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Green approaches to assess water quality in Reconquista River

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Introduction

Reconquista River is one of the most polluted rivers in Argentina[1,2]. This study addresses water quality in densely populated regions impacted by untreated organic and inorganic pollutants from industrial and urban sources. The objective is to assess water quality through physicochemical analyses while incorporating an Analytical GREEnness metric approach[3] to evaluate the sustainability of the analytical methods employed. By focusing on the greenness of these methodologies, the aim is to optimize as sustainable as possible workflows for environmental analysis without compromising the overall analytical performance. To complement this, multiparametric measurements will be used to investigate the role of phytoplankton communities as bioindicators of ecosystem health. This approach is proposed as a sustainable and innovative alternative for water quality assessment, aligning with the principles of green chemistry.

Materials and methods

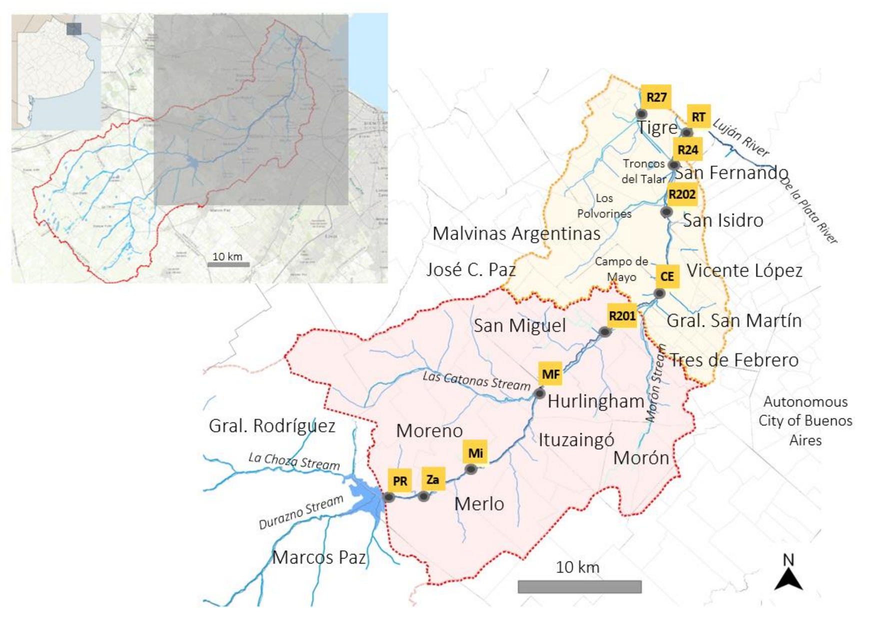


Fig 1. Sampling sites in the middle basin (red zone) and lower basin (orange zone) of the Reconquista River basin. PR: Roggero dam, Za: Zapiola bridge, Mi: Emilio Mitre bridge, MF: Martín Fierro bridge, R201: Provincial Route N°201, CE: CEAMSE, R202: Provincial Route N°202, R24: Provincial Route N°24, R27: Provincial Route N°27, RT: Tigre River.

Conventional Physicochemical Analysis

In situ	pH DO NTU EC ORP
Gravimetry	TSS TVSS
Respirometry	BOD_5
Spectrophotometry	COD, NH_4^+, NO_3^-, NO_2^-, TP, PO_4^{3-}, SO_4^{2-}
Titration	Hardness, Alkalinity, Cl^-

Low Impact Analysis

X ray fluorescence	As Cr Cu Fe Mn Ni Ti V Zn
HS-SPME-GC-MS	VOCs

Phytoplankton Analysis

Direct microscopy	Richness
Inverted microscopy	Abundance

Green assessment

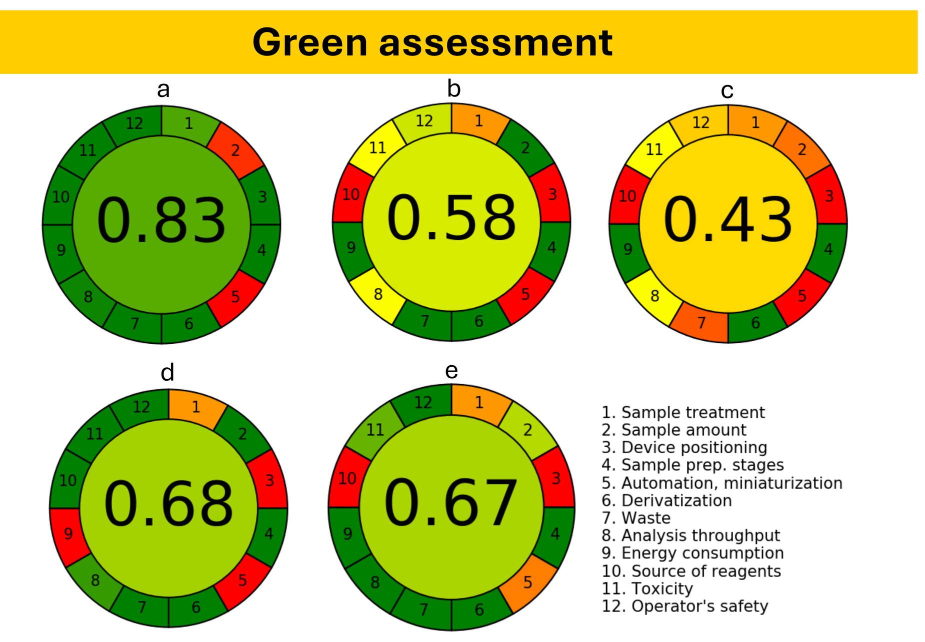


Fig 2. AGREE scores for a) in situ analysis, b) spectrophotometry, c) titration, d) HS-SPME-GC-MS, e) X ray fluorescence.

The lowest score for titration and spectrophotometry methods are due to large sample size, the amount of waste generated and the use of toxic reagents. Miniaturization and the use of specific electrochemical sensors could enhance a sustainable approach.

Results: Conventional Physicochemical Analysis

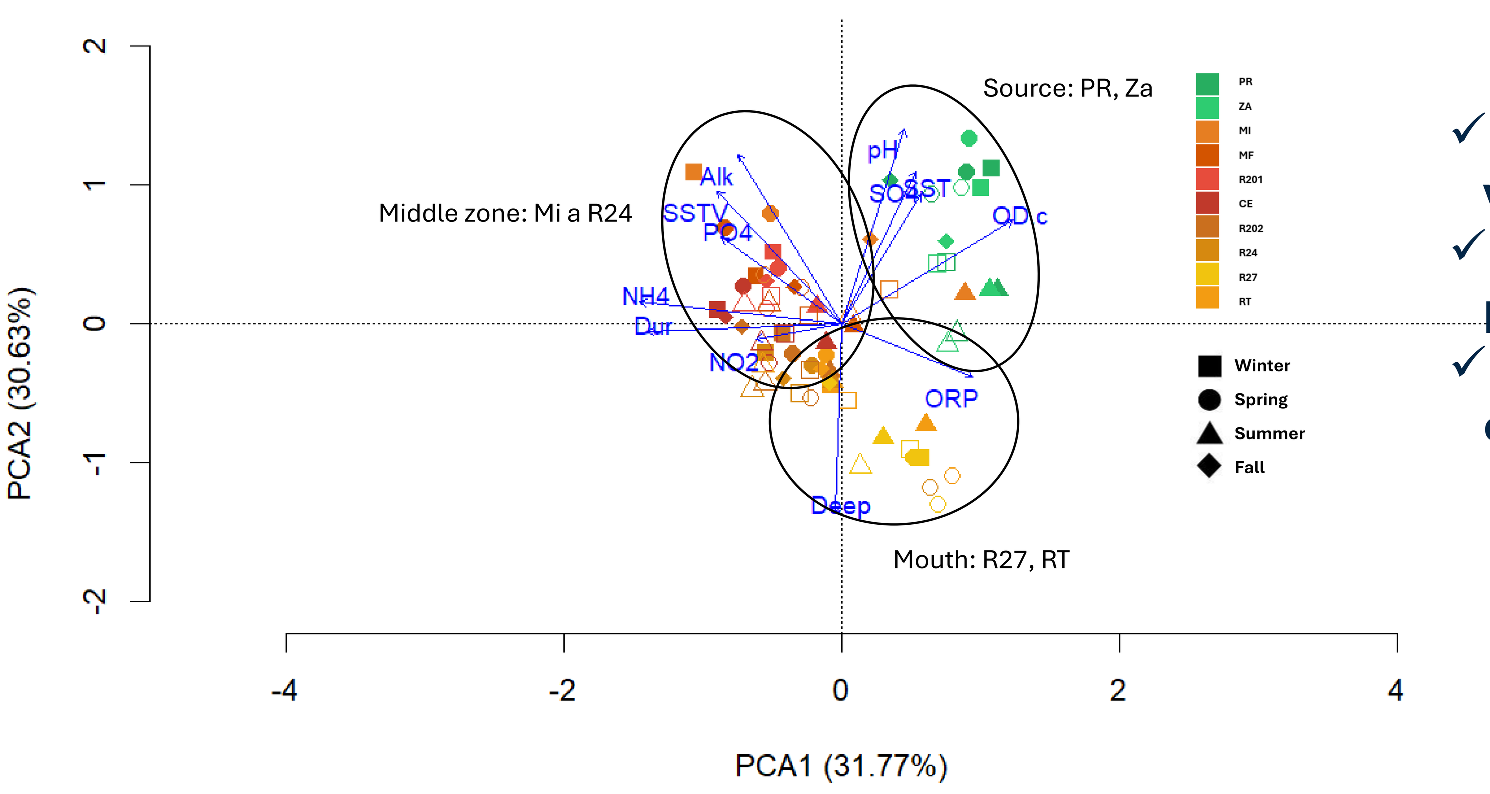


Fig 3. Principal component analysis performed for Reconquista River sampling sites in different seasons for two years. Full symbol: 1st year, void symbol: 2nd year.

- ✓ Pollution trends exhibit no significant seasonal variation.
- ✓ The sites are order in the groups according to pollution level.
- ✓ PCA and WQI accurately reflect field observations.

Beron Water Quality Index for urban rivers[4] considers temperature, chloride, ammonium, BOD5 and DO levels using the following equation:

$$WQI = \frac{\sum_{i=1}^{n} q_i}{\sum_{i=1}^{n} w_i}$$

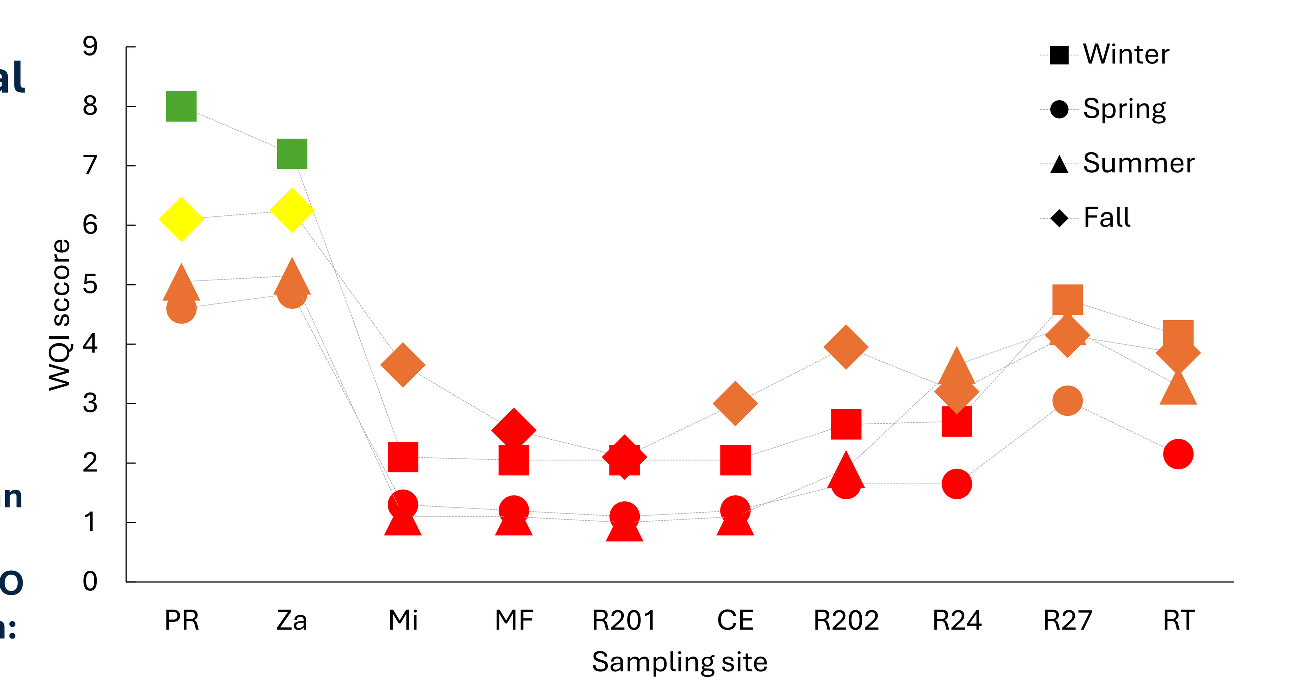


Fig 4. WQI scores for sampling sites in different seasons. • 8-10: mild pollution, • 6 -8: moderate pollution, • 3-6: high pollution, • 0-3: very high pollution/sewage like.

Results: X ray fluorescence

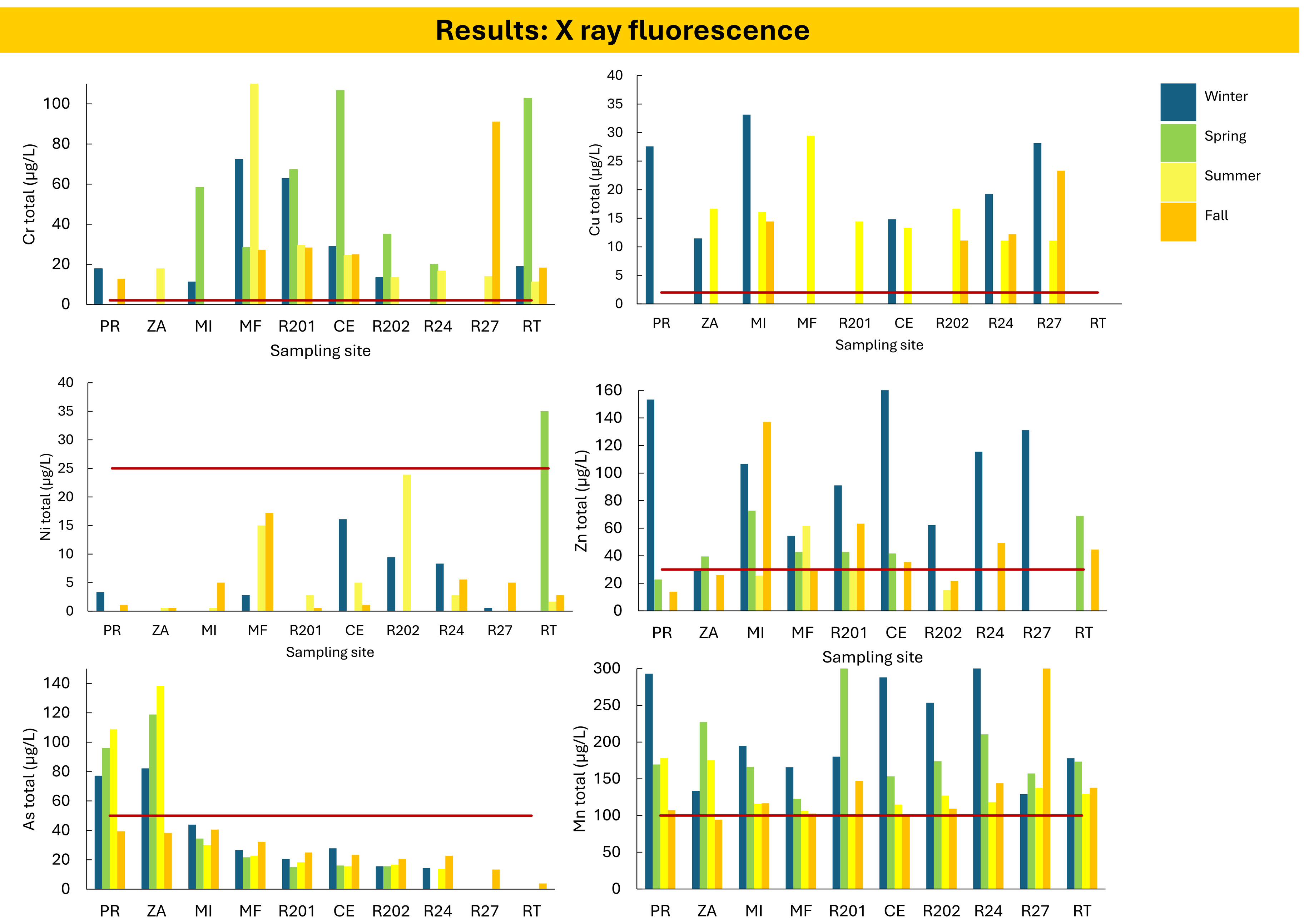


Fig 5. Metals and metalloids levels for sampling sites in different seasons. Red lines indicate aquatic life protection limits (µg/L): Cr= 2; Cu= 2: Ni=25; Zn= 30; As=50; Mn= 100.

Metal and metalloid levels show no spatial or seasonal trends. Cr, Zn, and Mn concentrations frequently exceeded aquatic life protection limits, primarily in the middle sampling zone.

These preliminary results highlight various approaches to assess water quality. In situ analysis is recommended due to its superior environmental sustainability compared to titration and spectrophotometry, which should be replaced with greener alternatives. X-ray fluorescence results indicate pollution with heavy metals, while phytoplankton analysis demonstrates its suitability for assessing water quality in an urban river and must be extended in time as its strong seasonal variation. VOCs analysis is still exploratory and need to be optimized.

Results: Phytoplankton Analysis

The abundance of phytoplankton classified in morpho-functional groups[5] shows strong seasonal variations and differences related to pollution levels in each season. The group 9b is more important in sewage like sites in spring and summer and group 5a and 5b most abundant in winter and fall, respectively.

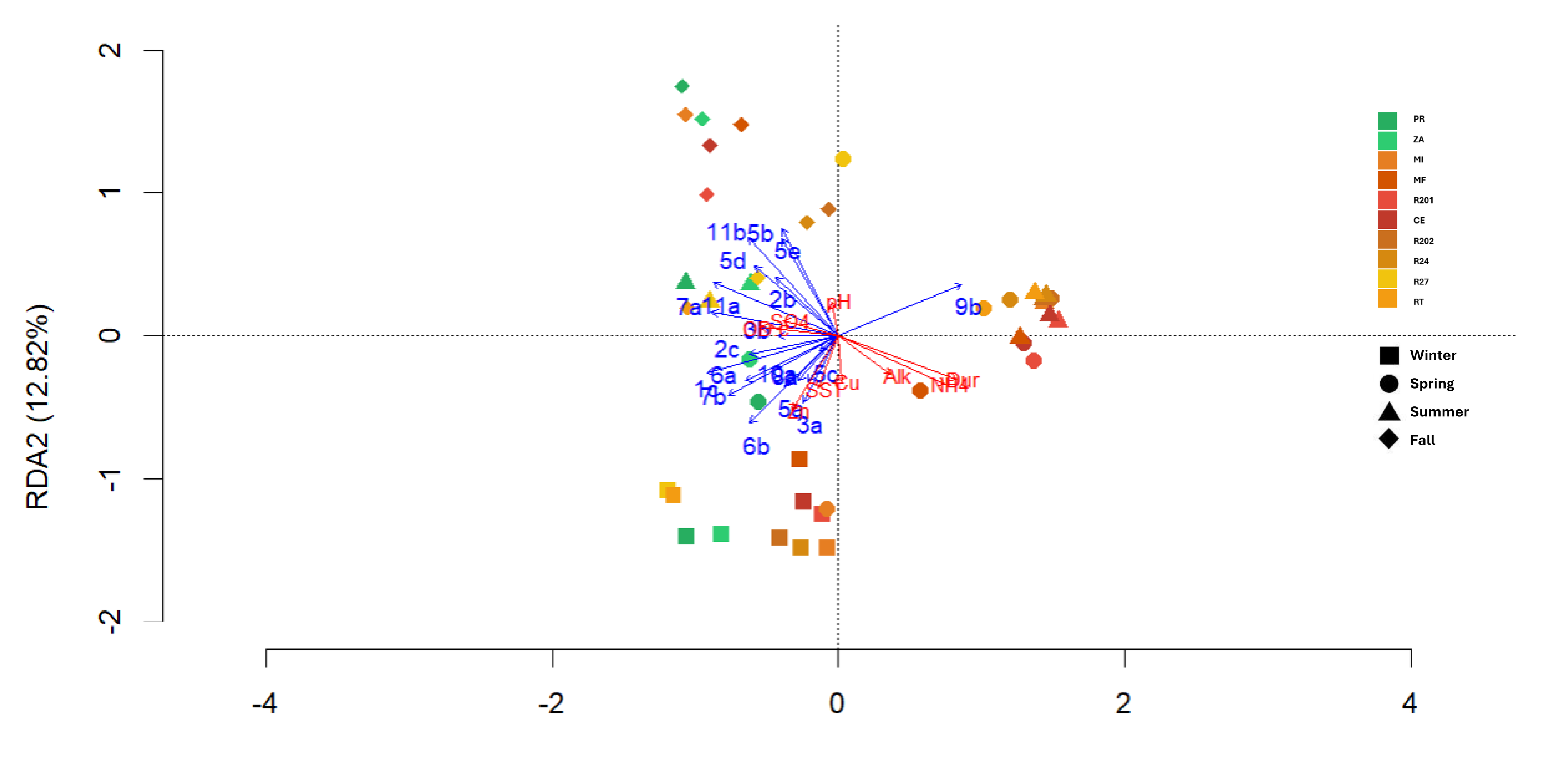
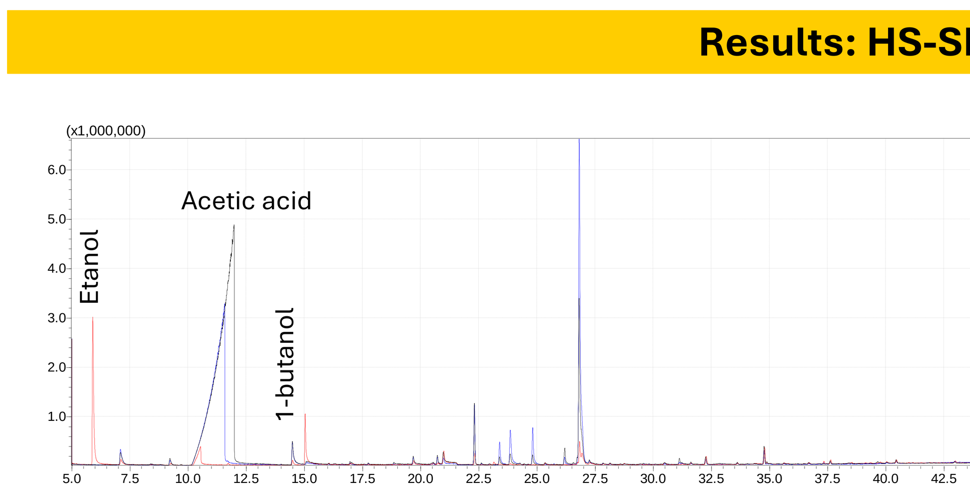


Fig 6. Redundance analysis for abundance of phytoplankton classified in morpho-functional groups (response variable) and abiotic matrix (explanatory variables).

Results: HS-SMPE-GC-MS



Headspace Solid-Phase Microextraction coupled with Gas Chromatography-Mass Spectrometry (HS-SPME-GC-MS) is a robust green analytical method for the detection and identification of volatile organic compounds. This method serve for the identification of volatiles contaminants and indicators of heterotrophic activity that could complement the phytoplankton analysis.

References

1. Castañé, P. M., Rovedatti, M. G., Topalián, M. L. and Salibián, A. Spatial and temporal trends of physicochemical parameters in the water of the Reconquista river (Buenos Aires, Argentina). Environ Monit Assess 117, 135–144 (2006).
2. Salibián, A. Ecotoxicological Assessment of the Highly Polluted Reconquista River of Argentina. Reviews of Environmental Contamination and Toxicology 35–65 (2006).
3. Pena-Pereira F., Wojnowski W. and Tobiszewski M. AGREE—Analytical GREEnness Metric Approach and Software. Analytical Chemistry 92 (14), 10076-10082 (2020).
4.Berón, L. Evaluación de la Calidad de las Aguas de los ríos de La Plata y Matanza-Riachuelo, mediante la utilización de índices de calidad de agua. Secretaría de Vivienda y Ordenamiento Ambiental, Ministerio de Salud y Acción Social, Argentina, 38 pp. (1984).
5- Salmaso N. and Padisák J. Morpho-Functional Groups and phytoplankton development in two deep lakes (Lake Garda, Italy and Lake Stechlin, Germany). Hydrobiologia 578, 97–112 (2007).