Nirvana

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In situ nano-enhanced bioremediation for nitrate impaired aquifers due to agricultural activity

Layman's report

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Full name: In situ nano-enhanced bioremediation for nitrate impaired aquifers due to agricultural activity

Acronym: NIRVANA

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Coordinator: Cetaqua Andalucía

Consortium: Aguas de Murcia (EMUASA) and Aquatec

Demonstrative site: Zarandona, Vega del Segura Aquifer (Murcia, Spain)

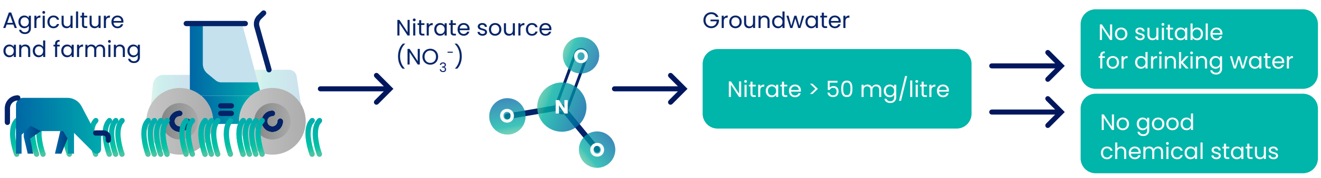
A touch of context

Nitrate is a chemical compound that is easily dissolved in water. From a chemical point of view, nitrate is made up of nitrogen and oxygen in a ratio of 1 to 3: there is one atom of nitrogen for every 3 of oxygen, which is why we represent it graphically as NO_3^-. When nitrate comes into contact with water it dissolves completely and therefore moves with the water, eventually underground until reaching an aquifer.

Nitrate in water has two possible origins: one natural, and the other due to contamination. Natural nitrate is present in water in low concentrations, typically below 5 or 10 mg/L.

The main anthropogenic sources of nitrate are the use of fertilisers in agriculture, animal excrements from farming, and urban wastewater.

Water with more than 50 mg/L does not comply with the European regulation on the quality of water intended for human consumption, and would not then be drinkable. In addition, groundwater bodies with nitrate concentrations above 50 mg/L do not comply either with the environmental objectives set out in the Water Framework Directive, and should consequently be defined as in "bad chemical status".

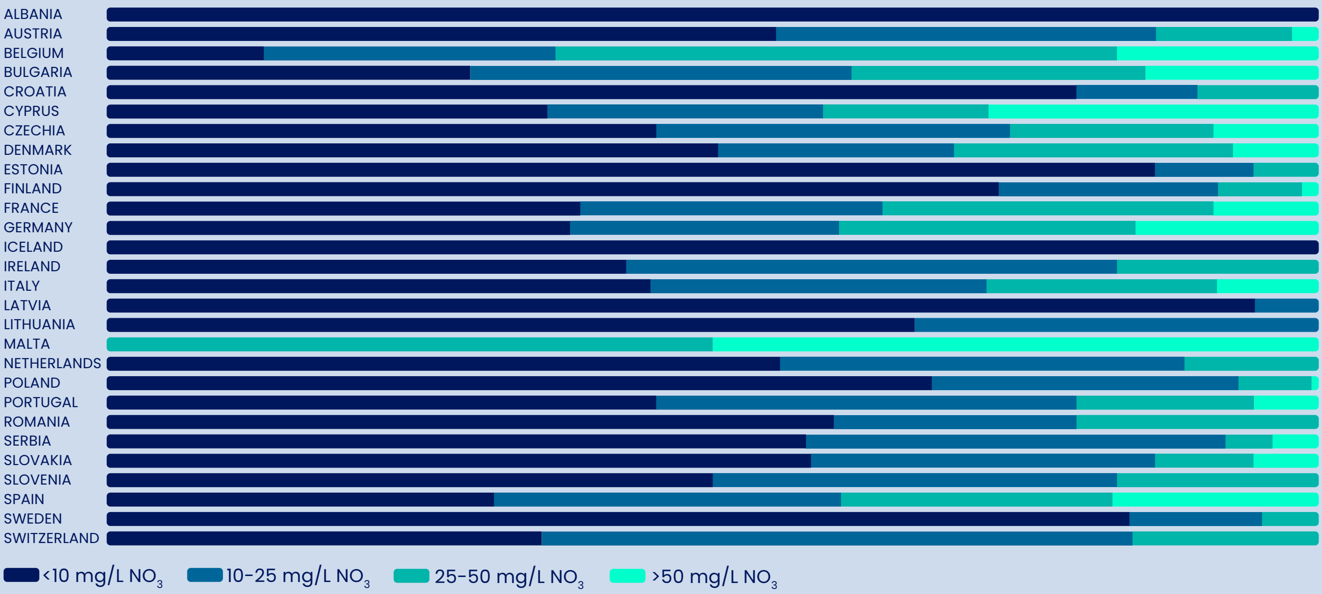


More than 350 groundwater bodies in Europe have an annual mean concentration of nitrate higher than the established limit and, in consequence, have a "bad chemical status". If we consider those with mean annual concentrations between 25 and 50 mg/L, therefore in risk of exceeding the limit, the number rises to 750.

In summary, the extensive use of fertilisers in agriculture, farming activities and discharge of untreated wastewater have resulted in nitrate pollution of aquifers, leading to the degradation of groundwater quality and the pollution of drinking water supplies. All this together limits the potential use of a natural resource which constitutes the largest reservoir of liquid freshwater in the world, and is an important resource especially as drinking water (75% of the European population depends on groundwater).

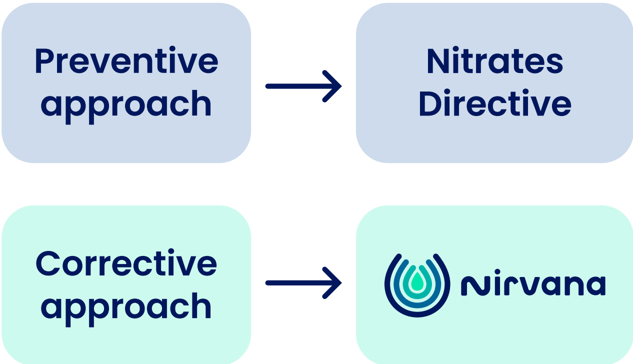
Classification of EU groundwater bodies according to their annual mean concentration of nitrate

Source: European Environment Agency.



How can we face excessive nitrate contents in groundwater?

There are two possible approaches to fight against nitrate contamination of groundwater: preventive and corrective.



Preventive measures are those aimed at avoiding the entry of nitrate into the natural environment, such as water treatment plants or advising farmers to apply the exact amount of fertiliser needed by the plant.

Corrective measures are aimed at solving the problem when it already exists, i.e. they reduce the amount of nitrate in already polluted waters. The denitrification technology proposed in the LIFE NIRVANA project is included in this category.

The main preventive measure is the Nitrates Directive (Directive 91/676/EC). It aims to reduce the input of nitrate into the environment and EU waters. It was published in 1991 and more than 30 years later nitrate is still the main responsible for the poor quality of the European aquifers and the abandonment of many drinking water production wells.

The solution, therefore, must come from a combination of both preventive and corrective measures.

Different nitrate removal techniques

There are currently several techniques for the elimination of nitrates in water. These can be classified into two groups:

- **Separation techniques**, as their name suggests, aim to separate nitrates from the water flow to be treated, concentrating them in a second waste product (brine) which has to be subsequently treated. These techniques are electrodialysis, reverse osmosis and anionic resins.
- The **transformation techniques** aim to transform nitrates into other harmless chemical compounds through biological or catalytic pathways.

The first techniques are currently the most widely used for the treatment of natural waters polluted by nitrates. Although they give very good results, they are expensive, do not solve the problem as they do not transform the nitrate into a harmless compound, and generate a brine concentrated in nitrates, with no direct economic value and which must be treated appropriately.

Among the transformation techniques, biological processes are currently widely used in wastewater and industrial water treatment and are incorporated in many treatment plants, giving very satisfactory results. However, this technology, although suitable for wastewater, cannot be used for drinking water treatment due to the possible bacterial contamination of the treated water and the presence of organic residues after water treatment.

LIFE NIRVANA, a novel technology for groundwater denitrification

The objective of the LIFE NIRVANA project is to demonstrate under real conditions an innovative technology for in situ groundwater denitrification based on the controlled injection of nanoparticles of zero-valent Fe (nZVI).

Iron nanoparticles have been successfully used for in situ groundwater remediation of chlorinated organic compounds at full scale. Laboratory experiments have demonstrated high potentiality and promising results for nZVI-induced biological denitrification, however no pilot or full scale demonstration study exists to date. Therefore, the novelty of LIFE NIRVANA project is to evaluate for the first time the performance of in situ groundwater biological denitrification with nZVI under real conditions and in a close-to-market context.

The proposed denitrification technology has been designed considering two different scale applications: local and full scale. 'Local' corresponds to single pumping wells, whereas 'full scale' addresses a complete nitrate-impaired groundwater body or a well-defined sector inside a groundwater body. Therefore, the implementation of the LIFE NIRVANA denitrification technology will contribute to:

- Recover former drinking water wells currently inactive due to nitrate concentrations above the legal limit (50 mg/L)
- Achieve a "good chemical status" in European groundwater bodies currently suffering from high nitrate concentrations.

LIFE NIRVANA pumping well

The specific goals established for the technology are the following:

- Reduction of nitrate concentration below 30 mg/l
- Reduction of total OPEX and CAPEX compared to other denitrification systems
- Reduction of CO_2 emissions compared to conventional pump and treat biological denitrification technologies
- Reduction of ~100% of the waste generated
- Preparation of a technical guide for in situ groundwater denitrification with nZVI based on the project results

What are iron nanoparticles and what are they for?

Iron nanoparticles, also known as nanoparticles of zero-valent iron or nZVI, are tiny particles of iron (Fe) with very interesting properties for many applications, among them groundwater remediation. They are highly reactive because of their small size (25-100 nm, i.e. 1,400 times smaller than a hair), large surface area (20-25 m^2 per gram) and reductive and sorption properties.

Iron nanoparticles are commercially available products which have been successfully used for in-situ groundwater remediation of chlorinated organic compounds (solvents, for instance).

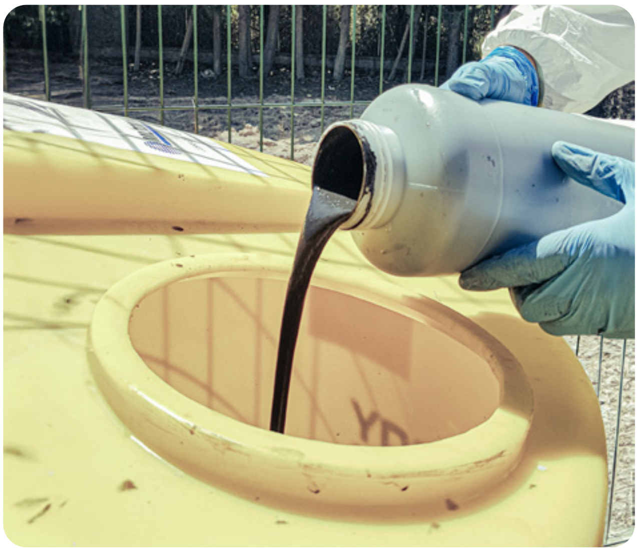
The main advantages of iron nanoparticles are:

- Large specific surface area, thereby significantly more reactive
- They can reach contaminants in deep aquifers or in areas not accessible by other methods due to their small size
- There are no ecotoxicity-related problems. In fact they may enhance the growth of bacteria which can further reduce the contaminant
- Concentrations required are small and thus, operational costs are limited

Iron nanoparticles are usually available as a dry powder or water slurry, each of them showing some advantages and disadvantages.

To minimise the fast degradation of iron nanoparticles when produced as water slurries, they can be coated with a biodegradable organic substance which can, in fact, acts as organic substratum for microorganisms present in the aquifer. These are the iron nanoparticles used in the LIFE NIRVANA project.

Slurry of iron nanoparticles

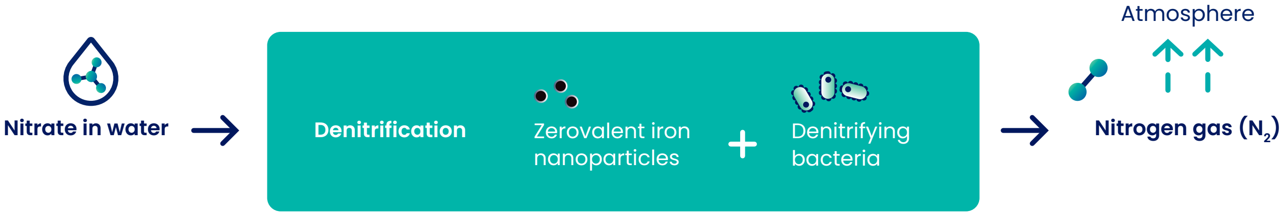


Pouring of iron nanoparticles into a mixing tank

Product	Advantages	Disadvantages
Dry powder	Slow degradation Reduced shipping costs	Its application requires dispersion and dosing units
Water slurry	Direct application Custom amount and concentration	Faster degradation Higher shipping costs

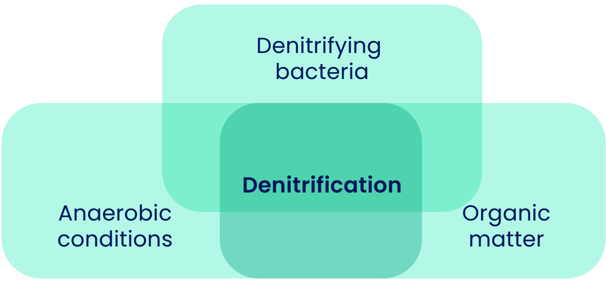
Iron nanoparticles and organic matter: the perfect blend

LIFE NIRVANA proposes a novel technology for the treatment of aquifers contaminated with nitrate. Nitrate is removed from the aquifer by means of a process called denitrification. Denitrification consists of the transformation of dissolved nitrate (NO_3^-) into the gas N_2, which automatically leaves the aquifer and reaches the atmosphere, where it has no toxic effect. In fact, the air we breathe contains 78% of N_2.



Groundwater denitrification requires the coexistence at the same time and place of the following three elements:

- Denitrifying bacteria
- Anaerobic conditions
- Organic matter



Denitrifying bacteria are the microorganisms responsible for denitrification, i.e. they have the ability to transform nitrate into N_2. They are ubiquitous in nature, therefore it can be considered that they are present in the subsurface.

Denitrification can occur when anaerobic conditions exist in the aquifer, and they are reached by the injection of iron nanoparticles.

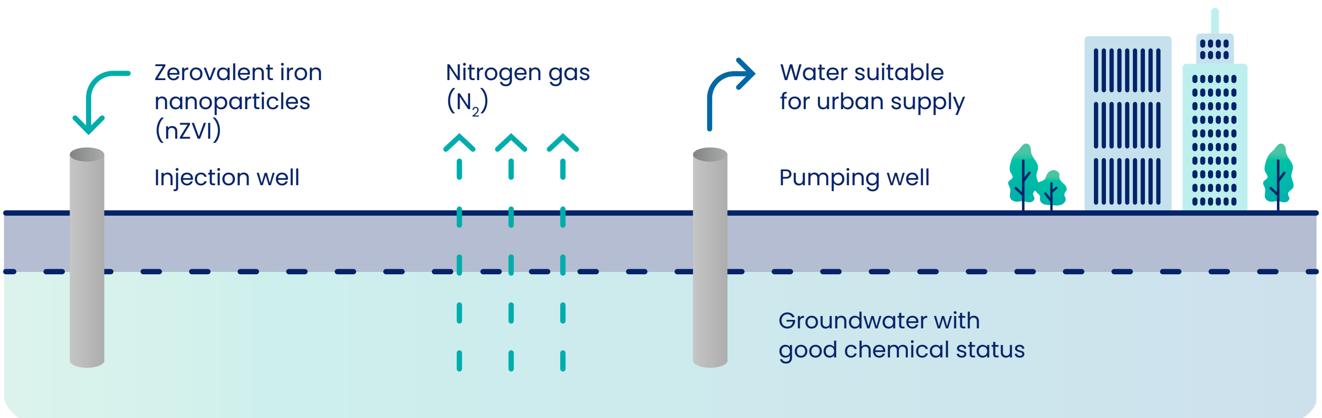
Natural groundwaters have very low contents of organic matter which limits the development of denitrifying bacteria. Therefore, the addition of an external source of organic matter is necessary for groundwater denitrification. This can be done by:

A. Adding the organic matter simultaneously with iron nanoparticles by using organic-coated particles, or

B. Adding the organic matter in a different stage

The combination of iron nanoparticles and organic matter allows to reach the perfect conditions for denitrification in the aquifer and, therefore, a net removal of nitrogen (nitrate) from groundwater.

As a result, the groundwater body could recover proper chemical status and become suitable for new uses, such as supply for human consumption. Therefore, NIRVANA is expected to promote more sustainable water resource management by increasing the volume of groundwater suitable for drinking consumption.



What has been the chosen pilot site?

The performance of the technology has been assessed in one of the pumping wells managed by EMUASA (one of the project's partners), which is nowadays used for irrigation of urban gardens in Murcia city. The selected pilot site is representative of other European nitrate-impaired groundwater bodies made up of unconsolidated deposits.

The well is located in **Vega Media y Baja del Segura** aquifer (SE Spain), which has been contaminated with high nitrate concentrations for decades, making its waters unsuitable for drinking consumption.

The pilot site consists of the following elements:

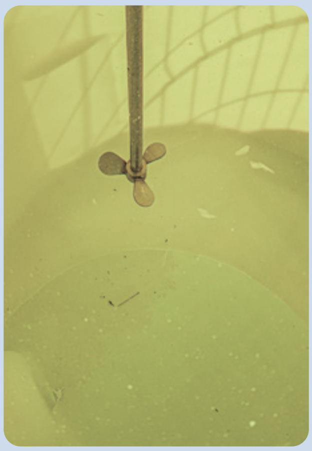
- One **pumping well**
- 2 **injection wells**, used for the introduction of iron nanoparticles and organic matter into the aquifer
- 7 **monitoring wells:**
  - 2 of them situated before the treatment zone
  - 4 of them located between the injection wells and the pumping well
  - 1 monitoring well placed after the treatment
- A 500-litre **tank** equipped with a mechanical mixer for diluting the iron nanoparticles and the acetate with water before injection
- **Injection pump**
- Other elements: Flow metres, water valves, and manometres.

Groundwater movement at the pilot site, which

Monitoring wells

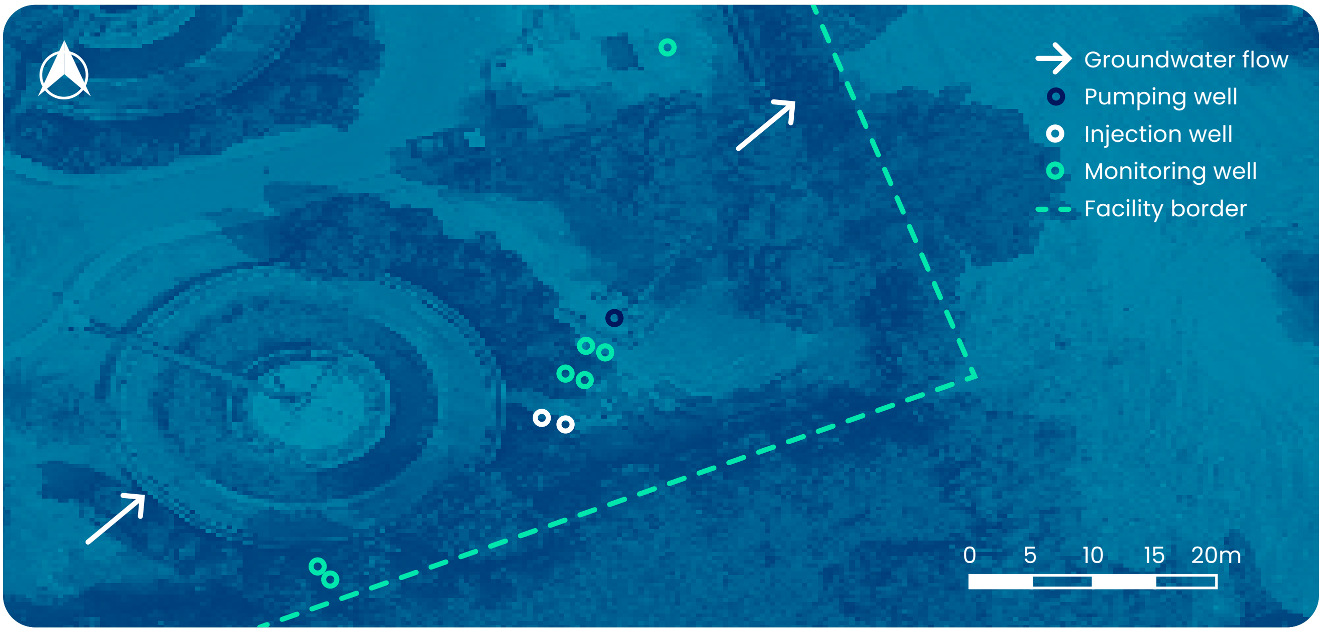
Injection well

500-litre tank used for iron nanoparticles mixing and dilution, equipped with a mechanical mixer.

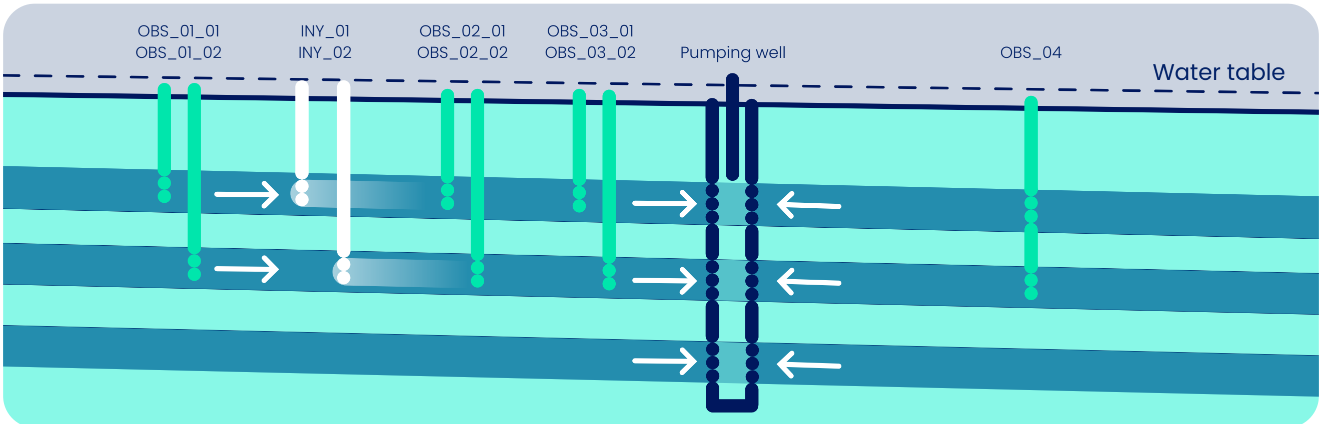


flows from southwest to northeast, determined the configuration design.

The treatment has been carried out in two different permeable levels because of the multi-layered nature of the aquifer at the pilot site.



LIFE NIRVANA pilot site



Cross-section of the LIFE NIRVANA site

There is no need to pump the water

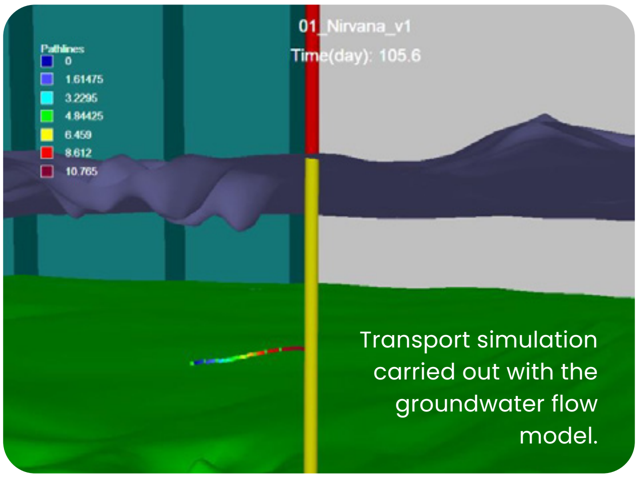
Unlike conventional denitrification treatments, LIFE NIRVANA technology does not require pumping of groundwater because the treatment takes place directly into the aquifer. For this reason it is called a "in situ" method as opposed to "pump&treat" or "ex situ" systems. This has the following advantages:

- Lower energy costs and CO_2 emissions
- Reduced space requirements since no plant needs to be built on the ground
- It allows the treatment of large volumes of water
- Two applications:
  - Single pumping wells
  - Large areas such as a contaminated aquifer or a defined sector into an aquifer

The project also includes the scaling-up of the technology. It has been carried out in the Campo de Cartagena - Mar Menor system (SE Spain), where a severe ecological degradation affects this valuable ecosystem due to an excess nitrate input from the aquifer.

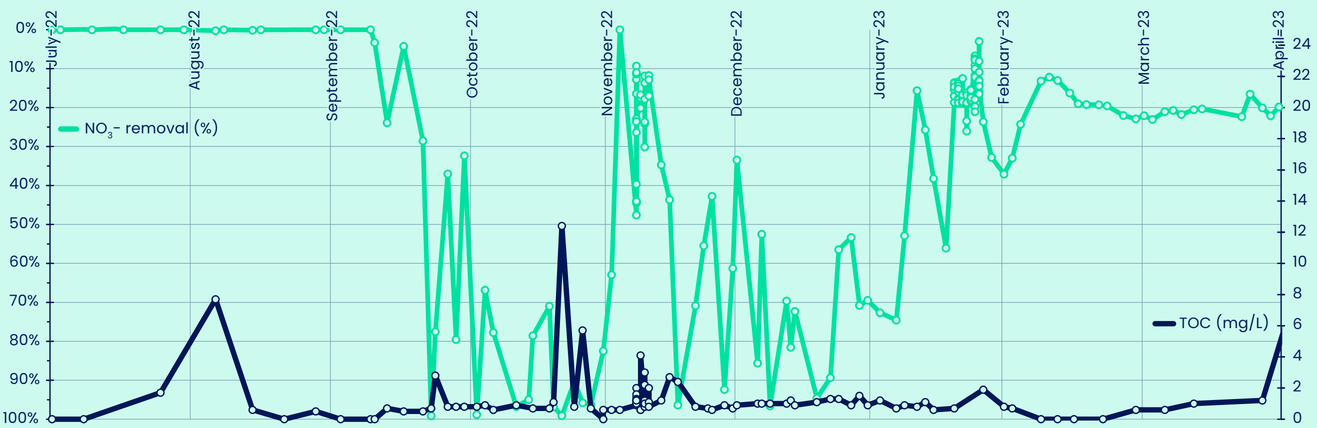
What has been achieved?

- Local characterisation of groundwater at the pilot site, including the preparation of a flow model of the aquifer, which will allow us to reproduce the aquifer's behaviour under specific -controlled- conditions.



Transport simulation carried out with the groundwater flow model.

- Configuration design of the denitrification site: number of injection and monitoring wells, location, distance between them and the pumping well, drilling depth.
- Drilling of 2 injection wells and 7 monitoring wells, and installation of other required equipment: nitrate and pH sensors, mixing tank, injection pump, water valves, manometres, etc.
- Performance of several tracer tests with salt (NaCl) before the beginning of the site operation, aiming at the characterisation of groundwater flow velocity, residence time and dilution rates inside the aquifer.
- Operation of the denitrification site for a year and a half: collection of more than 2,000 water samples, analyses of 20,000 parameters, and around 300 injections conducted.
- Nitrate removal rates reached up to 99%.
- Testing of 7 different injection strategies during the pilot site operation.
- Testing of 3 different iron nanoparticles produced by diverse EU manufacturers, with different characteristics and composition.
- Long-term nitrate removal rates up to 50%.
- No ammonium (NH_4^+) generation.
- Demonstration of the scaling up of the technology to larger treatment areas, using the Campo de Cartagena - Mar Menor ecologically-degraded system (SE Spain).
- Numerical modelling simulating the removal of nitrate, developed for three intensive-monitoring periods.
- Implementation of environmental, economic and social assessments of the proposed denitrification technology, and comparative analysis with two alternative treatments.
- OPEX reduction by 18%, CAPEX reduction by 50% and CO_2 emissions reduction by 45% compared to conventional treatments.
- No waste generation.
- Development of a Business Plan for a potential commercialization of the proposed technology at both national (Spain) and European scales.
- Preparation of a technical guide on the application of the proposed in situ groundwater denitrification methodology.
- Performance of 3 replication studies of the proposed technology in France, Portugal and Spain, including technical and economic assessments and expected results.
- Dissemination of project results through newsletters, audiovisual media (including a 3D virtual tour of the pilot site and some videos), attendance to specialised conferences, organisation of events with stakeholders and visits to the pilot site.



Temporal evolution of nitrate removal (%).

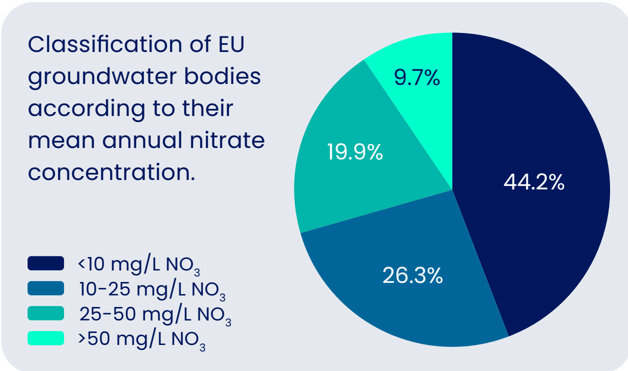
What's next: Project continuation

To ensure the continuity of the in situ groundwater denitrification methodology proposed in LIFE NIRVANA after the end of the project, a Replication Plan and a Business Plan have been developed.

Replication Plan

The objective of the Replication Plan is to identify other places at EU level (either aquifers, groundwater bodies or single wells) where the technology could be implemented.

The Replication Plan incorporates general guidelines for the implementation of the proposed technology in the environmental (River Basin District authorities), drinking water production and industry sectors, as well as conclusions and recommendations on the selection, implementation, operation and optimization of the NIRVANA denitrification treatment. It also includes a technical guide on the application of the proposed in situ groundwater denitrification methodology.



According to the most updated data available (2018-2020), 10% of all EU groundwater bodies have an annual mean concentration of nitrate higher than the legal limit, and then have a 'bad chemical status'. In addition, 20% of all groundwater bodies show mean annual concentrations between 25 and 50 mg/L and, in consequence, are at risk of failing to achieve a good chemical status. The countries with the highest number of groundwater bodies exceeding 50 mg/L are Spain, Germany, Italy and France.

Three replication studies have been carried out in three different aquifers selected from those identified in the previous section:

Country	Aquifer	Groundwater body
France	Lens-Liévin aquifer	FRAG303 - Craie de la vallée de la Deûle
Spain	Bárig aquifer	080.150 - Bárig
Portugal	Campina de Faro aquifer system	PTM19 - Campina de Faro - Subsistema Faro

They have been selected as meeting one of the following requirements:

- Presenting very high nitrate pollution (nitrate concentrations around 100 mg/L)
- Testing of the proposed technology in consolidated/fractured aquifers, instead of the demonstrated unconsolidated one in the LIFE NIRVANA project
- Groundwater-dependent surface water bodies or ecosystems

Lens-Liévin aquifer is located in Northern France, close to the Belgium border. It is part of groundwater body FRAG303 - Craie de la vallée de la Deüle. It consists of an unconfined chalk aquifer. The replication study has been carried out in a 60 m-deep well formerly used for the production of drinking water. The proposed configuration design consists of 3 injection wells arranged radially around the pumping well.

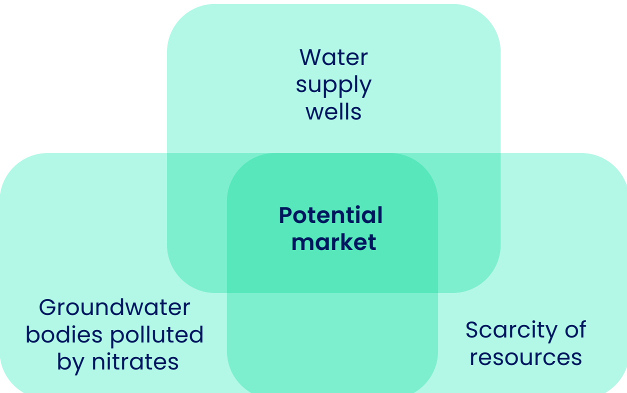
Bárig aquifer site is located in Eastern Spain. It is included in groundwater body 080.150 - Bárig, which is made up of limestones and dolostones. The selected site consists of one pumping well, still in use, which provides drinking water to a nearby town. The proposed configuration design also consists of 3 injection wells arranged radially around the pumping well.

Campina de Faro aquifer system is located in Southern Portugal, on the Atlantic coast. It is included in groundwater body PTM19 - Campina de Faro - Subsistema Faro. It consists of a porous aquifer principally made up of sands and gravels. Groundwater discharge from Campina de Faro aquifer constitutes a main vector for nitrogen transport to the protected coastal lagoon Ria Formosa. For this reason, the proposed configuration design for this site corresponds to a set of 15 injection wells strategically located along a 3 km strip of coast, through which 3.9 Mm^3 of nitrate-contaminated groundwater reach every year the protected lagoon.

Business Plan

The company responsible for the design of the Business Plan and the future commercialisation of the LIFE NIRVANA groundwater denitrification technology is Aquatec, one of the project’s partners. Aquatec is a water and environmental technology company offering consultancy services, design, integrated project development, installation and commissioning of advanced solutions for the optimisation of water cycle processes and environmental conservation.

The aim of the business plan is to define concisely, in the current market context, the existence and need for a product that solves an objective problem in the field of bioremediation. In order to do this, it is essential to define and understand the potential market, which results from the synergy of three entities: wells closed due to exceeding the nitrate limit, water bodies in poor chemical condition and scarcity of resources. In the current market context, customer segmentation thus defines a potential market segmentation and delimits a sales model, commercialization and marketing plan aimed at different target audiences.



The Business Plan has been designed for two possible applications: single wells and full scale. Full scale corresponds to the implementation of the technology in larger areas or for large volumes.

The Business Plan incorporates a cost study of the proposed technology, which is composed of CAPEX and OPEX costs. CAPEX includes drilling costs and all necessary equipment such as a tank with a built-in mechanical mixer, injection pump, flow metres, piping or water valves. Since CAPEX costs are very dependent on the depth of treatment, they are calculated for different drilling depths: up to 25 m, 50 m, 100 m and above 100 m. CAPEX costs also include optional equipment such as measurement probes or iron nanoparticles dispersion and dosing units, to be incorporated upon the customer's request.

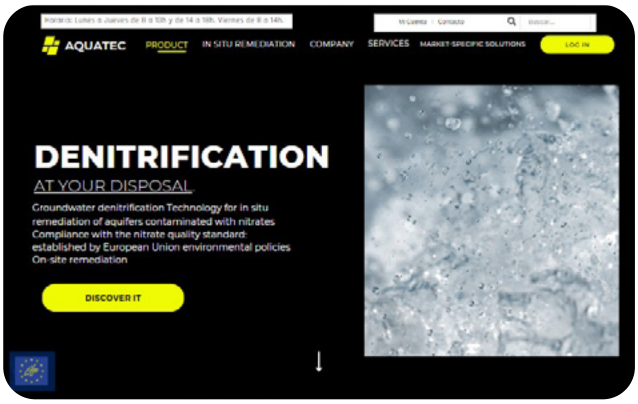
OPEX costs include iron nanoparticles and acetate supply, maintenance of injection wells, energy costs, and personnel costs.

The sales model consists of the request of a customer charge or fee for the use of the denitrification technology, which is established per single well under treatment. The fee is renewed annually and it includes other services such as remote technical consultancy.

The potential market for the LIFE NIRVANA denitrification technology is constituted by:

- All groundwater bodies classified as having bad chemical status because of nitrate, and wells used for the production of drinking water complying one of the following conditions:
- Abandoned because of excessive nitrate contents
- Currently in use but showing nitrate concentrations above the established legal limit (50 mg/L) or near this limit (>40 mg/L)

The marketing plan considers the setting up of a dedicated website designed for two potential customers: small users and large operators. The marketing and sales strategies are designed in such a way that they should foster both upselling (generation of more revenue by inviting the customer to purchase more expensive items, upgrades, or other add-ons), and cross-selling (selling of an additional product or service to an existing customer).



Benefits and impacts

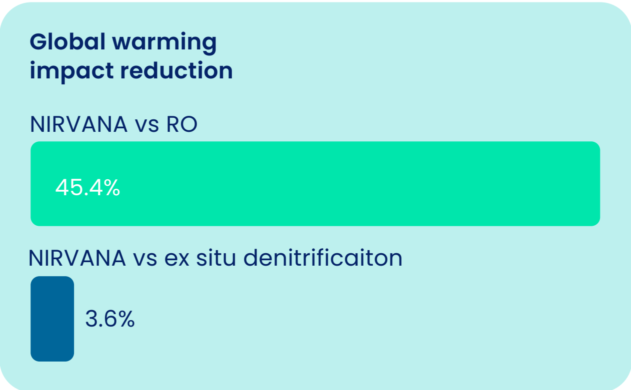
The performance of the groundwater denitrification technology of LIFE NIRVANA project has been assessed from an environmental, economic and social standpoints by its comparison with three different scenarios: the baseline conditions and two alternative technologies for removing nitrate.

Scenario	Description
Baseline conditions	Situation before the project implementation (no treatment)
Reverse osmosis (conventional alternative)	Reverse osmosis constitutes, in fact, the most commonly implemented solution to recover drinking water production wells with excessive nitrate concentrations
Ex-situ biological denitrification	Treatment based on aerobic granular sludge technology

Environmental assessment

LIFE NIRVANA shows a notorious reduction on the selected impacts in comparison with the conventional alternative, in particular:

- LIFE NIRVANA technology reduces CO_2 emissions up to 45% compared with reverse osmosis and up to 3.6% compared to ex-situ biological denitrification.
- In terms of reductions of the N equivalent emissions, LIFE NIRVANA allows to reduce these emissions more than 99% in comparison to reverse osmosis.
- The main impacts of the LIFE NIRVANA project are the usage of chemicals, followed by the electricity consumption, and drilling works.



Economic assessment

The main cost source of the LIFE NIRVANA technology is represented by chemicals, in particular iron nanoparticles and the CO_2 necessary for the regular maintenance of the injection wells. On the contrary, electricity represents a marginal cost.

The main results of the comparative economic assessment are the following:

- OPEX savings of 0.19 €/m^3 compared with reverse osmosis
- Total costs (OPEX + CAPEX) savings of 0.17 €/m^3 compared to reverse osmosis, and similar compared to ex-situ biological denitrification
- NIRVANA has the lowest electricity costs

Social assessment

- The local community appears to be aware of the water challenge addressed by LIFE NIRVANA and understands the risks and impacts involved
- Opinions on the impact on the local economy vary. Some believe the project identifies business opportunities, adds value to the target market, and can revitalise the local economy. Others are unsure of its contribution or whether the model can be widely adopted.
- The project has improved information availability and transparency in groundwater management in the region
- The project is recognized as a driver of innovation that can stimulate other innovative projects in the region and influence innovative policies.

Conclusions: contributing to a sustainable management of groundwater

For decades excessive concentrations of dissolved nitrate in EU groundwaters have been constituting a major environmental problem, mainly for two reasons: the water cannot be supplied as drinking water to the population, and the environmental objectives set out by the European policy -particularly the Water Framework Directive- are not fulfilled.

There are two possible approaches to face this problem: one preventive, represented by the Nitrates Directive, which has been in force for more than 30 years without the expected results, and the other corrective, which includes the LIFE NIRVANA project.

LIFE NIRVANA has demonstrated the efficiency of a novel technology to carry out in situ denitrification of groundwater contaminated with nitrates, which generates no waste and has lower operating (OPEX) and capital (CAPEX) costs, and reduced energy consumption and CO_2 footprint compared to conventional treatments. Unlike the latter, LIFE NIRVANA treatment can be implemented in situ (inside the aquifer), reducing energy costs and CO_2 emissions derived from water pumping.

The proposed denitrification technology presents two possible applications: single wells, especially suitable for former drinking water wells closed because of nitrate contamination; and full scale application, contributing to achieve a good environmental status of groundwater bodies or dependent surface ecosystems currently suffering from high nitrate concentrations.

One of the project outputs is a detailed technical guide on the application of the proposed in situ groundwater denitrification technology. This guide, along with three technical and economic replication studies conducted in European sites currently affected by nitrates, will pave the way for the future development of the LIFE NIRVANA technology. Its potential commercialisation is also supported by the design of a business plan suited to both national (Spain) and European scales.

Within the framework of the project it has been demonstrated that LIFE NIRVANA technology is a competitive alternative to conventional treatments for recovering drinking water wells affected by excessive nitrate concentrations, contributing to a more sustainable management of groundwater resources. It can also be suitable for large scale applications aiming at achieving a good status of water bodies and ecosystems with nitrate contents above the established environmental limit.

NIRVANA, a shared challenge among...

CETAQUA
WATER TECHNOLOGY CENTRE

Cetaqua Andalucía is a model of public-private collaboration that was created to ensure the sustainability and efficiency of the water cycle while taking regional needs into account.

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AGUAS DE MURCIA

Aguas de Murcia (EMUASA) is a joint venture service company, with 51% owned by the City of Murcia and 49% owned by HIDROGEA, within the Agbar Group, the first private operator of urban water management in Spain and one of the world leaders in the industry.

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AQUATEC

Aquatec, water and environment technology company from the group AGBAR, is a hydrogeological consulting and engineering firm that provides global solutions that contribute to sustainable development in the water sector through innovation in the design, construction and operation of drinking water treatment plants, wastewater treatment plants, groundwater facilities, tertiary treatment of reused water and reverse osmosis desalination plants.

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