

Demonstration of Variability: Concentration of Polynuclear Aromatic Hydrocarbons (PAHs) in Soil.

PAHs are organic compounds consisting of highly conjugated ring systems containing only carbon and hydrogen atoms¹⁻⁵. They are produced as a result of incomplete combustion of hydrocarbons originating from oil, tar and coal. They are considered powerful carcinogens, mutagens and teratogens, and thus represent a significant risk to human health. For this reason, PAHs are closely monitored pollutant in the environment¹⁻⁵.

The introduction of PAHs into the body happens via ultrafine particulate matter

less than 2.5 μm in diameter. The upper

respiratory tract is unable to eliminate these ultrafine particles from inhaled air, therefore providing an absorption pathway for PAH compounds through the alveoli of the lungs. It therefore is imperative that the PAH concentration of soil in potentially contaminated sites is determined to avoid possible health hazards.

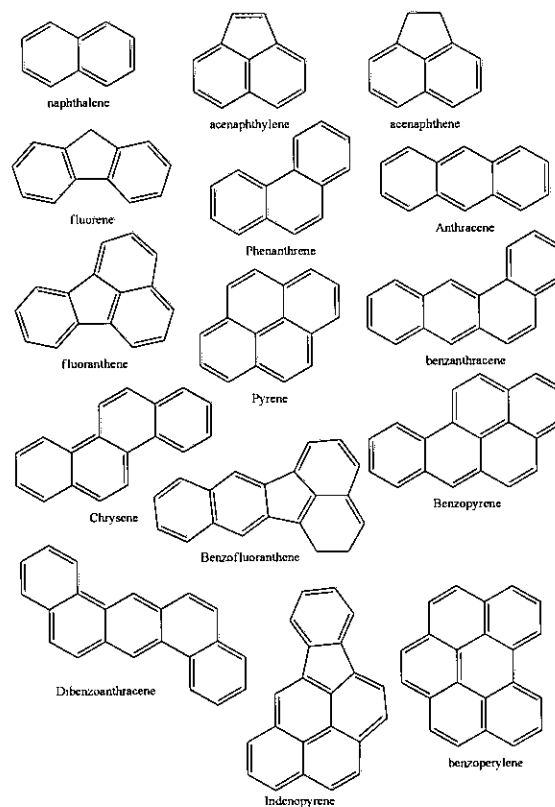
In chemical analysis, typically a single value is sought that summarises some property of a large collection of material (in this case the concentration of PAHs). In very thorough analyses, a sample grid is implemented to gain information regarding the concentration distribution over a large sample space⁶. What is often overlooked however is the inherent variability within even the smallest samples, which often gives rise to unfounded chemical determinations. In

the following demonstration, fifteen 10-g

samples of soil originating from a single jar were analysed and the concentration of 15 different PAH species were determined.

For each 10-g sample, a routine

analytical procedure was utilised consisting of a solvent extraction followed by GC-MS detection. This detection method is very robust and sensitive enough to be able to accurately quantify PAH concentrations down to the sub-ppm scale^{3,6,7}. Due to the degree of accuracy inherent in this technique, any discrepancy that arises between each soil sample is in fact indicative of a *real discrepancy*, owing to the non-homogeneity of the gross soil sample.



remaining samples PAH concentrations were summed as shown in Figure 1.4.

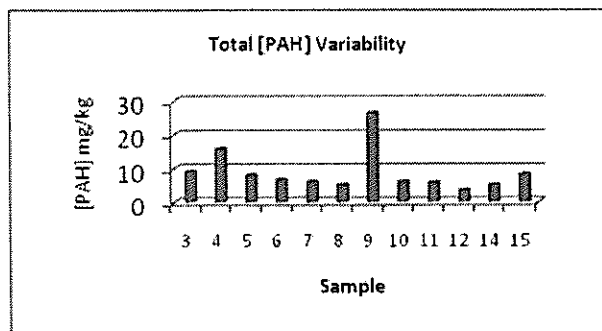


Figure 1.4: Total PAH variability with outliers (most variates data) removed.

The total PAH concentration was

determined to be $8.88 \pm 12.50 \text{ mg} \cdot \text{kg}^{-1}$ of

(1) Baek, S. O.; Goldstone, M. E.; Kirk, P. W. W.; Lester, J. N.; Perry, R. *Chemosphere* **1991**, *22*, 503 - 520.

(2) Dipple, A. In *ACS Symposium Series 283*; ACS: Washington, DC, 1985.

(3) Lawrich, R. J.; Hays, M. D. *Journal of Analytical Chemistry* **2007**, *79*, 3635 - 3645.

(4) Otson, R.; Leach, J. M.; Chung, L. T. K. *Journal of Analytical Chemistry* **1987**, *59*, 1701 - 1705.

(5) Wang, H.; Campigia, A. D. *Journal of Analytical Chemistry* **2008**, *80*, 8202 - 8209.

(6) Skoog, D. A.; West, M. W.; Holler, F. J.; Crouch, S. R. *Fundamentals of analytical chemistry*; Thompson Brooks Cole: Belmont, CA, 2004.

(7) Woodget, B. W.; Cooper, D. *Samples and standards*; Wiley: London, 1987.

soil. Note that the uncertainty (95% confidence interval) is larger than the determination itself. In the past, sampling theory has allowed for equations to be developed⁷⁻¹⁷ that will allow an analyst to calculate the size and quantity of sample required to arrive at a reasonable determination. With further research, a similar set of equations can be produced to overcome the sampling quandary outlined here.

References:

(8) Pittard, F. F. *Pierre Gy's sampling theory and sampling practice*; CRC Press: Boca Raton, FL, 1989.

(9) Devore, J. L.; Farnum, N. R. *Applied statistics for engineers and scientists*; Duxbury Press: Pacific Grove, CA, 1999.

(10) Miller, J. C.; Miller, J. N. *Statistics and chemometrics for analytical chemistry*; Prentice-Hall: Upper Saddle River, NJ, 2000.

(11) Herrington, B. L. *Journal of Chemical Education* **1937**, *14*, 544.

(12) Bishop, J. A. *Journal of Chemical Education* **1958**, *35*, 31.

(13) Kratochvil, B.; Reid, R. S.; Harris, W. E. *Journal of Chemical Education* **1980**, *57*, 518 - 520.

(14) Bauer, C. F. *Journal of Chemical Education* **1985**, *62*, 253.

(15) Hern, J. A. *Journal of Chemical Education* **1988**, *625*, 1096.