What is representative of the environment in the laboratory

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Abstract

Successful bioremediation of soil at gas works sites is assessed by accurately collecting and analysing representative samples for total and leachable PAHs and comparing these with the risk derived site specific data using standard methods. Analytical procedures are standardised to reduce error. Unfortunately standardisation does not explore where the sub-sample is selected and whether the test chosen is representative. Differences in laboratory sample selection, preparation, and extraction methods are so great that results can be meaningless even when standard methods are used. This paper examines the various approaches adopted in regard to analysing total and leachable PAHs. We found that results are being presented that are internally precise and accurate but are not representative.

Key Words

Polycyclic aromatic hydrocarbons (PAHs), grinding, ultrasonic, soxhlet.

Introduction

The aim of any investigation, remediation or validation is to deliver data that is: representative of what is sampled; precise; accurate; and reproducible. A sample can be precise, reproducible and accurate but the question must still be asked as to whether it is representative of the environment. This cannot be answered by the laboratory but only by the investigator. The investigator must question whether a laboratory test represents what they are wishing to measure, as each test is designed for a specific purpose i.e. to measure a specific aspect of the soil environment (e.g. Curtis and Narayanan 1998). This paper explores the ways in which current laboratory techniques and testing can vary between laboratories; how these variations influence data; and how individual PAH's physiochemical properties effect how a sample behaves under the differing preparation methods and extraction techniques.

Error one: Random elevated concentrations (nugget effect)

The Enhanced Bioremediation process generally involves material to be screened, mixed and turned regularly (e.g. Van Deuren *et al.* 2002). The mixing occurs several times and turning at least 15 times; this results in a relatively homogenised stockpile. During the process the stockpiles are sampled at discrete time intervals for operational reasons. It is common for stockpiles to exhibit a single random elevated organic compound (PAH) concentration approximately 1 to 3 months after the commencement of treatment. Historically this single elevated result has been attributed to the 'nugget effect' which is considered to be spatial variability within the sample selected from the container, resulting in the sample not representing the remainder of the container (i.e. an imprecise result) (e.g. Starks 1986; Don Scott 2000). The 'nugget effect' occurs as residual PAHs in the soil mass have been degraded and removed but PAHs in coke have not. Therefore consistent results depend on creating a homogenous sample and not sampling areas that have a greater amount of coke in the sub sample than is generally found within the greater mass of the sample. Data presented from a bioremediation project in Australia (Table 1) shows the variability of two (SR8-0.3m) and four (SP13-1) samples analysed from a single container. This clearly shows that although the data presented by the laboratory is accurate and precise it is not representative of the stockpile or soil environment.

Table 1. Replicates within a single Jar.

	SP13-1	SP13-1 Dup	SP13-1 Trip	SP13-1 Quad	SR8 -0.3m	SR8 -0.3m Dup
Phenanthrene	18	1.2	1.1	1.4	NT	NT
Anthracene	8.6	<1.0	<1.0	<1.0	NT	NT
Pyrene	15	2.3	2.5	3.4	NT	NT
BaP	11	1.3	1.9	2	100	0.23
Total PAHs	123	12	14	18	964	2.5

Note: units=mg/kg; NT = not tested.

Error Two: Sample preparation procedure

Currently there is no standardised method of preparing soil samples in the UK prior to the analysis of PAHs. The method undertaken to separate the gravel (>2 mm) from the soil (<2 mm) can include crushing, grinding, sieving or hand selection. Obviously the extent or ferocity of the grinding or crushing will influence whether clay aggregates and/or gravel size particles are broken down.

Three months into a large bioremediation project in the UK (remediating 50,000 m^3 of tar products plant and gas works spoil), every sample in all 15 stockpiles increased by a similar factor, particularly for 5 and 6 ring PAHs, as apparent at Day 35 in Figure 1 (data for one stockpile only). All stockpiles were influenced and then showed degradation from this unusual peak indicating this was not solely due to the nugget effect. An investigation was undertaken, which included a review of sources of error such as: non homogenous sample; sampling method; equipment; transport; laboratory preparation method; laboratory extraction methodology; and calculations. The investigation concluded that the only explanation was the sample preparation technician at the laboratory being on leave.

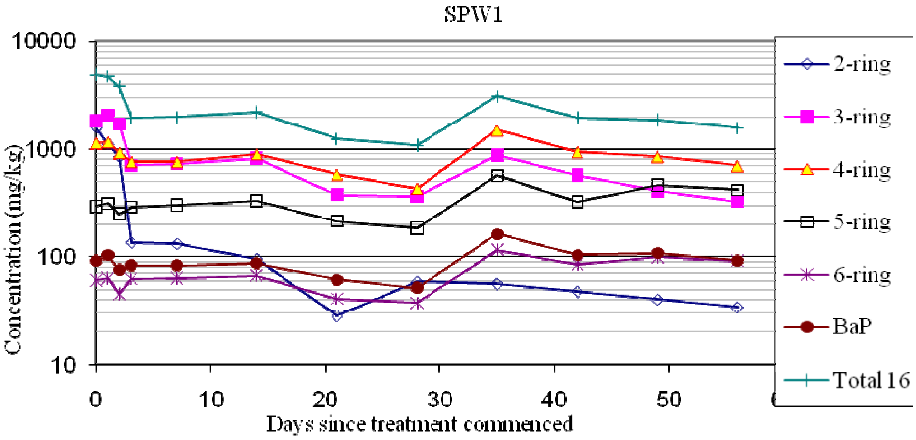

Figure 1. PAH Degradation with time – Northern England (note: logarithmic scale on y-axis).

To further investigate whether the presence of black carbon (i.e. ash, coke, clinker, slag and coal) being crushed during sample preparation was influencing the result of analyses, a single bulk homogenised sampled was prepared by eight methods. These eight methods were identified as potential sources of error based on observations when the samples were accompanied through the laboratory (data not shown). The eight sample preparation methods are summarised in Figure 2 with data presented in Table 2.

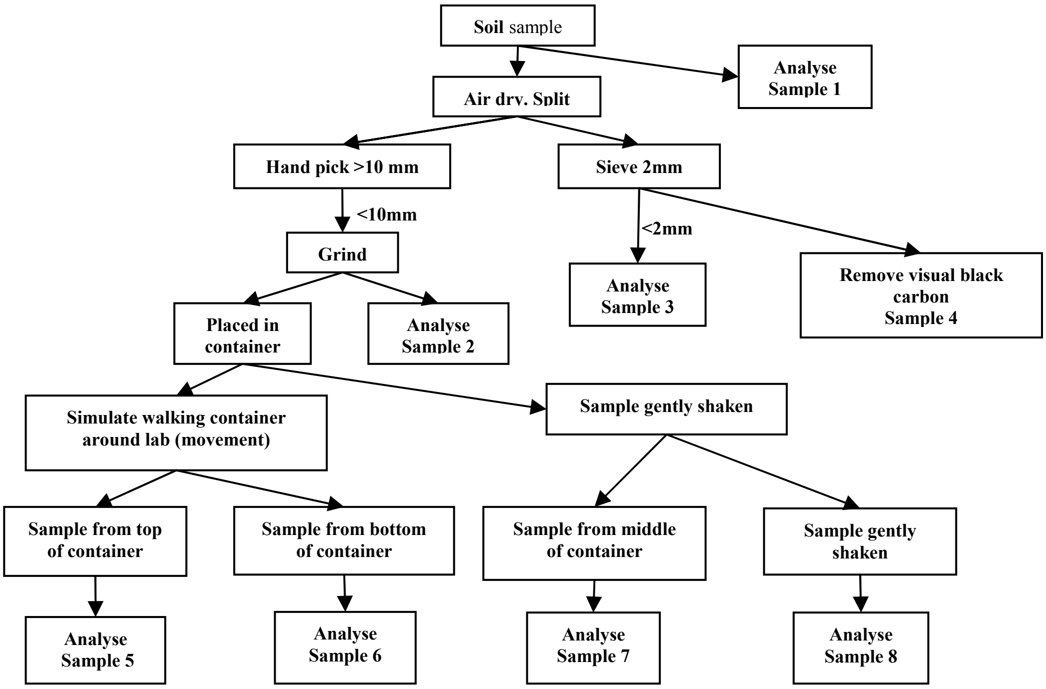

Figure 2. Summary of sample preparation method.

The PAH concentration ranged from 1239 (Sample 5) to 5777 (Sample 8) mg/kg from the same sample but subjected to different preparation methods (Table 2).

Table 2. Influence of sample preparation on single sample.

Sample	1	2	3	4	5	6	7	8
Phenanthrene	141	76	55	53	40	77	87	190
Anthracene	286	132	83	80	61	130	140	300
Pyrene	653	439	460	480	230	480	520	1100
BaP	265	154	180	180	78	160	170	370
Total PAHs	3494	2314	2252	2264	1239	2548	2740	5777

Note: units=mg/kg.

Error Three: Extraction method

The extraction of organic compounds from soil, sediment, sludges, and waste solids can be undertaken by several methods including: (i) Soxhlet extraction (USEPA Methods 3540 and 3541) (ii) ultrasonic extraction (USEPA Method 3550); (iii) accelerated solvent extraction (USEPA Method 3545A); and (iv) steam distillation. Currently there is no single standard method for the analysis of nonpolar trace organics

PAH contaminated material at MGP sites and most brownfield sites is not freshly contaminated but rather aged and often contains black carbon. To investigate the impact of extraction method on the aged material we commissioned a blind trial with three laboratories using field duplicates for a gas works soil containing black carbon. Sample preparation techniques were uniformly specified between the laboratories but extraction was not specified. Laboratory A and B used a soxhlet extraction whilst Laboratory C used ultrasonic extraction.

The results are summarised in Table 3 and show the total PAH extracted for ultrasonic extraction ranged from 260 to 1300 mg/kg whilst the soxhlet ranged from 1374 to 2653 mg/kg. The soxhlet extraction was 1.5 to 5.6 times more efficient than ultrasonic extraction for total PAH in the presence of black carbon and was not influenced by ring number. This supports ASTM comments that ultrasonic extraction is less efficient with very nonpolar compounds in certain circumstances.

Table 3. Comparison of extraction methods.

Sample	SPW6A			SPW5A			SPW3A			
Extraction	Sox	Sox	U/S	Sox	Sox	U/S	Sox	Sox	Sox	U/S
Laboratory	A	B	C	A	B	C	A	A	B	C
Phenanthrene	274	290	42	244	300	120	371	435	450	210
Anthracene	148	170	39	132	180	180	195	210	270	230
Pyrene	165	220	32	209	320	150	283	324	410	180
BaP	49	62	9	63	84	34	92	93	110	39
Total PAHs	1479	1577	260	1374	1755	880	2175	2351	2653	1300

Note: units=mg/kg; Sox = Soxhlet; U/S = Ultrasonic.

Conclusions

In the UK samples for analysis for metals and PAHs are prepared by air drying, removing stones (but not oversized coke) and grinding to 0.150 mm or 2 mm. Unfortunately the grinding of coke in the sample results not only in more PAHs being analysed but also creates the opportunity for the "nugget effect" to occur, biasing the results upwards. In summary we found that:

- Samples are more susceptible to the "nugget effect" as treatment proceeds as residual PAHs in the soil mass have been removed by bioremediation but PAHs in coke have not. Therefore the results depend on creating a homogenous sample and not sampling areas that have a greater amount of coke in the sub sample than is generally found within the greater mass of the sample.
- The grinding of soil samples during laboratory preparation produces errors which are dependent on the amount and type of gravel sized fractions present. It can act to both increase or decrease the compound concentration and thereby does not provide a reproducible representation of the environment.
- Soxhlet extraction of samples containing Black Carbon might be too aggressive and result in the decaying or swelling of silica and some silicates thereby not providing an accurate representation of the environment.

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