A CASE STUDY OF POLYCYCLIC AROMATIC HYDROCARBON CONTAMINATION AROUND A FORMER GASWORKS SITE

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Introduction

In the UK, the production of coal gas for lighting purposes began in the 19th century[1]. The by-products of this process were often stored at the site, and this has led to the ground in and around gasworks being contaminated with a variety of wastes and chemicals, including Polycyclic Aromatic Hydrocarbons (PAH). Although PAH are neither very soluble in water nor volatile, they can migrate with groundwater flow as floating particles and become entrained in soil or sediments. They are readily accumulated by shellfish, and PAH contamination in shellfish is of concern regarding human consumption as many PAH form carcinogenic metabolites. Coal gas provided the major source of town gas until the late 1950s when many gas works took advantage of cheap refinery products and converted to oil-gas plants. Following the introduction of natural gas from the North Sea, the manufactured gas production declined and a majority of town gas works closed in the 1970s.

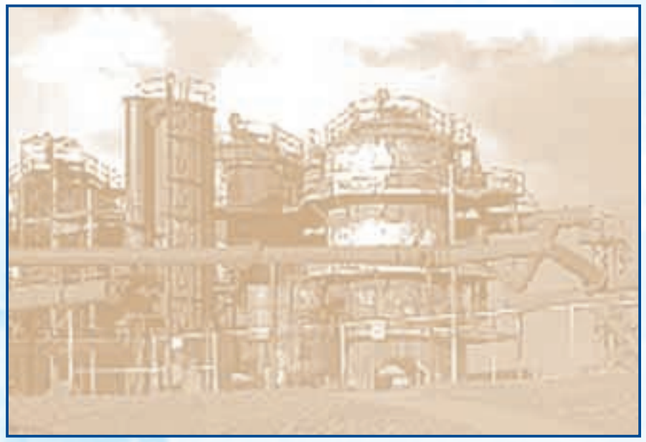

Figure 1: Coal gas works circa 1920

Methods

Concentrations of PAH have been determined in sediments, mussels and crustacea in the vicinity of a former gasworks site on the south coast of England.

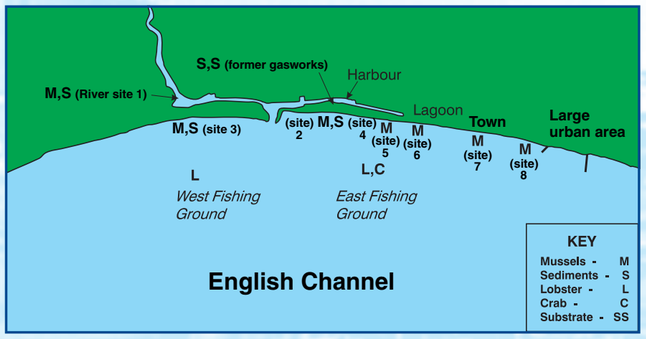

Figure 2: Map of study area and sampling points

Figure 3: PAH analysis by gas chromatography-mass spectometry

The PAH were extracted from the samples using alkaline saponification and analysed using a GCQ ion trap mass spectrometer[2]. Analyses were conducted within an analytical quality control scheme, and a procedural blank and a reference material were analysed within each batch of samples.

Results

Elevated PAH concentrations were found in mussels both from the beach below the former gasworks site, and from sites further to the east in the direction of the longshore drift. The significance of these concentrations was assessed using a toxic equivalency approach. The concentrations of individual PAH were summed on the basis of their comparative potency as carcinogens and the PAH concentrations expressed as benzo[*a*]pyrene equivalents (BaPEs) [3,4] (Table 1). The BaPE values obtained ranged from zero in crustacea collected within a mile of the shore, to 336 µg kg^{-1} wet weight in mussels from the beach below the gasworks site. Mussels from these beaches are not commercially exploited.

Table 1: Summed concentrations of PAH expressed both in concentrations (SPAH) and as benzo[a]pyrene equivalents (µg kg^{-1} wet weight for biota and dry weight for sediments)

Species and tissue	Location	∑PAH	BaPEs
mussel	bottom of beach below former gasworks site 2	3060	245
mussel	bottom of beach below former gasworks site 2	6450	336
mussel	beach to west of harbour site 3	57	1.9
mussel	River commercial bed site 1	80	2.7
mussel	groyne on beach below former gasworks site 4	1260	63
mussel	beach to east of harbour site 5	1960	209
mussel	beach to east of harbour site 5	2820	298
mussel	below Lagoon (westerly groyne) site 6	1410	117
mussel	below Lagoon (easterly groyne) site 6	926	75
mussel	Town beach (westerly groyne) site 7	1440	85
mussel	Town beach (west central groyne) site 7	778	53
mussel	Town beach (east central groyne) site 7	585	31
mussel	Town beach (easterly groyne) site 7	1107	50
mussel	large urban area (westerly groyne) site 8	308	12
mussel	large urban area (easterly groyne) site 8	301	12
lobster claw	West fishing grounds	34	0.5
lobster tail	West fishing grounds	28	0.4
lobster hepatopancreas	West fishing grounds	143	2.1
lobster hepatopancreas	East fishing grounds	130	0.2
lobster claw	East fishing grounds	9.1	0
lobster tail	East fishing grounds	4.9	0
spider crab body	East fishing grounds	16	0
edible crab body	East fishing grounds	14	0
Sediment type	**Location**	**∑PAH**	**BaPEs**
sand	bottom of beach below former gasworks site 2	133	14
sand	beach to west of harbour site 3	7	1.4
sand/mud	River site 1	8234	872
sand	beach below former gasworks site 4	88	5.7
sand	beach below former gasworks site 4	401	26
substrate	former gasworks site	458094	61598

Very high concentrations of PAH were found in the substrate, an ash like material present at the former gasworks site. This had a PAH profile consistent with the major source of contamination being coal or coke tar produced as a by-product during the period of gas production. Coal and coke tars contain a wide range of parent PAH compounds and the acquisition of full-scan GC/MS data allows the isomer distributions within these classes to be used for fingerprinting purposes. The PAH profiles seen in the mussels both from the beach below the former gasworks and from beaches to the east were found to be similar to those from the former gasworks site. This technique also revealed an extremely close match between the isomer distributions of two groups of PAH (of molecular weight 278 and 302 Daltons) found in coal tar[5] in another pair of samples. These were the substrate from the former gasworks site, and the sediment sample from the river upstream of the harbour, which supported a commercial mussel bed.

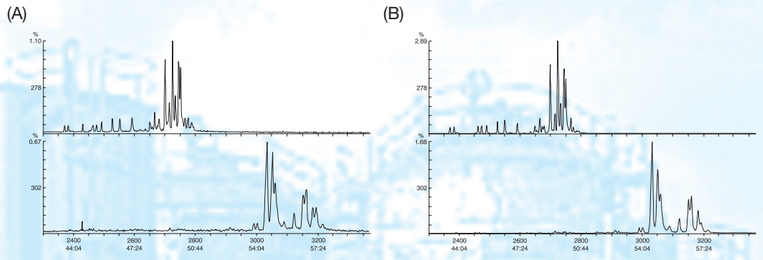

Figure 4: Mass chromatograms for PAH of molecular weight 278 and 302 Daltons (A) in sediment from the River and (B) in substrate from former gasworks site

This suggested :

1. PAH from the former gasworks site were being transported underneath the beach directly below the gasworks site and to the sea, although whether this was as a result of groundwater flow or tidal flushing is not known.
2. PAH are also being transported from the harbour to the river, probably in association with fine particulate material which is subsequently deposited to the river sediments. PAH contamination of the mussels from the commercially classified shellfish bed in the river, was, however, much lower than that seen on the beaches below the harbour. (Table 1 and Figure 2).

Figure 5: Mussels on groyne at site 4

The phenanthrene : anthracene ratio proved to be a sensitive indicator of the spread of PAH contamination due to the gasworks leachate. Figure 6 shows the ratio plotted against the mussel sampling locations, moving from west to east in the direction of the residual flow. The ratio is high initially in mussels from the commercial bed in the river (9.0), typical of oil contamination or a mixed source. Mussels from beach sites between the river and town were lower (2.4 to 3.3), and closer to the value of 1.26 seen in the substrate taken from the former gasworks site. Low values indicate that the major source there was from combustion processes rather than oil. The ratios rose again to values around 5 in mussels from the most distant site, showing that the influence of the gasworks leachate was reduced at that location.

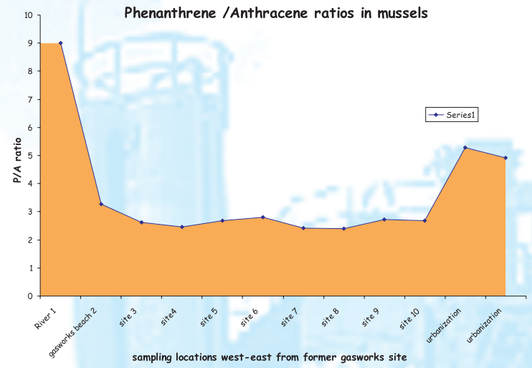

Figure 6: Phenanthrene : Anthracene ratios in mussels, plotted against sampling location

Conclusion

- This study has demonstrated the extent of PAH contamination, deriving from the former gasworks site, in local biota and sediments. As a result, the local councils have placed notices along the beach recommending that the mussels not be harvested.
- This is however unlikely to be an isolated incident. As the UK had around 1800 coal carbonisation sites prior to the advent of natural gas from the UK continental shelf, and many of these would have served as gasworks in coastal communities or by rivers and estuaries.
- Severe contamination of the ground underlying gasworks sites is a common feature, and the mobility of PAH and other contaminants will be dependent on the ground structure and water movement beneath these sites.
- Coal and coke tars contain a much wider range of high molecular weight PAH than crude oils. Many of these additional PAH compounds are also known or suspected carcinogens[6], but were not determined in this study, and are compounds for which toxic equivalency factors have not yet been developed.
- The BaPE values reported in this study are therefore minimum estimates at the present time and state of knowledge. A wider range of PAH will need to be determined in the future as knowledge of their sources and effects develops.

References

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