An environmental forensics approach to differentiating sewage and manure nitrate inputs into surface waters
Cecilia Fenech¹, Luc Rock², Kieran Nolan³, John Tobin¹, Anne Morrissey⁴*
Corresponding Author*
¹School of Biotechnology, Dublin City University, Dublin 9, Ireland, ²School of Planning, Architecture and Civil Engineering, Belfast, BT9 5AG, N. Ireland, ³School of Chemistry, Dublin City University, Dublin 9, Ireland, ⁴Oscail, Dublin City University, Dublin 9, Ireland

Keywords: Chemical markers, environmental forensics, isotopes, nitrate, pharmaceuticals, SPE-LC-MS/MS.

In recent years, there has been increasing interest in environmental forensics applications in the area of nitrate source determination. Although nitrate is naturally found within the environment as part of the nitrogen cycle, anthropogenic sources such as synthetic nitrate fertilizer have greatly increased nitrate loads within ground and surface waters. Such elevated loads have led to severe impacts on aquatic ecosystems and has also given rise to health considerations in humans and livestock. Therefore, the identification of nitrate inputs is essential in preserving water quality and achieving sustainability of our water resources. This would allow for more effective remediation of contaminated sites and also the application of the polluter pays principle.

To date, stable isotopic compositions of nitrate (δ¹⁵N, δ¹⁸O) have been largely used to identify nitrate sources (Fig. 1) (Xue et al., 2009). This is because isotopes of the same element have slightly different chemical and physical properties, which result in mass-dependent isotope fractionation (Kendall and Caldwell, 1998). However, sewage and manure have overlapping δ¹⁵N and δ¹⁸O values, due to their similarity in that they are both essentially animal wastes. This has made their differentiation on this basis unviable. Nevertheless, the specific differentiation between sources of faecal contamination is of particular importance as the risk to humans is usually considered to be higher from human faecal contamination (sewage) than from animal faecal contamination since viruses, which represent an important basis of illness resulting from faecal exposure, are highly host specific (Field and Samadpour, 2007).

The use of co-occurring discriminators of sewage and manure in order to differentiate between sewage and manure nitrate inputs is hence required. In the present study, human and veterinary specific chemical markers are being assessed as markers of sewage and manure contamination respectively. Chemical markers such as pharmaceuticals, their metabolites and food additives are considered to be the most suitable co-occurring discriminators for sewage and manure. This is because such chemical markers are relatively water soluble and non-volatile, and their natural background levels within surface waters are low (Benotti and Brownawell, 2007). In addition, they are commonly persistent, in order to avoid the substance becoming inactive before achieving their effect (Enick and Moore, 2007).

Furthermore, through the careful selection of the suite of chemical markers, specific information about the sample being analysed
could be elucidated in addition to evidence about the source of nitrate being human (sewage) or veterinary (manure). This includes whether the source of sewage is raw or treated. A suite of 10 chemical markers suitable for the differentiation of sewage and manure within surface waters has been identified. An SPE-LC-MS/MS method for their simultaneous determination within surface waters has subsequently been developed. The limits of detection and quantification lie in the ng L\(^{-1}\) range, which corresponds to the concentrations at which such chemical markers occur within surface waters.

Through the additive contribution of information obtained through the chemical marker and isotopic analysis, the various point and diffuse sources of nitrate contamination could be identified. A monitoring campaign is hence being carried out in order to confirm the methodology’s applicability.


Acknowledgments

This work was performed as part of the EU Framework 7 project “ATWARM” (Marie Curie ITN, No. 238273)”

Disclosures

The authors have nothing to disclose.