



Comparative water sampling methodologies for the recovery of post-blast 2,4,6-trinitrotoluene explosive residues

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Introduction



Representative sampling is difficult to achieve due to the heterogeneous nature of explosive contaminations and environmental conditions



Water is a fluid medium, therefore highly heterogeneous environment



Traditional sampling methods often produce highly variable results



Any given sample should reflect the distribution and composition of the residues in the environment



Two experiments launched comparing three sampling methods for bulk and trace contamination - grab, composite and 3-D MIS

Representative sampling defined in literature

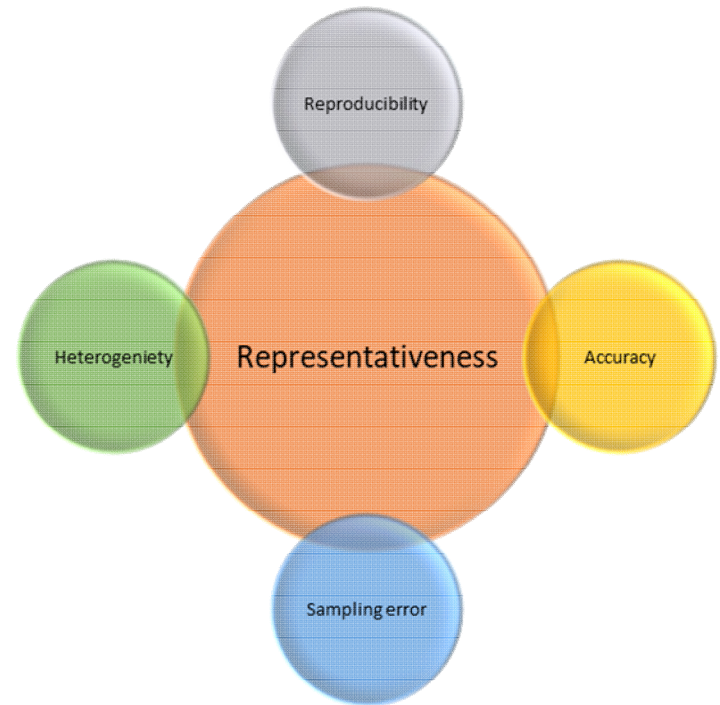
The process of choosing a sample that accurately represents the area of the environment being sampled while being small to be handled and transported easily to the laboratory (15)

Accuracy and reproducibility as well as precision, constitute the definition of representativity (2,17)

Representative sampling is nothing more than representative mass reduction (9,17)

Representativeness within science is defined through uncertainties that are fit for purpose (1)

Incorrectly extracted samples cannot be representative (18)



Experimental set up

- 100 g TNT fill & 20g PENO (80% PETN + 20% marker) used to trigger TNT
- Top of IBC cut off
- QC measures: Duplicate samples, Field blanks, Background samples
- Water collection through strategic placement of four paddling pools



Pipe bomb for HO/LO



Heterogeneity

The biggest source of error in sampling

All samples are heterogenous, at all scales

Distribution heterogeneity - caused by segregation of the sample (e.g. settling)

Constitutional heterogeneity - fundamental property of a material caused by differences in particle size and/or composition



Source: Staake, 2023

Grab sampling



Collecting a lump of material from a lot in a single operation



Each primary increment is processed and analysed separately, which increases both time and analysis costs



While this method is a very simple, approximative and cost-effective, it is far from ideal due to several inherent sampling errors



Failure to address heterogeneity and its representation limited to a specific moment and location (15)



Despite these drawbacks, grab sampling is outlined as the preferred method for water sample collection in the SIBCRA guidance

Composite sampling

Combining multiple samples into a single bulk sample

Reduces time and materials needed for analysis

Sample splitting

Increased volume from combining liquid samples can lower detection sensitivity

Concentrating the analytes using standard filtration methods can combat this issue

Potentially produce false negatives

Multi-increment sampling

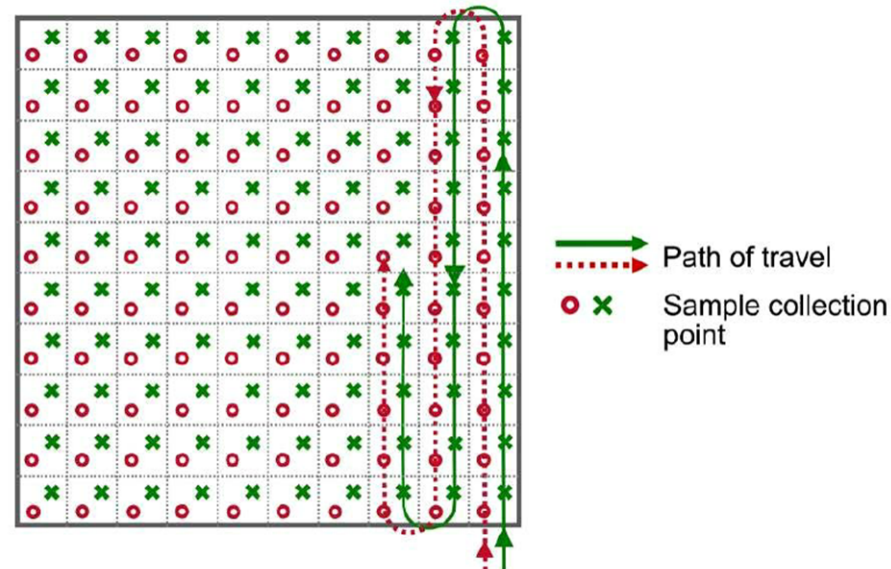
Considered the most representative method

Systematic sampling, pooling several primary increments into one overall sample

Sampling area is divided into a grid

A single grab sample is taken from approximately the same location within each square to form the pooled sample

To ensure representation of the full body of water- spatial aspect and be conducted three-dimensionally



Source: Walsh et al., 2014

Sampling modes



Random sampling – Sampling locations are randomly assigned within the lot, either along the time axis or geometrical axes, depending on case



Stratified random sampling – The lot is divided into sub-lots (called strata) before sampling. Within each stratum, increments, or samples are selected randomly



Systematic sampling – Samples are cut at equal distances (lags) along the time (or geometric) axes of the lot

High-order detonations vs Low-order deflagrations

- Most widely utilised approach
- Entails detonating an explosive donor charge around the unexploded ordinance
- Any live explosive material within the UXO detonates with it
- Highly effective
- This method produces loud underwater blasts that harm marine ecosystems (8)
- Smaller donor charges, which do not detonate the UXO
- Method pierces the UXO shell
- Thus, minimizing environmental damage
- Allowing it to burn out without detonation
- There is limited information about the effectiveness of low-order deflagrations

HO vs LO

IBC A



Pipe bomb fragments IBC A



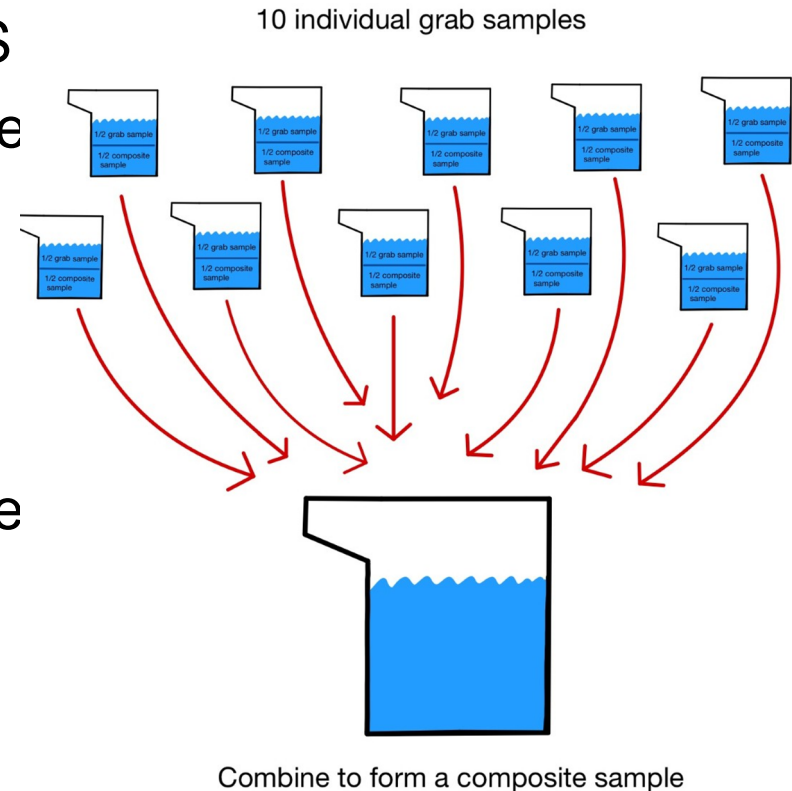
Pipe bomb fragments IBC C

IBC C



Methodology – Sample splitting

- Grab $\Rightarrow$ Composite $\Rightarrow$ 3-D MIS
- Sample location was chosen by sample not through algorithm or VSP
- 12 grab samples, in duplicates
- 6 from the surface of the IBC and one from each of the paddling pools
- 50% retained as individual grab sample (hazard mapping)
- 50% of each sample pooled into composite sample



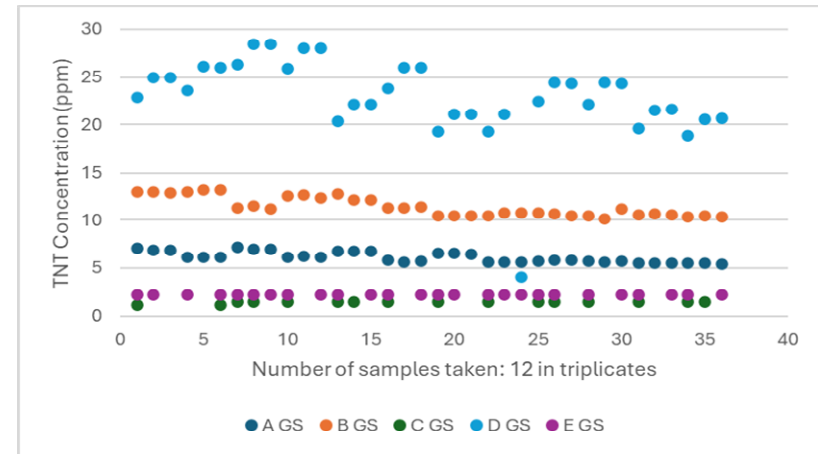
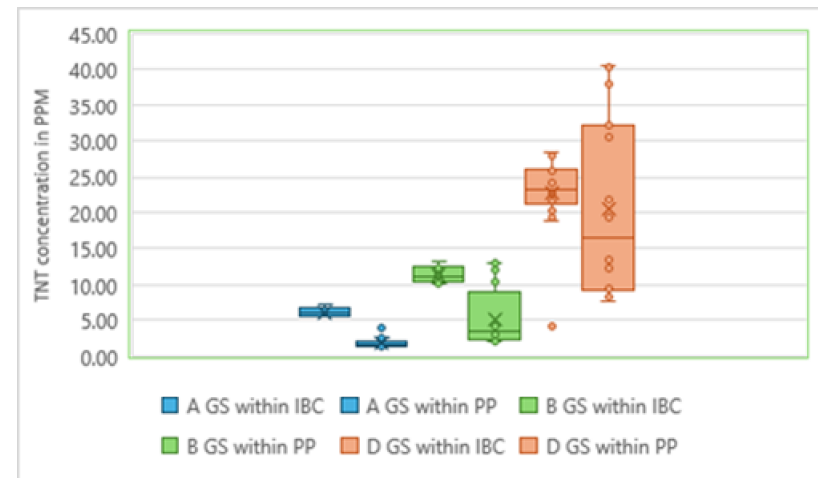
Methodology - 3D-MIS

- Sectioning the lot within the metal cage surrounding the IBC into 12 sub-lots across two layers
- 12 subsamples, six from layer one and six from layer two, were collected in duplicates
- Each subplot was sampled roughly in the same location



Results - Grab samples

- Mean values for LO ranged between 6.12 and 22.9 ppm
- Mean values for the HO range between 1.4 and 2.16 ppm
- TNT was detected in all LO samples
- TNT was detected in 44% of HO 'C', 72% in HO 'E' and 53% in HO 'F'
- Quantitative analysis was only possible for HO 'C' and 'E'
- Grab samples taken from the paddling pools, had a higher variance and an overall lower concentration of TNT
- The higher the residual concentration, the higher the variance within the samples



Results - Composite samples



As 40% of the composite sample originating from the paddling pools, the results were notably biased



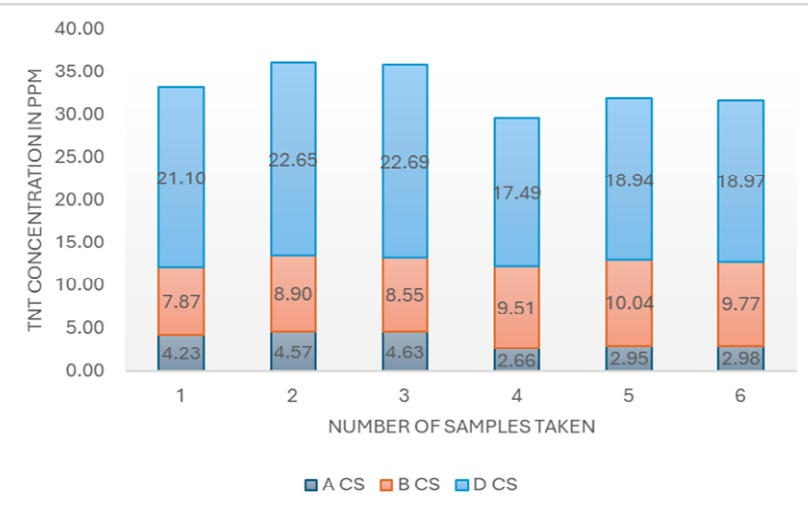
Quantitative analysis was only possible for LO samples



Limiting factor – further dilution of trace contaminant



With increasing concentrations, increase in standard deviation is observed



Results – 3D MIS



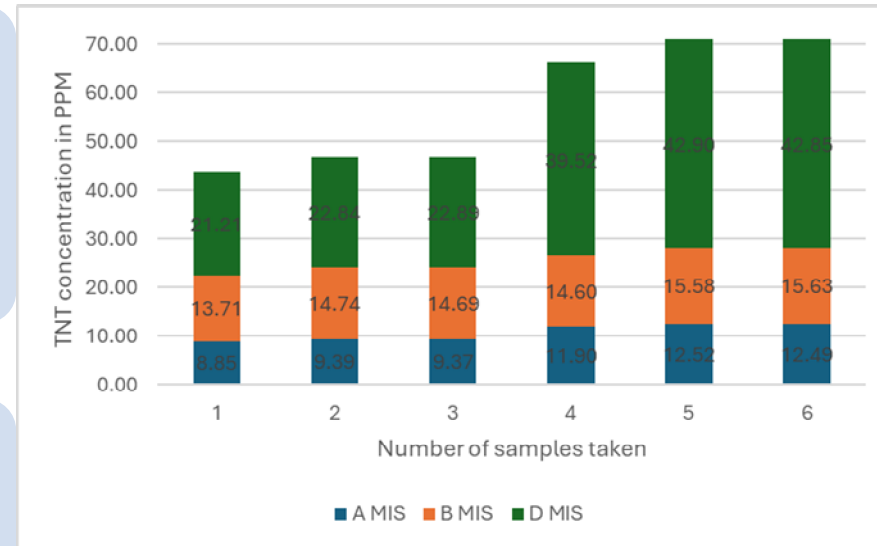
Samples were only taken for LO



Following HO, only 1/4th of the water remained in the IBC, hence samples would not represent the body of water



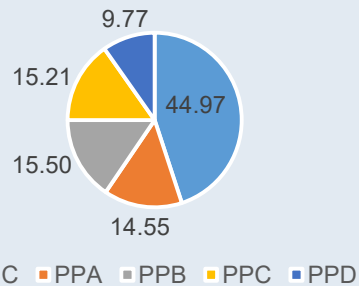
Limitation – labour intensiveness, requires substantial planning, equipment and time



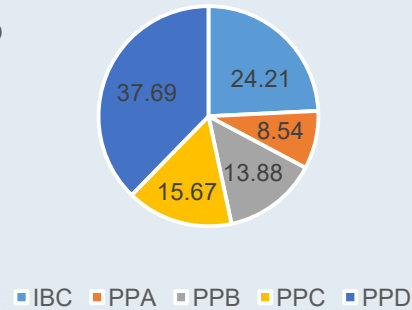
IBC	Sampling method	Mean	SD
A	MIS	10.76	1.72
B	MIS	14.83	0.71
D	MIS	32.03	10.74

Key findings

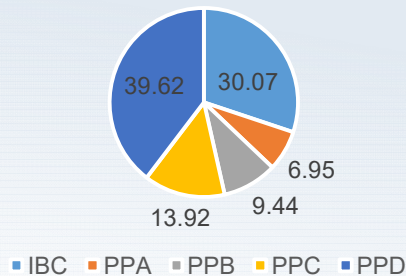
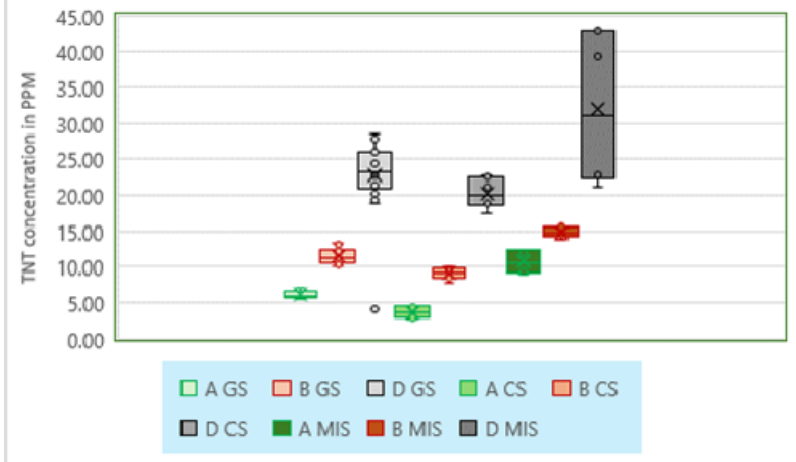
IBC A



IBC D



IBC B



- CS showed the lowest concentration, while the GS was found to be in the middle and the MIS showed the highest detected concentrations of TNT
- The closer the concentration of the analyte of interest is to the LoD of the equipment, the greater the number of samples required for reliable detection
- There is a need to select appropriate sampling methods based on the specific objectives and scope of the sampling
- GS useful for hazard mapping, intelligence, determination of level of heterogeneity
- CS significantly reduces the time taken for analysis, while requiring meticulous planning and coordination
- 3-D MIS shows need for spatial sampling of heterogeneous materials

Questions?



References

1. Analytical Methods Committee. (2016). Representative sampling? Views from a regulator and a measurement scientist. *Analytical Methods*, 8(24). <https://doi.org/10.1039/c6ay90077a>
2. Andrewes, P. (2023). Physical sampling practices and principles: Is it an underappreciated facet of dairy science? In *International Dairy Journal* (Vol. 136). <https://doi.org/10.1016/j.idairyj.2022.105491>
3. B. Geelhoed, M.J.J. Koster-Ammerlaan, G.J.C. Kraaijveld, P. Bode, D. S. Dihal, & H. Cheng. (2009). An experimental comparison of Gy's sampling model with a more general model for particulate material sampling. *Fourth World Conference on Sampling and Blending*.
4. Bodnar, M., Namieśnik, J., & Konieczka, P. (2013). Validation of a sampling procedure. In *TrAC - Trends in Analytical Chemistry* (Vol. 51). <https://doi.org/10.1016/j.trac.2013.06.011>
5. Burke, N., Zacharski, K., Adley, C. C., & Southern, M. (2021). A comparison of analytical test methods in dairy processing. *Food Control*, 121. <https://doi.org/10.1016/j.foodcont.2020.107637>
6. Dominy, S. C. (2007). Sampling - A critical component to gold mining project evaluation. *Australasian Institute of Mining and Metallurgy Publication Series*.
7. Esbensen, K. H., & Wagner, C. (2014). Theory of sampling (TOS) versus measurement uncertainty (MU) - A call for integration. In *TrAC - Trends in Analytical Chemistry* (Vol. 57, pp. 93–106). Elsevier B.V. <https://doi.org/10.1016/j.trac.2014.02.007>
8. Fox, T. (2022). *Marine Unexploded Ordnance, Clearance and Marine Licensing* | Ashfords. <https://www.Ashfords.Co.Uk/Insights/Articles/Marine-Unexploded-Ordnance-Clearance-and-Marine-Licensing-What-Developers-Need-to-Know>. <https://www.ashfords.co.uk/insights/articles/marine-unexploded-ordnance-clearance-and-marine-licensing-what-developers-need-to-know>
9. Gy, P. (1998). *Sampling for analytical purposes* (John Wiley & Sons, Ed.). Wiley.
10. Gy, P. (2004). Sampling of discrete materials - A new introduction to the theory of sampling: I. Qualitative approach. *Chemometrics and Intelligent Laboratory Systems*, 74(1), 7–24. <https://doi.org/10.1016/j.chemolab.2004.05.012>
11. Huizer, M., ter Laak, T. L., de Voogt, P., & van Wezel, A. P. (2021). Wastewater-based epidemiology for illicit drugs: A critical review on global data. In *Water Research* (Vol. 207). <https://doi.org/10.1016/j.watres.2021.117789>
12. Kabir, A., Furton, K. G., Paixão, T. R. L. C., Antunes, J., Coltro, W. K. T., Salles, M. O., Lião, L. M., Dennany, L., Brozek-Mucha, Z., Sharma, V., Vaz, B. G., & de Araujo, W. R. (2019). Forensic Analytical Methods. In T. R. L. C. Paixão, M. O. Salles, & W. K. T. Coltro (Eds.), *Forensic Analytical Methods* (1st ed.). Royal Society of Chemistry, 2019. <https://doi.org/10.1039/9781788016117>
13. Kruskal, W., & Mosteller, F. (1980). Representative Sampling, IV: The History of the Concept in Statistics, 1895-1939. *International Statistical Review / Revue Internationale de Statistique*, 48(2). <https://doi.org/10.2307/1403151>
14. Kuiper, H. A., & Paoletti, C. (2015). Food and feed safety assessment: The importance of proper sampling. *Journal of AOAC International*, 98(2). <https://doi.org/10.5740/jaoacint.15-007>
15. Madrid, Y., & Zayas, Z. P. (2007). Water sampling: Traditional methods and new approaches in water sampling strategy. *TrAC - Trends in Analytical Chemistry*, 26(4). <https://doi.org/10.1016/j.trac.2007.01.002>
16. Minkinen, P. O., & Esbensen, K. H. (2009). Grab vs. composite sampling of particulate materials with significant spatial heterogeneity-A simulation study of "correct sampling errors." *Analytica Chimica Acta*, 653(1). <https://doi.org/10.1016/j.aca.2009.08.039>
17. Petersen, L., Dahl, C. K., & Esbensen, K. H. (2004). Representative mass reduction in sampling - A critical survey of techniques and hardware. *Chemometrics and Intelligent Laboratory Systems*, 74(1), 95–114. <https://doi.org/10.1016/j.chemolab.2004.03.020>
18. Petersen, L., Minkinen, P., & Esbensen, K. H. (2005). Representative sampling for reliable data analysis: Theory of Sampling. *Chemometrics and Intelligent Laboratory Systems*, 77(1-2 SPEC. ISS.). <https://doi.org/10.1016/j.chemolab.2004.09.013>
19. Staake, J. (2023, February 13). *70 Easy Science Experiments Using Materials You Already Have On Hand*. <https://www.Weareteachers.Com/Easy-Science-Experiments/>.
20. Stoeppler, M. (Ed.). (1997). *Sampling and Sample Preparation*. Springer Berlin Heidelberg. <https://doi.org/10.1007/978-3-642-60632-8>
21. Temple, T. J., & Ladyman, M. K. (2020). *Global Approaches to Environmental Management on Military Training Ranges* (T. J. Temple & M. K. Ladyman, Eds.; 1st ed.). IOP Publishing. <https://doi.org/10.1088/978-0-7503-1605-7>
22. Walsh, M. R., Walsh, M. E., Gagnon, K., Hewitt, A. D., & Jenkins, T. F. (2014). Subsampling of Soils Containing Energetics Residues. *Soil and Sediment Contamination*, 23(4). <https://doi.org/10.1080/15320383.2014.8382>