable dust, pig slurry, road dust and in soils (Mantseva *et al*., 2002; Raszyk *et al.,* 1998; EA, 2007; Petersen *et al*., 2003; Berset and Holzer, 1995).

Methodology

Whilst a wide range of studies have been undertaken (primarily in the laboratory) examining PAH degradation in soils and in particular interactions with microbial communities (e.g. Obuekwe and Semple, 2011), there are few field-based studies that have examined potential soil accumulation following repeated biosolids applications.

In order to assess the potential for long-term soil accumulation, archived biosolids samples and soil samples from the Defra/United Kingdom Water Industry Research-UKWIR/Scottish Government/Environment Agency/Welsh Government funded "Long-term Sludge Experiments (LtSEs)" were utilised. The LtSEs are a multi-site field study that was set up in 1994 to examine the impacts of heavy metals in sludge on soil fertility and microbial activity (e.g. Gibbs *et al.*, 2006; Chaudri *et al.*, 2007; Chaudri *et al.*, 2008).

The nine experimental sites (6 in England, 2 in Scotland and 1 in Wales) *viz*: Gleadthorpe (GLE), Woburn (WOB), Watlington (WAT), Pwllpeiran (PWL), Rosemaund (ROS), Bridgets (BRI), Hartwood (HAR), Auchincruive (AUC) and Shirburn (SHI) were selected to represent a range of soil physical and chemical properties, in particular clay and organic matter contents, throughout Britain (Figure 1).

Figure 1: Location of "Long-term Sludge Experiment" sites

Annual applications of sludge cakes containing elevated levels of Zn, Cu and Cd, and low-metal sludges were applied over the period 1994-2004 (i.e. 11 years). In the case of elevated metal sludge, cakes Zn and Cd additions were at the maximum permitted metal loading rates detailed in the Sludge Use in Agriculture Regulations (SI, 1989) and Code of Practice for Agricultural Use of Sewage Sludge (DoE, 1996), with the low-metal sludges applied to supply the same quantity of organic matter.

Results and discussion

Achieved samples of the sludges applied between 1994 and 2004 were analysed for PAH concentrations with concentrations; mean PAH concentrations in the low-metal sludge cake were 2.6 mg/kg dm, in the Zn rich sludge were 11.2 mg.kg dm and in the Cd rich sludge were 5.6 mg/kg dm. The estimated PAH loading (sum of the 9 EU priority congeners) over the 11 year period at the seven sites in England and Wales were calculated (Table 3).

Table 3: Long-term (1994-2004; 11 years) dry solids and PAH loadings to "Long-term Sludge Experiment" sites

Sludge cake type*	Total dry solids loading rates (t/ha) at sites							PAH loading rates (kg/ha) at sites**						
	Gle	Wob	Wat	Pwl	Ros	Bri	Shi	Gle	Wob	Wat	Pwl	Ros	Bri	Shi
Low-metal	19.6	28.7	29.7	29.4	29.0	29.4	29.5	0.11	0.11	0.11	0.11	0.11	0.11	0.11
Zinc rich	32.6	33.7	32.1	31.9	32.7	39.6	32.1	0.31	0.34	0.30	0.30	0.32	0.35	0.31
Cadmium rich	37.4	35.6	35.7	36.0	36.3	36.0	36.3	0.16	0.15	0.15	0.15	0.16	0.15	0.16

* Treatments are a combination of zinc or cadmium rich sludge and low-metal sludge in approximately a 70:30% ratio for the zinc rich treatment, and a 60:40% ratio for the cadmium treatment.

** PAH concentrations are the sum of Acenaphthene, Benzo(a)pyrene, Benzo(b+k)fluoranthene, Benzo(ghi)perylene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Phenanthrene, Pyrene (i.e. 9 congeners).

The archived soil samples from spring 2005 (i.e. following 11 years of biosolids additions) were analysed for PAH concentrations (Table 4).

Table 4: PAH concentrations in soil samples from the "Long-term Sludge Experiment" sites

Treatments	PAH concentrations in soil (mg/kg dry matter)*						
	Gleadthorpe	**Woburn**	**Watlington**	**Pwllpeiran**	**Rosemaund**	**Bridgets**	**Shirburn**
Untreated control	0.69	0.50	0.22	0.17	0.17	0.19	0.36
Low-metal	0.56	0.51	0.34	0.20	0.17	0.24	0.33
Zinc rich	0.63	0.49	0.30	0.18	0.23	0.21	0.33
Cadmium rich	0.68	0.50	0.36	0.19	0.30	0.23	0.38
Statistical significance	NS (P>0.05)	NS (P>0.05)	NS (P>0.05)	NS (P>0.05)	NS (P>0.05)	NS (P>0.05)	NS (P>0.05)

* PAH concentrations are the sum of Acenaphthene, Benzo(a)pyrene, Benzo(b+k)fluoranthene, Benzo(ghi)perylene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Phenanthrene, Pyrene (i.e. 9 congeners).

The results clearly show that at all seven sites in England and Wales, there were no significant increases ($P>0.05$) in soil PAH concentrations above the untreated control.

Conclusions

The results from all seven sites following repeated biosolids applications over an eleven year period, showed that there were no significant increases ($P>0.05$) in soil PAH concentrations (sum of the 9 EU congeners of concern) above the untreated control. The lack of any statistically significance increase in soil PAH concentrations above the untreated control, and the similarity of PAH concentrations across the four treatments at each site, demonstrate the dominance of background (soil) PAH concentrations. In summary, the repeated application of biosolids did not significantly impact on overall soil PAH concentrations.

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