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无机态氮素转化机制及水土体氮源识别方法

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摘要: 氮素在生物生命活动中起着至关重要的作用, 是有机分子的基本组成元素, 也是土壤的主要养分。对于氮污染的研究首先要明确各种氮形态转化机制, 这是解决各种氮科学问题的基础, 也是研究者容易忽略的重点。本文论述了氮素在生态系统中的转化过程及作用机制的基础, 归纳总结了近年来国内外有关水土中氮源分析的研究方法及氮同位素分馏作用, 重点综述了地表水及地下水体中氮源识别方法与应用, 包括定性识别和模型识别方法。指出利用水化学方法与多种同位素方法相结合能够有效识别水土氮污染源。针对传统亚硝化反应中氧原子来源识别中的问题, 提出了反应过程的现代观点, 解释了二次氧化反应过程中 $\delta^{18}\text{O}-\text{NO}_3^-$ 的富集原理。提出盆地含水层中原生铵态氮对地下水污染具有重要贡献, 并给出了新的研究设想。

关键词: 氮素; 硝酸盐; 氮同位素; 识别; 水土; 原生污染

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Mechanism of Inorganic Nitrogen Transformation and Identification of Nitrogen Sources in Water and Soil

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Abstract: Nitrogen plays a vital role in biological activities as the basic element of organic molecules and the main nutrient of soil. In the study of nitrogen pollution, the first step is to understand the transformation mechanism of various nitrogen forms. Based on the transformation process and the mechanism of nitrogen in the ecosystem, this review summarizes the research methods of nitrogen source analysis and nitrogen isotope fractionation in soil and water, and categorically reviews the applications of nitrogen source identification in surface water and groundwater. We showed that it is more effective to identify the sources of soil and water nitrogen pollution by combining hydrochemical methods with the multi-isotope approach. The importance of primary nitrogen sources should also be quantified to study groundwater pollution. A new approach to determine the source of oxygen atoms during nitrosation was also presented, and the enrichment principle of $\delta^{18}\text{O}-\text{NO}_3^-$ during secondary oxidation was explained. Finally, the contribution of primary ammonium nitrogen to groundwater pollution was discussed, and innovative research ideas were provided.

Key words: N; nitrate; nitrogen isotopes; identification; water and soil; primary pollution

地球上氮素(N)总量在众多元素中位列第四, 在生物生命活动中起着至关重要的作用, 是蛋白质、遗传材料以及叶绿素和其它关键有机分子的基本组成元素^[1,2]。同时在生态系统中也是农业土壤的最主要养分之一^[3]。多样的氮素形态决定了氮素复杂的转化过程, 而明确各种形态的转化机制是利用氮素、氮同位素研究解决各种科学问题的关键。

当前, 高频率肥料的施用、生活污水的肆意排放及大量的工业生产活动造成了严重的生态系统破坏。这引起水体、土体中的无机态氮素(铵态氮、硝态氮及亚硝态氮)不断增高, 影响着人类安全健康^[4]。超标的氮化合物有致癌、致畸的作用, 于20世纪后半叶才逐渐引起科学界的重视。为有效控制氮污染扩散及污染恶化, 首要问题就是判定区域介质的污染来源和媒介。由于不同来源的氮素有不同的同位素特征, 从20世纪70年代开始, 价态稳定的硝酸盐氮便成为首要的关注对象, $\delta^{15}\text{N}-\text{NO}_3^-$ 开始广泛应用于识别各类氮污染源^[5~15]。然而, 反硝化等作用的分馏致使不同来源的氮素有重叠的同位素

值。90年代开始, $\delta^{18}\text{O}-\text{NO}_3^-$ 作为辅助性同位素协助识别氮源^[16~22]。近年来, 水化学指标、多种元素同位素方法及数学统计耦合方法共同识别氮源的技术越来越受到青睐^[23~32]。

理解氮素在各个圈层中的转化机制, 对于判别污染源及分析污染过程意义重大。然而, 对比国内外的相关资料, 研究者通常挑选同位素分馏较大的反应过程进行重点论述, 对氮素的转化过程分析还不够全面, 在实际分析中, 可能会造成氮源的遗漏, 以及造成水化、土壤地化指标异常原因解析不全面。在实际场地中对于不同区域或介质采用的同位素分析方法也大不相同, 需要首先理解场地的氮素转化过程。本文从氮素各个形态的具体转化过程出发, 综述了利用同位素方法

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识别氮源的研究进展及发展趋势. 针对传统亚硝化反应中氧原子来源识别中的问题, 提出了反应过程的现代观点, 解释了二次氧化反应过程中 $\delta^{18}\text{O}-\text{NO}_3^-$ 的富集原理. 提出盆地含水层中原生铵态氮对地下水污染具有重要贡献, 并给出了新的研究设想.

1 氮素转化机制

生态系统中氮素具有 3 种存在形态, 即有机氮、

无机氮与分子态氮, 其在大气、水及土壤等圈层的相互转化及运动构成了氮素的生物地球化学循环^[33], 如图 1 所示. 其中, 无机态氮在土壤氮素中占较小比例, 却是植物吸收氮的主要形态, 特别是硝态氮和铵态氮^[34]. 在实际生态系统中, 远远不止图 1 所示的过程. 比如在采用分段崩落法的矿山, 炸药爆炸前几个月, 就已经大量埋藏于钻孔, 短时间内硝酸铵会随着地下水入渗到地下含水介质中^[35]. 以下将重点分析无机态氮在水体和土体的转化过程.



各反应机制引自文献[36~43]

图 1 氮素转化过程示意

Fig. 1 Diagram of nitrogen conversion process

1.1 矿化作用

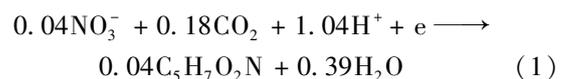
矿化作用 (mineralization) 是指有机氮 (TON) 通过矿质化转变为铵态氮 (NH_4^+) 的过程. 有机氮是沉积物氮素主要赋存形态, 约占总氮的 76.38% ~ 92.02%^[36]. 1964 年 Bremner^[44] 将有机氮分为氨态氮、非酸解未知态氮、氨基酸氮、酸解性未知氮和氨基糖态氮等形态. 各组分含量占全氮的比例顺序为: 氨基酸氮 > 非酸解未知态氮 > 酸解未知氮 > 铵态氮 > 氨基糖态氮, 土壤可矿化氮主要来自酸解氮, 特别是氨基酸态氮和铵态氮^[45].

TON 矿化过程分为两个步骤: 首先通过解聚作用将有机大分子化合物分解为生物单体-可溶性有机氮 (DON), 之后 DON 被氨化生成铵态氮. 土壤蛋白质、氨基多糖和核酸等有机氮的矿化过程中, 会产生氨基酸、氨基糖、嘌呤和嘧啶等中间产物. 矿化过程涉及的酶类, 如水解酶、氧化酶、脱氨酶和裂解酶等, 主要来自植物根系、土壤动物和微生物分泌^[37]. 矿化过程受土壤质地、温度湿度及耕作方式等多种因素影响^[46,47], TON 的测定方法也呈现多样化^[48,49].

天然的铵盐主要来自于 TON 的矿化, 一般来说, 矿化作用不会产生明显的氮同位素分馏效应^[50], 富集系数 (ϵ) 一般在 -1‰ ~ 1‰ 之间^[38]. 因此, 在溶解氧含量较低的还原条件下, 即弱硝化作用下, 自然状态下的 $\delta^{15}\text{N}-\text{TON}$ 与 $\delta^{15}\text{N}-\text{NH}_4^+$ 结果相差不大. 且地下水体中 $\delta^{15}\text{N}-\text{NH}_4^+$ 与沉积物中相似^[51]. 通常, 地下含水介质中碳氮比 (C/N) 介于 20 ~ 25 之间有利于矿化作用^[52].

1.2 同化作用

同化作用 (assimilation) 指生物将无机态氮转化为有机态氮的过程, 即在自养微生物作用下无机氮被吸收利用过程. 由于反应趋于优先利用较轻的 ^{14}N , 在反应物的无机氮中发生 ^{15}N 富集, 在生成物有机氮中产生 ^{14}N 的富集. 同化作用前后, 形成反应物与生成物中氮的同位素分馏. 水体中同化作用引起的氮同位素分馏范围较大, ϵ 范围在 -27‰ ~ 0‰ 之间^[38]. 同化反应硝态氮转化为有机氮过程如公式 (1) 所示^[53].

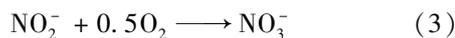
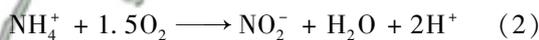


在同化作用中,铵态氮和硝态氮都存在的情况下,大多异养微生物更倾向于吸收铵态氮^[54].对于自养微生物来讲,可以利用 CO₂ 将硝酸盐同化为生物细胞的蛋白质(有机质),例如,微藻和蓝藻等化能自养生物及光能自养生物作用过程中,氢、还原态硫及铁等无机物可以提供能量补充. NH₄⁺ 作为微生物更倾向于利用的氮源,在反应中含量不足时,多种细菌和几乎所有的微藻类生物会将 NO₃⁻ 还原为 NH₄⁺ 继续利用并大量增长^[39].

1.3 硝化作用

1.3.1 自养硝化作用(AN)

自养硝化作用是传统观点所认为的硝化作用,指在好氧条件下 NH₄⁺-N 在硝化细菌的作用下(以 CO₂ 为碳源)依次被氧化成 NO₂⁻-N 和 NO₃⁻-N 的过程.这两个阶段分别是在氨氧化细菌(AOB)和亚硝酸盐氧化菌(NO₂-N)的作用下完成的,因而又称为氨氧化过程和亚硝化过程^[37].硝化细菌优先利用¹⁴N-NH₄⁺,将其转化为¹⁴N-NO₃⁻,造成剩余 NH₄⁺-N 中¹⁵N-NH₄⁺ 所占比例增加,发生¹⁵N 的富集.经历两个阶段的连续反应,并且每阶段均发生不同程度的氮同位素分馏,因此自养硝化作用分馏明显,其富集系数(ε)一般在 -12‰ ~ -29‰ 之间^[38].在硝化作用主导氮素转化过程,铵态氮浓度与硝态氮、亚硝态氮浓度之和呈负相关关系,相关曲线越接近 1:1,则硝化作用越强^[51].自养硝化作用可以用公式(2)和(3)表示.



1.3.2 异养硝化作用(HN)

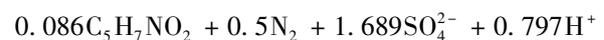
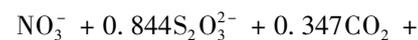
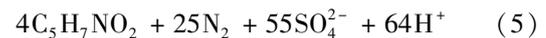
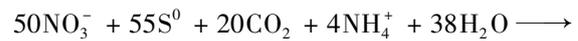
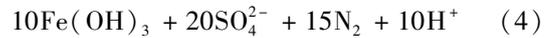
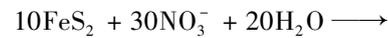
该作用由异养硝化微生物主导,以有机碳(TOC)为碳源,将还原态氮转化为氧化态氮,在底物利用类型上,无机氮和有机氮可以同时被利用,区别于自养硝化作用,底物类型只能是无机氮^[55-57].异养微生物有两种氧化途径,一种是异养硝化细菌,将硝化活性与好氧反硝化过程联系起来,形成硝化-反硝化耦合过程,消散有氧呼吸受限时的还原当量^[58].另一种作用更强的异养硝化途径则由真菌主导,尤其是在酸性土壤中^[59].HN 机制较难研究,目前仅限于个别菌株.主要原因包括反应底物类型广泛、异养硝化微生物多样、不同微生物具有的关键酶及编码基因差异等^[60].

1.4 反硝化作用

1.4.1 自养反硝化作用(AD)

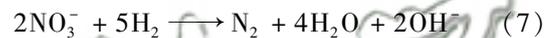
在硫氧化自养反硝化过程中,富 NO₃⁻ 的地下水可以促进含水层中硫化物生成硫酸盐和酸性物质,降低水体 pH,该过程以 HCO₃⁻ 和 CO₂ 作为碳源,单

质硫和硫代硫酸盐等硫氧化物都可作为电子供体.因此,当硝酸盐被还原成氮气时,硫被氧化成硫酸盐,硫及其化合物则用于细胞合成^[61-64].硫氧化自养反硝化过程如公式(4)~(6)所示.



(6)

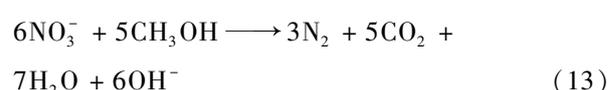
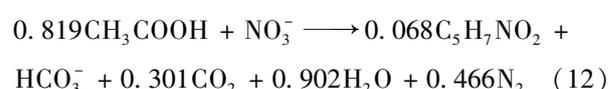
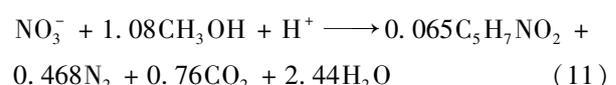
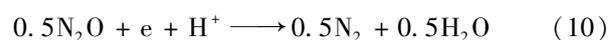
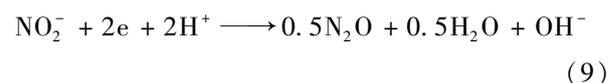
以氢为营养的自养反硝化过程中,氢气则作为电子供体参与反应,方程式如式(7)所示.



在利用自养反硝化去除超标的硝酸盐室内实验中,脱氮速率取决于许多因素,包括单质硫颗粒的大小和碱度来源.小颗粒单质硫的使用可以增加反硝化速率,因为小颗粒单质硫增加了细菌附着表面积,从而增大硫的溶解度^[65].

1.4.2 异养反硝化作用(HD)

许多细菌通过将离子氮氧化物还原为气态产物来实现厌氧生长,尽管存在大量的异养和自养反硝化菌这种以硝酸盐或亚硝酸盐代替氧气作为电子受体的呼吸过程会产生三磷酸腺苷(ATP),称为异养反硝化或异化硝酸盐还原,受 DO 浓度的影响,通过抑制硝酸还原酶来抑制硝酸还原.然而,某些种类的细菌在有氧气存在的情况下也会发生反硝化作用^[39].异养反硝化过程中,微生物以 TOC 为碳源,以 NO₃⁻ 为电子受体,将 NO₃⁻ 还原为 N₂.异养反硝化公式如(8)~(10)所示,有机质参与反应的具体公式如(11)~(13)所示^[66].

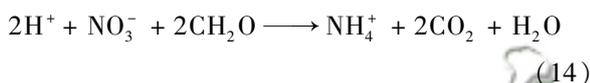


如公式(11)~(13)所示,在异化途径中,硝酸盐和亚硝酸盐作为电子受体被有机和无机电子供体

氧化. 在此过程中, 大多数微生物脱氮系统使用异养菌, 这需要有有机碳源, 如甲醇、乙醇、葡萄糖或乙酸盐. 由于地表水或地下水通常缺乏有机碳, 而有机碳是异养反硝化的重要电子供体, 因此维持过程需要增加外部碳源^[67].

1.5 异化硝酸盐还原为铵(DNRA)

异化硝酸盐还原为铵(DNRA)是一个厌氧还原过程, 该过程会消耗 NO_3^- . 反应方程式(14)所示, 假定异养反硝化和 DNRA 反应 NO_3^- 的消耗分配是由有机质有效性控制的, 则当碳(电子供体)供应受限制时, 异养反硝化过程主导反应过程; 否则, 当 NO_3^- (电子受体)供应受限制时, DNRA 作用主导氧化还原反应^[40~42]. 但也有研究表明, 加入有机碳可以促进微生物的呼吸作用, 一定程度上促进 DNRA 过程进行^[68,69], DNRA 的反应方程式如下所示.



另外, 研究表明还原条件下, 硫化物可以作为 DNRA 过程的指示剂, 当沉积物中检测到硫化物时, DNRA 是主要的硝酸盐还原过程, 反之则过程终止^[70]. 硫化物能够促进 DNRA 过程, 因为其可以作为电子供体为反应过程提供电子, 促进无机化能自养硫细菌将硝酸盐氧化为铵^[71~73].

1.6 厌氧氨氧化反应(ANAMMOX)

该过程指在还原环境条件下, 各类微生物以 NH_4^+ 作为电子供体, 以 NO_2^- 为电子受体, 结合转化为氮气的过程^[74]. 类似反硝化过程, 该反应也是水体脱氮的主要途径, 此类研究当前颇受关注. 通过稳定同位素标记法标记 $^{15}\text{N}\text{-NO}_3^-$ ^[75] 人为干扰研究发现, 反应受温度、盐度影响较大, 极高温、高温及高盐度环境会严重降低厌氧氨氧化细菌的活性^[76~80]. 在自然条件下, 当水体中硝酸盐浓度较低时, 厌氧氨氧化反应(ANAMMOX)过程与 NO_3^- 和 NH_4^+ 浓度呈正相关关系^[76,81]. 而当硝酸盐浓度过高时, 会抑制反应速率. 而此时与异养反硝化反应速率呈现明显正相关关系^[82]. 尽管在红树林和其他厌氧土壤中的一些研究表明厌氧氨氧化反应活性很高, 但是反硝化和 DNRA 在土体中的协同作用明显占据主导地位^[83~86]. 此外, 在硫酸盐还原作用(SR)作用刺激下, 会使自养反硝化(AD)和厌氧氨氧化反应产生竞争关系, 因为 DNRA 过程需要跟 AD 竞争 NO_3^- ^[76].

对于 TOC 对厌氧氨氧化反应的影响, 普遍的共识是当 TOC 浓度较低时, 对反应过程影响较小. 而对于高浓度 TOC 反应影响结果则出现研究分

歧^[80,87].

1.7 氮同位素分馏作用

在地下含水层中, 氮素的各个反应过程包括物理过程和生物化学过程, 每个作用过程有着不同的分馏值, 且针对同一个作用过程, 不同的研究者也给出了不同的富集系数. 分馏作用包括热力学平衡分馏和动力学非平衡分馏, 比如氨挥发过程就包括两个作用过程, 铵(NH_4^+)和氨(NH_3)在溶液中的平衡分馏、液态氨(NH_3)和气态氨(NH_3)的平衡分馏属于热力学平衡分馏, 而氨在介质的扩散作用则为动力学不平衡分馏, 两个作用过程都会产生较大的同位素分馏. 表 1 为地下含水介质中氮素主要反应过程的富集系数范围.

表 1 氮素作用过程的富集系数

氮素反应过程	富集系数(ϵ)/‰	文献
同化作用	-27 ~ -1	[17,90]
矿化作用	-1 ~ 1	[17,38,90]
固氮作用	-3 ~ -1	[17,38,88,89]
反硝化作用	-40 ~ -5	[91,92]
硝化作用	-29 ~ -12	[17,38]

2 氮源识别的研究进展

2.1 同位素方法

2.1.1 氮氧同位素

利用氮氧同位素共同分析氮素来源的优势在于氧同位素可以区分个别同位素重叠判别效应, 更加明确氮源. 通过比对多位研究者对于 $\delta^{15}\text{N}\text{-NO}_3^-$ 和 $\delta^{18}\text{O}\text{-NO}_3^-$ 的研究结果, 得出了硝酸盐的基本来源(国内流域 $\delta^{15}\text{N}\text{-NO}_3^-$ 值参见文献[88]), 如图 2 和图 3 所示^[90]. 同时为了更精准确定 $\delta^{18}\text{O}\text{-NO}_3^-$ 对氮源识别的影响, 需要运用 MetaWin^[93] 等校正软件对 $\delta^{18}\text{O}\text{-NO}_3^-$ 的“有效贡献量”进行评估.

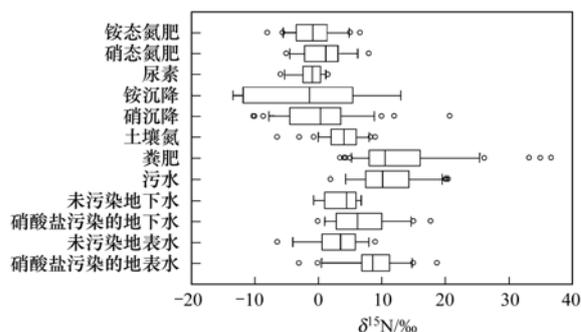


图 2 关于 $\delta^{15}\text{N}\text{-NO}_3^-$ 多种源和汇的箱型图^[90]

Fig. 2 Box diagrams of multiple sources and sinks of $\delta^{15}\text{N}\text{-NO}_3^-$

根据图 3 可知, 尽管 $\delta^{18}\text{O}\text{-NO}_3^-$ 识别氮素来源, 但由于仅限于区分为数不多的种类, 因此本方法也存在一定局限性. 综合图 2 和图 3, 为方便研究氮素

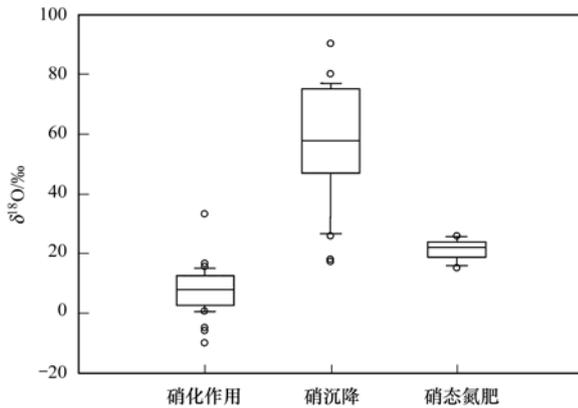


图3 关于 $\delta^{18}\text{O}-\text{NO}_3^-$ 多种源和汇的箱型图^[90]

Fig. 3 Box diagrams of multiple sources and sinks of $\delta^{18}\text{O}-\text{NO}_3^-$

来源,将两者绘于一幅图内进行初步指示(图4),并可以识别反硝化作用,当存在反硝化作用时,氮氧同位素数据点一般沿一定斜率(1:2.1~1:1.3)直线方向演化^[94~100].

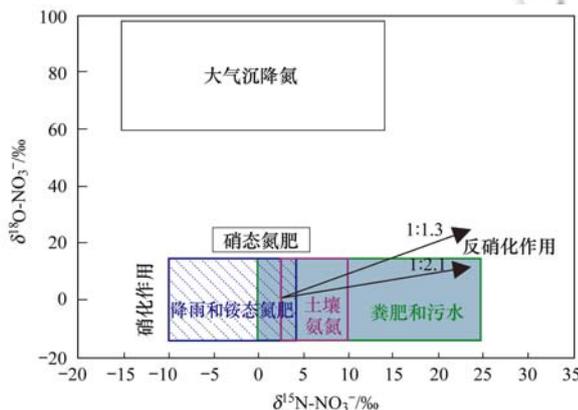


图4 氮氧同位素识别氮源示意^[97]

Fig. 4 Schematic diagram of nitrogen-oxygen isotope identification of nitrogen source

微生物参与的反硝化过程会经常模糊同位素的组成,该过程会同时修改 N 和 O 同位素比值,造成数据结果模棱两可的解释.对于判断体系中是否存在反硝化反应来讲,一般有以下方法.对比 $\delta^{15}\text{N}-\text{NO}_3^-$ 与硝酸根浓度值的趋势,若两者呈明显负相关关系,则可能存在反硝化反应^[7];若存在反硝化作用, $\delta^{15}\text{N}-\text{NO}_3^-$ 和 $\delta^{18}\text{O}-\text{NO}_3^-$ 与 $\ln(\text{NO}_3^- - \text{N})$ 呈线性关系^[90,96,101~103];氮氧同位素数据点沿一定斜率(1:2.1~1:1.3)直线方向演化.

2.1.2 同位素与水化学结合

结合阴阳离子浓度及同位素数据可以为氮源识别提供可靠的信息,因为人为活动造成的化学组分异常会主导自然条件下的污染物源,化学指标同时可以指示水体运动路径及地表地下水体的交互过程^[51,104].

例如,若地层中 $\text{NH}_4^+ - \text{N}$ 浓度与 $\delta^{15}\text{N}-\text{NH}_4^+$ 为正

相关关系,则考虑反应过程以吸附作用为主导;且铵态氮与 Ca^{2+} 浓度比值接近 2:1 [$2\text{NH}_4^+ + \text{CaX} \rightarrow \text{Ca}^{2+} + (\text{NH}_4)_2\text{X}$].若二者呈负相关关系,则考虑以化学反应为主导^[50,105~107].另外,粪肥中的氮素会以尿素的形式水解为 NH_4^+ ,进而转化为 NO_3^- ,水解的尿素会使介质 pH 升高,并且有利于形成 NH_3 造成氮损失,致使 $\delta^{15}\text{N}-\text{NH}_4^+$ 升高.

一般情况下,若存在离子浓度值异常升高(Ca^{2+} 、 Na^+ 、 K^+ 和 Cl^- 等),则可能是由于人为次生污染的原因,因为弱透水层会充当地表水与地下水交互的媒介将氮污染物带入含水层. Min 等^[108]于 2002 年的研究发现在地下水运动过程中,当水化学类型由 $\text{Ca}-\text{HCO}_3$ 转变为 $\text{Na}(\text{K})-\text{Cl}$ 型时,更多是由于生活污水和粪肥的影响.农业活动会使水体富集高浓度的 Cl^- ,而 HCO_3^- 浓度则占比降低.若该类阴阳离子浓度符合正常水平,则超标的氮素很可能来源于原生污染.

总的来说,由盆地内部局部补给的地下水渗滤形成的局部水流系统受益地表面过程影响极易受到污染,人为活动密集的地下水开采影响着局部水流系统.相比之下,大尺度规模的地下水流系统,其补给来源为高海拔区的老地下水,与大气没有或只有有限的接触交互, CO_2 和 O_2 浓度一般较地表水偏低,水岩交互作用的时间尺度更长.地下水研究中需要结合水化学指标共同指示氮源,有些指标可以直接指明某个化学过程的强弱关系,避免单一证据造成的误判.

2.1.3 多种同位素方法

一般情况下,深层地下水与局部地下水存在混合过程.由于区域地下水的还原条件,使得反硝化反应可以正常进行,在氧化还原反应过程中,同位素数据为水化学研究提供了有用的补充信息,特别是在水化学数据不确定的情况下.运用多种同位素辅助氮源识别的方法近年来颇受关注,主要有以下 3 个优点:①能够移除、简化部分化学作用的影响,使氮源的判定更加精准;②能够共同指示或辅助指示氮源.比如, $\delta^{18}\text{O}-\text{SO}_4^{2-}$ 同样可以指示 SO_4^{2-} 是否受到大气沉降的影响, $\delta^{34}\text{S}-\text{SO}_4^{2-}$ 可以指示是否来源于硫酸化物的氧化作用还是蒸发岩的溶解,间接说明水体中氮素的化学作用;③共同指示氮素的物源.比如, C/N 、 $\delta^{13}\text{C}-\text{TOC}$ 及 $\delta^{15}\text{N}-\text{NO}_3^-$ 可以共同指示古气候环境,解释有机质来源的植物种类^[109].

对于地表径流中氮源的判定,由于其受大气影响明显,需要去除大气氮沉降的影响.据统计,部分河流中大气贡献的硝酸盐约占 46%,而地下水中占比 3%~6%.因此,对于单纯利用 N、O 同位素共同

识别氮来源的文章,要大胆质疑.对于氮源的研究,务必结合当地水文地质条件和水化学背景,查明是否存在人为因素下的污染源.目前,采用 $\delta^{17}\text{O}$ 同位素能移除大气沉降对于氮源的部分贡献影响,更好地说明其他的氮源或生物化学作用对样品产生的影响^[110].

地下水中 SO_4^{2-} 会受到不同的驱动作用,包括还原性无机硫的氧化作用、石膏的溶解、农业肥料及有机土壤硫的矿化作用. $\delta^{34}\text{S}\text{-SO}_4^{2-}$ 与 $\delta^{18}\text{O}\text{-SO}_4^{2-}$ 可以指示水体是否受到人为污染,辅助指示氮素来源.比如,原生土壤中, $\delta^{34}\text{S}\text{-SO}_4^{2-}$ 与 $\delta^{18}\text{O}\text{-SO}_4^{2-}$ 一般分别为 $0\sim 6\text{‰}$,且 SO_4^{2-} 浓度较低;而农化产品和粪肥作为肥料的话, $\delta^{34}\text{S}$ 的平均值一般为 5‰ , $\delta^{18}\text{O}$ 范围平均值为 12‰ ,也有其他研究者得出 $\delta^{34}\text{S}$ 为 $-0.9\text{‰}\sim 5.8\text{‰}$ 的结论,现在 $\delta^{18}\text{O}$ 采用 $3.8\text{‰}\sim 6\text{‰}$ 作为指示粪肥的硫酸盐源.对于污水来说,平均 $\delta^{34}\text{S}$ 为 9.6‰ , $\delta^{18}\text{O}$ 为 10‰ ,在污染源识别研究过程中,认为相比较于表层渗滤水,污水管网渗水影响可以忽略不计.同时,更高的硫同位素与低浓度的硫酸盐也能指示地层中可能存在较强的细菌硫酸盐还原作用.若 $\delta^{34}\text{S}$ 值高于 20‰ , $\delta^{18}\text{O}$ 高于 12‰ ,认为高浓度硫酸盐来源于石膏的溶解,因为石膏溶解不会引起同位素分馏效应^[111].

水中 $\delta^2\text{H}$ 与 $\delta^{18}\text{O}$ 也是辅助指示氮源的重要指标.研究地表水的同位素与地下含水介质的氢氧同位素关系,可以确定水体来源,指示地下水是否受到现代水的影响,进一步指示是否受到人为污染.早在20世纪90年代,Connolly等^[112]便利用氢氧同位素研究了地下含水介质的水体来源,指出含水层中的水不全是来源于大气降水.并且文献^[113~115]详细介绍了地层水的来源与发展.

硼同位素也于上世纪末期开始应用于硝酸盐氮污染源的识别^[13,116,117].硼在水溶液中是高度可溶的,在几乎所有的水体类型中都以微量成分的形式存在,且 $\delta^{11}\text{B}$ 在不同的污染水体中的值域也不同.一般来讲,若地层中地下水受污水污染, $\delta^{11}\text{B}$ 范围在 $-7.7\text{‰}\sim 12.9\text{‰}$ 不等,而不同种类的动物粪便值域大不相同,范围一般在 $6.9\text{‰}\sim 42.1\text{‰}$,肥料中的 $\delta^{11}\text{B}$ 值域则为 $8\text{‰}\sim 17\text{‰}$ 之间,这些值域已被成功应用到辅助区分多种氮素来源^[13,116~118].Seiler等^[118]使用 $\delta^{15}\text{N}\text{-NO}_3^-$ 和 $\delta^{18}\text{O}\text{-NO}_3^-$ 值与 $\delta^{11}\text{B}$ 值结合,对美国内华达州地下水中的生活污水和化肥污染进行了区分.

2.2 模型识别

2.2.1 质量平衡混合模型

质量平衡混合模型一般是基于两种同位素,利

用元素质量平衡原理识别氮素的多种来源,量化每种来源的氮素贡献比.前人多用 $\delta^{15}\text{N}\text{-NO}_3^-$ 和 $\delta^{18}\text{O}\text{-NO}_3^-$ 计算氮污染源贡献量,识别超标的硝酸盐主要污染源,并根据识别结果加以模型控制,识别了每种污染源的贡献比例^[119~121].但是该方法在实际应用中具有相当大的局限性,下文将提及.

质量平衡混合模型基于两种同位素识别量化3种氮源的计算方法如公式(14)所示:

$$\begin{aligned} \delta^{15}\text{N} &= f_1\delta^{15}\text{N}_1 + f_2\delta^{15}\text{N}_2 + f_3\delta^{15}\text{N}_3 \\ \delta^{18}\text{O} &= f_1\delta^{18}\text{O}_1 + f_2\delta^{18}\text{O}_2 + f_3\delta^{18}\text{O}_3 \\ 1 &= f_1 + f_2 + f_3 \end{aligned} \quad (14)$$

式中, $\delta^{15}\text{N}$ 和 $\delta^{18}\text{O}$ 是混合物 NO_3^- 中的同位素测试值; $f_1\sim f_3$ 是3种氮源各自的贡献比.

2.2.2 稳定同位素混合模型(SIAR)

质量平衡混合模型在运用中没有考虑氮素的时空变异性,也不考虑氮同位素的变异性,因此不能识别同位素分馏带来的同位素变化结果.同时,实际情况的氮源更加复杂,仅仅依赖公式(14)不能准确识别氮源.Parnell等^[122]运用R统计计算程序开发了同位素混合模型开源软件包以满足氮源识别要求,程序基于贝叶斯框架建立了一个基于狄利克雷分布的逻辑先验分布来估计可能的比例源贡献,然后确定每个源对混合物的比例贡献的概率分布.该方法已经成功应用于量化多种氮源的贡献比例研究^[123~125].该方法可用公式(15)表达:

$$\left. \begin{aligned} X_{ij} &= \sum_{k=1}^K p_k (S_{jk} + C_{jk}) + \varepsilon_{ij}, \\ S_{jk} &\sim N(\mu_{jk}, \omega_{jk}^2), \\ C_{jk} &\sim N(\lambda_{jk}, \tau_{jk}^2), \\ \varepsilon_{ij} &\sim N(0, \sigma_j^2). \end{aligned} \right\} \quad (15)$$

式中, X_{ij} 表示不同来源的第*i*种混合物的第*j*个同位素的值, $i=1,2,3,\dots,N$, $j=1,2,3,\dots,J$; S_{jk} 表示第*k*种污染源的第*j*个同位素的值, $k=1,2,3,\dots,K$;与平均值 μ_{jk} 和标准偏差 ω_{jk} 皆符合正态分布; p_k 表示污染源中第*k*个来源的贡献比例; C_{jk} 表示第*k*个来源的第*j*个同位素分馏系数;与平均值 λ_{jk} 和标准偏差 τ_{jk} 皆符合正态分布; ε_{ij} 表示剩余误差,代表不同单个混合物之间不能确定的变量.

3 关于氮污染物研究的问题与设想

3.1 关于 $\delta^{18}\text{O}\text{-NO}_3^-$ 的问题

硝酸盐的产生过程中,其中的氮和氧同位素会出现不同的效果.在浅表海水中,或在氧化性含氧水域中,铵盐几乎全部来源于有机氮的矿化并最终氧化成硝酸盐.因此,与铵盐产生有关的氮同

位素效应以及硝化作用本质上不影响硝酸盐中 $\delta^{15}\text{N}$ 的产生,在此情况下,新生成的硝酸盐中的 $\delta^{15}\text{N}$ 主要是由新矿化的有机质中的 $\delta^{15}\text{N}$ 控制.而新产生的硝酸盐中的 $\delta^{18}\text{O}$ 明显不会依赖于新矿化的有机质中 $\delta^{18}\text{O}$ 组分.

现代生物化学研究已经揭示了 NH_4^+ 氧化为 NO_2^- 的机制,其中一个氧原子来源于 O_2 ,另一个来源于 H_2O ^[126],而 NO_2^- 氧化为 NO_3^- 过程中,氧原子全部来源于 H_2O ,因此,在此基础上,传统解释为 NO_3^- 中 2/3 的氧原子来源于水,1/3 来源于 O_2 ,更有学者基于此原理对氮素进行了识别研究^[17,127,128].

然而,生物化学研究也显示,生态系统中存在一种强的催化硝化菌可以交换 NO_2^- - H_2O 的氧原子.在 NH_4^+ 氧化为 NO_2^- 过程中,少于 1/2 的氧原子来源于 O_2 ,且在亚硝化单细胞菌的培养实验中对 $\delta^{18}\text{O}$ 标记发现,至少 50% 的氧原子与水中氧原子发生了交换^[129].所以在 NO_3^- 中,6 个氧原子至少有 5 个来源于 H_2O ,而且在 NO_2^- 氧化为 NO_3^- 过程中,也可能存在催化硝化菌的催化交换作用,进一步降低了 O_2 对 NO_3^- 中氧原子的贡献.图 5 显示了硝酸盐氧原子的来源.

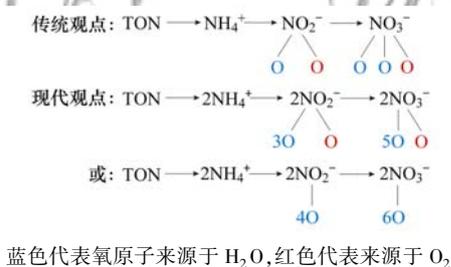


图 5 硝酸盐氧原子来源示意

Fig. 5 Schematic diagram of sources of nitrate-oxygen atoms

3.2 关于亚硝化反应与硝酸盐还原反应

在亚硝酸盐氧化为硝酸盐及硝酸盐还原为亚硝酸盐过程中,其中的 $\delta^{15}\text{N}$ - NO_3^- 和 $\delta^{18}\text{O}$ - NO_3^- 并不是 1:1 共变的.硝酸盐还原过程受反硝化作用影响会消耗 NO_3^- 及氮氧同位素,当还原产生的亚硝酸盐再次氧化为硝酸盐时,将会返还给硝酸盐相同的 $\delta^{15}\text{N}$,因此,反应过程中外界的 $\delta^{15}\text{N}$ - NO_3^- 从未发生变化.

然而,重新氧化为硝酸盐中的 $\delta^{18}\text{O}$ - NO_3^- 更可能比之前还原成亚硝酸盐的硝酸盐中 $\delta^{18}\text{O}$ - NO_3^- 偏高,这是因为反应过程中优先利用 ^{16}O 同位素,造成氧化为硝酸盐的亚硝酸中氧同位素偏重,致使产物硝酸盐比之前未反应前的硝酸盐 $\delta^{18}\text{O}$ - NO_3^- 偏重.故而,在反硝化过程进行中,二次氧化反应也可致使 $\delta^{18}\text{O}$ - NO_3^- 升高,这是一个容易忽略的因素.

3.3 关于原生氮污染的研究设想

氮污染来源包含原生污染和次生污染两类污染.两种来源的氮素会共同致使水体质量恶化,生态系统受损.全新世以来,特别是工业革命以来,人类活动对大自然的肆意破坏致使地表水、浅层地下水及表层土壤介质体受到严重污染,在此过程中,氮素作为生态系统中最重要元素之一,也在历史长河中逐渐富集,直接损害生物健康,危害人类生命安全,这是当前水土氮污染研究的热点.

然而,地球关键带研究的前期调查发现,原生污染对地下水劣质水成因也有相当的贡献比例,但是原生氮素污染对于地下水的硝酸盐含量贡献研究相对较少.第四纪以来,沉积环境、气候环境进行了多次交替演变,复杂的变化过程沉积了富含有机质的地层,岩土矿化过程是产生铵态氮的主要化学作用,因此,研究地下水氮素污染需要分析地层沉积时古气候环境,厘清地层氮素转化过程对于氮元素的贡献.

4 结论及展望

氮素在生态系统中起着至关重要的作用,是生物体生命活动的基本构成组分.尽管无机态氮污染的研究方法越来越复杂深入,但是明确各种氮形态转化机制,是解决各种氮科学问题的基础.本文搜集国内外研究成果,总结了有机和无机氮素之间的转化机制,并综述了氮素识别的定性定量常规方法及研究进展.

随着对水土体超标的氮化合物来源的逐步认识,国内外学者对全新世以来,人为活动造成的氮污染进行了氮源识别研究,能够识别污染来源并定量化各种源的贡献比例.然而,对于氮污染物的原生污染则缺乏系统性研究,并且对所识别的污染源,缺少实际的解决措施,这需要我们继续深化加强.针对地下含水介质中氮素的污染,本文提出了原生与次生污染物结合探索的研究设想,共同分析场地氮素超标原因.水土氮污染的研究需要继续研究氮素转化机制,在此基础上继续深入,而多种方法结合的氮污染源识别也有待更多的研究实例.

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