Nitrate source identification in various water bodies via isotopic fingerprinting

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15 years NO$_3^-$ management in Flanders: 1999-2014

"If you are uncertain about a status you will search for additional information before taking action"
NO$_3^-$ source apportionment

Xue et al. 2009
Economic value of including isotopes increases with potential damage costs

**Classical monitoring**

Water body status?

**Isotope monitoring**

Additional information via isotopes?

**Improved decision via better information**

Economic value from better decision making:

- Cost to get information

Cost-benefit analysis

![Graph showing the economic value of including isotopes increases with potential damage costs.](image-url)
Objectives

To quantify NO₃⁻ sources in surface water

To classify surface waters in NO₃⁻ pollution classes via stable isotopes in NO₃⁻

To assess if physicochemical data sets can be used to retrieve NO₃⁻ pollution classification
Methodology

• Select representative sampling points (30) for 5 different NO$_3^-$ pollution classes (= based on expert judgment)

• Estimate proportional NO$_3^-$ source contribution per NO$_3^-$ pollution class using a Bayesian isotopic mixing model (SIAR) (monthly sampling during 2 years)

• Re-classify the 30 sampling points in NO$_3^-$ pollution classes via a k-means clustering approach using the SIAR fingerprint as input data

• Build a decision tree model including physicochemical data (10 parameters, monthly sampling during 2 years) to retrieve the classification via expert and k-means clustering
Expert classification of 30 sampling points

Agriculture (Class A)

A: Agriculture
AGC: Agr. with ground water compensation
AH: Agriculture + Horticulture
G: Greenhouses
H: Households
Seasonal $\text{NO}_3^-$ source identification (2 year data)

$\delta^{15}\text{N}$ (‰)

$\delta^{18}\text{O}$ (‰)

NP

NF

NFR

Soil

M&S


AW  AS

AGCW  AGCS

AHW  AHS

GW  GS

HW  HS

NP

NF

NFR

Soil

M&S
One year $^{11}$B data

- class A
- class AGC
- class AH
- class G
- class H

Manure

Mineral fertilizer

Sewage

$\delta^{11}$B (‰) vs. $1/B$ (L $\mu$g$^{-1}$)
Classification of Nitrate Polluting Activities through Clustering of Isotope Mixing Model Outputs

Dongmei Xue,* Bernard De Baets, Oswald Van Cleemput, Carmel Hennessy, Michael Berglund, and Pascal Boeckx
K-means clustering results for winter (SIAR)

<table>
<thead>
<tr>
<th>Expert classification†</th>
<th>Sampling location</th>
<th>Three clusters via k-means</th>
<th>Four clusters via k-means</th>
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<td>cluster 3+</td>
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<td>cluster 1</td>
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</tbody>
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Silhouette: 0.6

4 classes: A, AGC, G and H based on $^{11}$B + 3-means clustering
Comparison of expert classification and k-means clustering

<table>
<thead>
<tr>
<th>Season</th>
<th>Cluster comparison</th>
<th>Rand index</th>
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<td>Summer</td>
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K-means clustering using SIAR output retrieves 70% of expert classification!
Retrieve expert (a) and 3-means clustering (b) classification via decision tree models.
Conclusions and future application

- Coupled “SIAR” – “k-means clustering” approach is a promising tool to determine the number of NO$_3^-$ pollution classes when expert knowledge for a basin is absent.

- Decision trees using physicochemical data can be applied to classify a larger number of monitoring points of that basin into the established NO$_3^-$ pollution classes.

- Away from Europe,…
Kinshasa, DR Congo
Nitrate concentration in groundwater boreholes
Range: 0.1 - 339.7 mg L⁻¹
Average: 39.2 ± 56.5 mg L⁻¹
Nyungwe - tropical mountain forest
Atmospheric N deposition

NH$_4^+$: 2.5 kg N ha$^{-1}$ yr$^{-1}$
NO$_3^-$: 5.2 kg N ha$^{-1}$ yr$^{-1}$

Compare with:
- Temperate forest (Belgium)
  ≈ 20 - 35 kg N ha$^{-1}$ yr$^{-1}$
- Temperate forest (south Chile)
  ≈ 8 kg N ha$^{-1}$ yr$^{-1}$
Nitrate leaching and source

- Loss of $\text{NO}_3^-$ = 19.7 kg N ha$^{-1}$ yr$^{-1}$
- $\text{NO}_3^-$ loss 4-fold higher than deposition

Plants use $\text{NH}_4^+$ and not $\text{NO}_3^-$
Bayesian mixing models (mixSIAR) account for uncertainty and isotope fractionation, hence a detailed temporal and spatial isotopic characterization of NO$_3^-$, and correct assessment of enrichment factor for soil and river denitrification is paramount.