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Review

The potential for a suite of isotope and chemical markers to differentiate sources of nitrate contamination: A review

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ABSTRACT

Nitrate is naturally found within the environment as part of the nitrogen cycle. However, anthropogenic inputs have greatly increased nitrate loads within ground and surface waters. This has had a severe impact on aquatic ecosystems and has given rise to health considerations in humans and livestock. Therefore, the identification of nitrate sources is important in preserving water quality and achieving sustainability of our water resources. Nitrate sources can be determined based on the nitrate nitrogen (N) and oxygen (O) isotopic compositions (δ^{15}N, δ^{18}O). However, sewage and manure have overlapping δ^{15}N and δ^{18}O values making their differentiation on this basis problematic. The specific differentiation between sources of faecal contamination is of particular importance, because the risk to humans is usually considered higher from human faecal contamination (sewage) than from animal faecal contamination. This review summarises the current state of knowledge in using isotope tracers to differentiate various nitrate sources and identifies potential chemical tracers for differentiating sewage and manure. In particular, an in depth review of the current state of knowledge regarding the necessary considerations in using chemical markers, such as pharmaceuticals and food additives, to differentiate sewage and manure sources of nitrate contamination will be given, through an understanding of their use, occurrence and fate, in order to identify the most suitable potential chemical markers.

Contents

Abbreviations: FIB, faecal indicator bacteria; WWTP, wastewater treatment plant; BOD, biological oxygen demand.

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1. Introduction

The nitrate ion (NO_3^-) occurs naturally as part of the nitrogen cycle. However, its ever-increasing concentrations have made it a ubiquitous contaminant of natural water resources. Nitrate arises from several point and non-point (diffuse) sources including synthetic and natural fertilisation, bacterial production, atmospheric deposition and leaking septic systems (Bordeleau et al., 2008). In addition, biogeochemical processes are known to modify nitrate concentrations such that different forms of nitrogen (NO_2, NH_4, NH_3) can potentially be transformed into nitrate (WHO, 2004).

Nitrate is considered to be a contaminant of concern because its presence within the environment has been linked to various environmental and health considerations. Such concerns have led to several pieces of legislation aimed at limiting nitrate concentrations. Within the European Union, these may be found in several pieces of legislation (Bouraoui et al., 2009), such as the Nitrates Directive (91/676/EEC), the Urban Wastewater Directive (91/271/EEC), the Water Framework Directive (2000/60/EC) and the Groundwater Directive (2006/118/EC). Other measures related to nitrate contamination include the Common Agricultural Policy reform, whereby subsidies have been decoupled from production levels and linked to the application of statutory minimum requirements and cross compliance leading to a decrease in fertiliser use (Bouraoui et al., 2009). However, at this point in time, there is no limit set for nitrates in rivers or lakes (EPA, 2009).

Determining the sources of nitrate contamination in water bodies and understanding the processes affecting local nitrate concentrations are necessary for a number of reasons. These include:

1. Improved management of water bodies for preserving water quality;
2. Actions for the remediation of contaminated sites can be targeted to the actual source making them more efficient, thus reducing public health and environmental considerations related to elevated nitrate concentrations;
3. More effective application of the ‘polluter pays principle’ in the context of nitrate contamination, since the inputs can be identified (Kendall, 1998; Kraft and Stites, 2003; Curt et al., 2004; Xue et al., 2009).

Unfortunately, the sources of nitrate within different regions may vary considerably even on a small scale (EEA, 2005). The relationship between nitrate concentrations in groundwater and surface water, and the quantity of nitrate introduced from a specific source is complicated by a number of factors. These include the occurrence of multiple inputs, the presence of overlapping point and non-point sources, the coexistence of several biogeochemical processes that alter nitrate concentrations, the presence of various factors affecting nitrate concentrations (such as human activity, geography and climate) and the occurrence of considerable temporal variations dependent upon precipitation levels leading to inter-annual variations (Kendall, 1998; Curt et al., 2004; EEA, 2005; Chen et al., 2010).

The present review provides an overview of the current state of knowledge in using isotope tracers to differentiate various sources. It then focuses on identifying potential chemical tracers for differentiating sewage and manure. In particular, an in depth review of the current state of knowledge concerning the necessary considerations in using pharmaceuticals and related compounds, such as food additives as chemical markers, to differentiate sewage and manure sources of nitrate contamination will be given. 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).

2. Methods of differentiating nitrate sources

In an effort to distinguish between sources of nitrate contamination, various approaches have been adopted. These have been applied with different degrees of success for source determination. However, to the authors’ knowledge, no one technique has been determined to be suitable to differentiate all sources of nitrate contamination. Furthermore, it is likely that a suite of techniques and indicators must be utilised in conjunction with each other in order to achieve successful differentiation.