Impact of Gravel Pits on Water Quality in Alluvial Aquifers

Igor Karlović 1,*, Tamara Marković 1, Andrew C. Smith 2 and Krešimir Maldini 3

1 Croatian Geological Survey, 10000 Zagreb, Croatia
2 British Geological Survey, Nottingham NG12 5GG, UK
3 Main Water Laboratory, Department of Monitoring, Josip Juraj Strossmayer Water Institute, 10000 Zagreb, Croatia
* Correspondence: ikarlovic@hgi-cgs.hr

Abstract: Gravel pits are considered potentially hazardous in terms of groundwater quality protection as they represent an open part of the aquifer system, increasing the aquifer’s vulnerability to contamination from the surface. The aim of this research was to determine the biogeochemical processes in gravel pits that have a positive effect on the groundwater quality in the alluvial aquifer in NW Croatia. The aquifer is situated below developed agricultural land, with high groundwater nitrate concentrations having been recorded over the last decades. The differences between two gravel pits and the surrounding groundwater were studied using in situ, hydrochemical, and isotopic parameters (δ15N-NO3 and δ18O-NO3), together with existing microbial data. The analyses of nitrogen species indicated that nitrate attenuation processes take place in gravel pits. Bacterial denitrification and nitrate uptake by algae were responsible for significant decreases in nitrate concentration. These processes were more effective in the inactive gravel pit, which has a longer water residence time and during warm periods, when microbial biomass, abundance, and activity were high. The seasonally variable microbial activity also affected trace metals, removing them from groundwater, possibly through the biosorption of metal ions. The presented research shows that the observed biogeochemical processes are associated with seasonal changes that affect the types and number of microbial communities and the chemical composition of water, resulting in gravel pits being groundwater remediation points.

Keywords: gravel pit; surface and groundwater quality; nitrogen species; denitrification; biosorption

1. Introduction

Gravel and sand are non-renewable natural resources which are used in the construction industry for various infrastructure projects (e.g., buildings, roads, and other concrete-based structures). With population growth, the demand for these mineral resources is increasing. The U.S. Geological Survey estimates that the world produced about 265 million metric tons of sand and gravel in 2020 [1]. The results of gravel and sand excavation include gravel pits, which change the morphology and drainage pattern of catchments [2]. The locations of gravel pits are conditioned by the position of natural deposits of sand and gravel, such as alluvial river deposits, streambeds, glaciofluvial deposits, etc. When sand and gravel extraction occur below the water table, groundwater naturally fills the gravel pit, forming a lake. The creation of gravel pits can therefore affect groundwater quality, which is especially important in areas that use groundwater as a source of drinking water. As a result of excavation, the protective soil cover is removed, which exposes the aquifer to the atmosphere and increases its vulnerability to contamination [3]. Another threat to groundwater quality is related to the illegal waste disposal in inactive gravel pits [4,5], which has an impact on both the gravel pit water and the downstream groundwater. Thus, it is very important to investigate the interaction between gravel pits and groundwater, particularly when gravel pits are formed in areas close to groundwater abstraction sites [6]. In general, limited attention has been paid to the positive effects of gravel pits on water quality.
quality compared to the negative ones. However, several studies have recognized that
gravel pits can mitigate groundwater nitrate contamination originating from agricultural
activity through assimilation by algae and/or bacterial denitrification [7–9]. Additionally,
the inflow and accumulation of nutrients into the gravel pits may cause eutrophication and
interfere with metal cycling [2]. There is potential to use gravel pits as nutrient filters and
to regulate groundwater nitrogen pollution, but it is important to understand the factors
responsible for nitrogen removal [10].

Groundwater reserves in Croatia are related either to alluvial aquifers in river valleys
with primary porosity or to karst aquifers with secondary porosity, the former of which
are suitable for gravel and sand extraction. In 2013, approximately 2.6 million m$^3$ of sand
and gravel were excavated in Croatia, one third of which was extracted from an alluvial
aquifer in the Drava River valley in the Varaždin region [11]. The groundwater of this area
belongs to strategic groundwater resources but also has a nitrate contamination problem,
originating mainly from agriculture. The origin, fate, and transport of nitrate within the
Varaždin aquifer have been studied extensively using hydraulic, geochemical, isotope,
microbiological, statistical, and modelling techniques [12], but a natural mechanism to
significantly reduce high nitrate concentrations in groundwater has not been identified.

Given the agricultural production and groundwater residence time [13], nitrate contamina-
tion in the Varaždin aquifer will likely continue for decades, so it is important to further
investigate possible processes that can contribute to the improvement of groundwater
quality. Therefore, the focus of this research is to investigate gravel pits as potential ground-
water remediation sites. In this context, we aimed to improve the understanding of the
biochemical processes affecting dissolved nitrate and metal concentrations in gravel pits.

Nitrate attenuation was evaluated by comparing our results with existing isotope and
microbial data, with emphasis on the influence of in situ parameters, seasonal differences,
and gravel pit activity. A sampling methodology that included collecting both filtered
and unfiltered water samples from the gravel pit allowed us to observe changes in metal
concentrations and discuss their relation to seasonal nitrate variations.

2. Materials and Methods

2.1. Study Area

The study was carried out within the Varaždin aquifer in the northwestern part
of Croatia (Figure 1). This area has a long-standing problem with nitrate groundwater
contamination, resulting mainly from sources related to agricultural production and the
sewage system [13,14]. The groundwater abstracted at well fields is used in the public water
supply network, excluding the Varaždin well field due to its high nitrate concentrations.
The aquifer was formed in the Quaternary as a result of the accumulation processes of
the Drava River [15], so its lithology is dominated by alluvial gravel-sand deposits. Mean
annual precipitation over the basin is 832 mm/a, with typical seasonal variations in air
temperature [16]. The groundwater flows in the SE direction and is recharged by surface
water and by the infiltration of precipitation [17]. Several gravel pits have been excavated
along the Drava River for sand and gravel mining (Figure 1). Among them, two small
gravel pits located in the central part of the aquifer and its adjacent observation wells were
selected as representative case studies. The water level in gravel pits represents a surface of
equipotential heads. Land use in the vicinity of the studied gravel pits is dominated by
agriculture. The agricultural fields are intensively cultivated (cabbage, maize, pumpkin,
potato), fertilized and are in contact with groundwater by rainfall infiltration through the
unsaturated zone. The gravel pits are recharged by groundwater and precipitation, without
inflow from surface waters. The origin of the nitrate in gravel pits is mainly related to
groundwater inflow, with concentrations in the central part of the aquifer exceeding the
threshold value of 50 mg/L [13]. However, flushing of the surface during rain events
occurs too.
The gravel pit in the village of Zelendvor is active, i.e., the excavation of gravel and sand is ongoing. The current surface area of the gravel pit is ca. 25,000 m². The thickness of the Quaternary sediments is around 12 m in this part of the study area, which limits the maximum depth of the gravel pit to between 10 and 12 m. The closest observation well, P-1530, is located about 2 km away in NE direction. The well is screened at its bottom at a depth of 7.5 m. The measured depth to groundwater, i.e., the thickness of the unsaturated zone, was between 5.80 and 6.33 m within the study period.

The gravel pit in the village of Šijanec is inactive and is used for recreational fishing. It is generally shallow, with water depths of up to 4 m, covering a surface area of approximately 12,000 m². The aquifer thickness at this site is around 35 m. There are high nutrient loads, and diverse communities of algae and bacteria that inhabit this gravel pit, most noticeable in the summer period when algal blooms of Microcystis sp. occur [18]. The closest observation well, PDS-5, is situated about 1 km from the gravel pit in the SE direction. The well is 31.0 m deep, with a 6 m long screen at a depth from 13.7 to 19.7 m. The measured depth to groundwater was between 2.63 and 5.52 m within the study period.

2.2. Water Sampling and Laboratory Analyses

Gravel pit water and groundwater samples were collected once a month for chemical analyses of nitrogen species and metal concentrations in water. Gravel pits were sampled from a boat in the central part of each gravel pit by submerging a bailer sampler below the water level, taking composite samples in the period from June 2017 to February 2020 at gravel pit Šijanec, and between June 2017 and December 2017 at gravel pit Zelendvor. The shorter period of sampling in the active pit was due to our inability to access the site from 2018 onwards. Neighboring observation wells were sampled on the same days as the gravel pits. Groundwater samples were collected after pumping at least three times the well volume, i.e., until the stabilization of in situ parameters. In situ parameters (temperature—T, pH, electrical conductivity—EC, dissolved oxygen—DO) were measured using a multiparameter WTW probe. Water samples for nitrate (NO₃⁻), nitrite (NO₂⁻), and ammonia (NH₄⁺) analyses were filtered in the field through a 0.45 µm cellulose membrane filter into 200 mL HDPE bottles. Separate water samples for metal analyses were collected...
into 100 mL HDPE bottles, both unfiltered and filtered through a 0.45 µm filter, and acidified with 6 M ultra-pure HNO₃. During the sampling campaigns, duplicate samples (unfiltered and filtered) were taken eight times from the inactive gravel pit and two times from the active gravel pit. Samples were kept cool in a refrigerator, transported to the laboratory, and measured on the same day. Gravel pit water samples for the isotopic analyses of δ¹⁵N and δ¹⁸O isotopes in nitrates were filtered through 0.2 µm membrane filters into HDPE 1000 mL bottles in the field, and upon arrival at the laboratory, they were frozen. The NO₃⁻ concentrations were measured using ion chromatography on Dionex ICS 6000, while NO₂⁻ and NH₄⁺ concentrations were analyzed using a spectrophotometer, the HACH DR 9000. The concentrations of metals in the water were measured using an inductively coupled plasma-mass spectrometry on the Agilent 8900 ICP-MS Triple Quad, following the procedure described in Karlovic et al. [19]. δ¹⁵N and δ¹⁸O isotope analyses were conducted at the Stable Isotope Facility of the British Geological Survey, following the analytical method described in Markovic et al. [16].

2.3. Methodological Approach

For this work, water sampling was conducted to compare the hydrochemical parameters of samples from the gravel pits with those of their closest observation wells, selected to represent the surrounding groundwater. In particular, in situ parameters and nitrogen species were observed over time to examine their interrelation and the changes in the water chemistry, and to explain possible mechanisms that reduce nitrate concentrations in gravel pits. Numerous authors have studied bacterial denitrification as an effective nitrate reduction process (e.g., [20–22]). The process is mediated by denitrifying bacteria and is mostly efficient under anaerobic conditions with available electron donors, such as dissolved organic carbon [23,24]. During denitrification, the decrease in nitrate concentration is accompanied by the enrichment of δ¹⁵N and δ¹⁸O [25]. Moreover, δ¹⁵N/δ¹⁸O ratios between 1.3 and 2.1 suggest the occurrence of denitrification [26–28]. Nitrate reduction in gravel pits has also been associated with nutrient uptake by primary producers such as algae [3,9,29]. In order to identify the biochemical processes that govern nitrate dynamics in gravel pit waters, the obtained results were compared to existing microbial [18,30] and groundwater nitrogen isotope data [16]. Besides nitrate reduction processes, the potential bioaccumulation of metals in gravel pits was studied by comparing metal concentrations between unfiltered and filtered water samples.

3. Results and Discussion

3.1. In Situ Parameters and Nitrogen Species

The measured in situ parameters and analyzed nitrogen species are presented in Table 1. The in situ parameters within individual gravel pits did not show significant changes with depth, which points to homogenized water in the gravel pit lakes. The high EC values indicate dissolved solids at the sampled locations, which is expected given that they are located in an agricultural area with an intensive input of nutrients into the system. The highest EC was measured in the groundwater, followed by a lower EC in the active pit, and the lowest EC in the inactive gravel pit. Higher variations in water temperature were observed in the gravel pits due to the influence of seasonal changes in air temperature, whereas the mean groundwater temperature indicates the mean annual temperature of the aquifer recharge area. The gravel pits had higher pH values than the surrounding groundwater, with a significant shift to more alkaline in the inactive gravel pit. All measurements of DO suggest that groundwater and gravel pit waters are oxygen saturated.
Table 1. In situ parameters and nitrogen species recorded in investigated gravel pits and in groundwater (observation wells). Data are shown as minimum and maximum values with mean values in parentheses.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Active Gravel Pit</th>
<th>P-1530</th>
<th>Inactive Gravel Pit</th>
<th>PDS-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC (µS/cm)</td>
<td>447 (572) 649</td>
<td>689 (693) 697</td>
<td>217 (334) 501</td>
<td>661 (685) 694</td>
</tr>
<tr>
<td>T (°C)</td>
<td>5.5 (16.8) 24.1</td>
<td>9.2 (14.5) 22.9</td>
<td>1.2 (15.5) 32.1</td>
<td>11.8 (12.6) 13.9</td>
</tr>
<tr>
<td>pH</td>
<td>7.52 (7.80) 8.14</td>
<td>7.33 (7.45) 7.53</td>
<td>7.04 (8.64) 10.67</td>
<td>6.91 (7.28) 7.45</td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>9.9 (12.8) 18.5</td>
<td>8.5 (9.7) 11.6</td>
<td>7.1 (12.9) 19.5</td>
<td>3.5 (8.2) 9.9</td>
</tr>
<tr>
<td>NO3⁻ (mg/L)</td>
<td>33.7 (54.2) 64.5</td>
<td>48.1 (88.7) 109</td>
<td>0.6 (15.8) 50.1</td>
<td>42.1 (76.5) 210</td>
</tr>
<tr>
<td>NO2⁻ (mg/L)</td>
<td>0.06 (0.16) 0.22</td>
<td>&lt;0.01 (&lt;0.01) 0.01</td>
<td>&lt;0.01 (0.09) 0.38</td>
<td>&lt;0.01 (0.01) 0.02</td>
</tr>
<tr>
<td>NH4⁺ (mg/L)</td>
<td>0.02 (0.15) 0.34</td>
<td>&lt;0.01 (0.02) 0.05</td>
<td>&lt;0.01 (0.27) 0.70</td>
<td>&lt;0.01 (0.04) 0.10</td>
</tr>
</tbody>
</table>

Although gravel pits are mainly recharged by groundwater, and the observation wells are not far away, significant differences in nitrate concentrations were observed (Table 1; Figure 2). Both observation wells had high nitrate levels, with mean concentrations exceeding the threshold value of 50 mg/L. This is influenced mainly by agricultural activity in this part of the aquifer [13,16]. Seasonal peaks of groundwater nitrate concentrations are associated with the rainy season, during which nutrient leaching from cultivated areas is increased, but also with the dry season, during which the absence of rain events is replaced by intensive irrigation. As a result, the highest nitrate concentration of around 210 mg/L was measured in a groundwater sample collected in summer (June 2017). Conversely, the nitrate concentrations of the gravel pits were lower than those of groundwater throughout the whole study period. Mean nitrate concentrations reduced more than 30 mg/L within the active gravel pit. An even greater decrease in nitrate concentrations was observed in the inactive gravel pit, with maximum values around the 50 mg/L threshold value. The nitrate concentrations of the gravel pits varied among hydrological periods, which is likely controlled by the inflow of groundwater nitrate concentrations, the dilution of lake water by rainwater, and nitrogen transformation processes. Low NO2⁻ and NH4⁺ concentrations have been recorded in groundwater samples, often below the detection limit. However, low NO2⁻ and NH4⁺ concentrations in gravel pit waters are generally observed during the colder parts of the year, when higher nitrate concentrations are recorded (Figure 3); conversely, peak NO2⁻ and NH4⁺ values are measured during the warmer parts of the year, when nitrate concentrations are seen to decrease. This reversal indicates seasonal changes in the dynamics among nitrogen species, possibly due to nitrogen transformation processes.

Figure 2. Time series showing the decrease in nitrate concentrations of the groundwater in the (a) active gravel pit and (b) inactive gravel pit.
while having low nitrate concentrations, an indication of denitrification. Moreover, the attenuation was assessed using nitrate isotope data from groundwater and inactive gravel pit (Figure 4). The pronounced separation of gravel pit samples from groundwater samples clearly shows changes in stable isotope composition. The gravel pit samples were enriched (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4). The pronounced separation of gravel pit samples from groundwater samples (Figure 4).

3.2. Nitrate Attenuation in Gravel Pits

The two main nitrate attenuation processes studied in this piece of research are denitrification and nutrient uptake by algae in gravel pits. Since both processes are microbial-catalyzed, the inclusion of previous microbial research in the studied gravel pits [18,30] in conjunction with nitrogen isotope data contributed to the interpretation of nitrate reduction in gravel pits. Nitrate entering the gravel pits is readily available for microorganisms to utilize, and high dissolved organic carbon concentrations [31] suggest that electron donors are also available. However, high levels of dissolved oxygen may be a limiting factor for denitrification at these sites, as the occurrence of denitrification is more favorable at dissolved oxygen concentration levels below 1–2 mg/L O2 [20]. Nevertheless, denitrification was assessed using nitrate isotope data from groundwater and inactive gravel pit (Figure 4). The pronounced separation of gravel pit samples from groundwater samples clearly shows changes in stable isotope composition. The gravel pit samples were enriched with $\delta^{15}$N while having low nitrate concentrations, an indication of denitrification. Moreover, the $\delta^{15}$N/$\delta^{18}$O ratio from a sample collected in winter (December 2019) was 1.1, having shifted to a value very close to the denitrification range. The $\delta^{15}$N/$\delta^{18}$O ratio of another gravel pit sample, collected in summer (June 2019), suggests the absence of denitrification.

![Figure 3](image1.png)
Figure 3. Relationship between the nitrate, ammonia, and nitrite concentrations of the (a) active gravel pit and (b) inactive gravel pit.

![Figure 4](image2.png)
Figure 4. Relationship between the nitrate concentration and nitrate isotopic composition ($\delta^{15}$N-$\text{NO}_3^-$) of the inactive gravel pit and nearby groundwater (values for groundwater are interpreted in Marković et al. [16]).
Although the potential for denitrification is higher in anaerobic conditions, the process has also been observed in aerobic conditions [32]. Furthermore, denitrification in gravel pits has been previously documented [7,8,10,33], implying that our high dissolved oxygen measurements do not completely exclude the possibility of denitrification. High DO measurements are due to the process of photosynthesis, where algal and bacterial communities generate oxygen as a byproduct, causing the supersaturation of oxygen in the surrounding water.

Seasonal variation in denitrification activity suggests that another process is responsible for nitrate attenuation in gravel pits throughout the year. In the inactive gravel pit, algal and bacterial communities are in competition for nutrients, with Cyanobacteria dominating in the summer period, followed by their breakdown and replacement with diatoms, dinoflagelatte, Bacillariophyceae, and Actinobacteriota in the winter period [18]. This competition is crucial for understanding how microbial dynamics govern nitrate reduction in gravel pits. Water temperature affects the rate of biochemical processes [34], but it also influences the survival time of microorganisms [35]. Both studied gravel pits showed decreases in phytoplankton biomass and abundance in the winter season [30], which coincided with the higher nitrate concentration. In the summer, high water temperatures, exposure to sunlight, low water levels, and increased nutrient load present favorable conditions for algal development in gravel pits and the consequent nutrient uptake by algae, which is responsible for the observed nitrate reduction. Additionally, higher summer pH in the inactive gravel pit, combined with lower EC and nitrate concentration, suggest that the activity of algae is more efficient in the inactive gravel pit. In the winter period, the effective nitrate utilizers diatoms [36] and dinoflagelatte [37] may assist in bacterial denitrification in nitrate reduction.

The rate of nitrate decrease is also related to the activity of gravel pits. Nitrate reduction is affected by the lake water residence time, i.e., a longer mean residence time likely results in increased nitrate uptake and a decrease in nitrate concentrations [3]. The residence time of water in the gravel pit may increase with time, as the permeability of its banks changes due to clogging [2]. Additionally, the post-excavation age of the gravel pit influences the ecosystem metabolism of the gravel pits [9], and Cyanobacteria favor lakes with a long residence time [38]. It is fair to assume that the active gravel pit has shorter water residence times due to the constant excavation of gravel and sand, which enables a continuous supply of nitrate through the inflow of fresh groundwater and affects the productivity of algae, resulting in a smaller decrease in nitrate concentration.

Overall, different mechanisms dominate nitrate attenuation in gravel pits depending on the season. Nitrate reduction in summer is due to nutrient uptake by algae, while the combined effect of bacteria and algae is present in winter. Although the research emphasis was on the comparison of the summer and winter seasons, the nitrate fate in gravel pits in other seasons is likely transitional between these two processes. The presented results are in accordance with [7,10], who identified denitrification and assimilation by algae as the main nitrogen removal mechanisms in gravel pits. Based on our observations, gravel pits act as a sink for nitrate within the studied aquifer system, therefore having a positive effect on groundwater quality.

3.3. Metal Bio-Removal in Gravel Pits

The seasonally variable activity of algae was also seen in the analysis of selected trace metals (Al, As, Cd, Cr, Cu, Fe, Mn, and Pb) in the gravel pit waters. The groundwater contained very low concentrations of such trace metals, measuring from below the detection limit of the instrument to the highest concentration, which was for iron around 34 µg/L (Table 2). Filtered gravel pit water samples were characterized by lower trace metal concentrations compared to unfiltered samples, close to the concentrations found in groundwater. During filtration, colloidal particles, algae, and bacteria are removed from samples, together with trace metals, which are bound to them. Gravel pit lakes are generally clear with low turbidity (low colloidal particle content), but during algal blooms,
the turbidity is higher. It is observed that during these blooms in the warm period of the year, trace metals were higher in unfiltered samples than in filtered ones. During the colder period of the year, the concentrations of trace metals in unfiltered and filtered samples were closer. This suggests the sequestration of metals from gravel pit waters by algae and Cyanobacteria, which is especially pronounced in the warm period when their activity is high.

Table 2. Comparison of metal concentrations in gravel pits (unfiltered and filtered pairs) and groundwater samples. Data are shown as minimum and maximum values with mean values in parentheses.

<table>
<thead>
<tr>
<th>Parameter (µg/L)</th>
<th>Inactive Gravel Pit</th>
<th>Active Gravel Pit</th>
<th>Groundwater</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unfiltered</td>
<td>Filtered</td>
<td>Unfiltered</td>
</tr>
<tr>
<td>Al</td>
<td>11.1 (144) 516</td>
<td>4.72 (9.98) 29.5</td>
<td>28.8 (84.3) 197</td>
</tr>
<tr>
<td>As</td>
<td>0.62 (1.32) 2.28</td>
<td>0.60 (0.83) 1.71</td>
<td>0.61 (0.81) 1.07</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;0.01 (&lt;0.02) 0.08</td>
<td>&lt;0.01 (&lt;0.02) 0.03</td>
<td>0.01 (0.02) 0.02</td>
</tr>
<tr>
<td>Cr</td>
<td>0.09 (0.38) 0.68</td>
<td>0.04 (0.12) 0.28</td>
<td>0.18 (0.30) 0.40</td>
</tr>
<tr>
<td>Cu</td>
<td>1.07 (2.77) 12.8</td>
<td>0.52 (1.63) 2.26</td>
<td>0.94 (1.50) 2.05</td>
</tr>
<tr>
<td>Fe</td>
<td>67.9 (366) 836</td>
<td>11.9 (23.2) 33.8</td>
<td>36.1 (112) 258</td>
</tr>
<tr>
<td>Mn</td>
<td>1.94 (20.7) 47.3</td>
<td>0.10 (0.47) 1.06</td>
<td>11.3 (25.8) 62.4</td>
</tr>
<tr>
<td>Pb</td>
<td>0.25 (1.19) 2.68</td>
<td>0.06 (0.57) 3.14</td>
<td>0.23 (0.36) 0.57</td>
</tr>
</tbody>
</table>

Determining the actual microbial processes of metal removal was outside the scope of this study, but biosorption may be one of them. According to Al-Amin et al. [39], different cyanobacterial species are reported to sequester metal ions by biosorption (occurring on the cell surface) and/or bioaccumulation (occurring inside the cell). Among them, Microcystis, the most dominant species in the inactive gravel pit during the summer period [18], is reported to have removal efficiencies by biosorption of Cd (II), Cu (II), and Cr (VI) between 24–76% [40].

Using the presented results and identified biochemical processes, natural groundwater remediation mechanisms within the studied gravel pits are depicted in a conceptual model (Figure 5).

![Figure 5](image-url)
recharges the gravel pit, where nitrate is reduced through uptake by algae in the summer period, combined with denitrification in the winter period. The nitrate decrease is more pronounced in the inactive gravel pit and in the warm period, when microbial activity is high. The metal ions are transported into gravel pits via groundwater, surface washout during rain events, and from machines for gravel extraction. The bio-removal of metals from gravel pit water is closely related to algal activity in summer, i.e., the presence of Cyanobacteria and their uptake capacity.

4. Conclusions

The main objective of this research was to explore the biochemical processes which take place in gravel pits and have a positive effect on groundwater quality. The conducted research provided the following conclusions:

- Highly active microbial systems are present in gravel pit lakes, where bacterial denitrification and nitrate uptake by algae are responsible for significant decreases in nitrate concentration, thus serving as a sink for nitrate within the studied aquifer system.
- These processes were more efficient in the inactive gravel pit that has a longer water residence time, resulting in increased nitrate uptake and decreases in nitrate concentrations.
- The bio-removal of dissolved metals from gravel pit water is mediated by cyanobacteria, probably by the biosorption of metal ions.
- All observed processes are more pronounced in the warm period when microbial biomass, abundance, and activity are high, which confirms that when favorable conditions are met, microorganisms are the key factor that governs the fate of nitrate and metals in the studied gravel pits.

Although this study has demonstrated the positive effects of gravel pits, there are some negative aspects that pose a potential risk to groundwater quality. The excavation of gravel pits removes the protective soil cover, thus increasing the vulnerability of aquifers to contamination from the surface. In our case, nutrients from agricultural land are easily transferred to groundwater by rainfall or irrigation. Opening new gravel pits could lead to evaporation losses from the lake water surface and to the emission of \( \text{N}_2\text{O} \) from the potential denitrification process. However, it has been considered that the denitrification activity of gravel pits does not modify the world stock of \( \text{N}_2\text{O} \). Additionally, human activities such as fish farming can affect groundwater quality by adding extra nutrients into gravel pits, leading to eutrophication. Of particular concern are cyanobacteria, as some species are toxic.

Gravel pits have the potential to be significant nitrate sinks in aquifers below agricultural land and represent a unique approach to groundwater remediation. Considering both the positive and negative aspects of gravel pits, their overall impact on groundwater quality remains unclear. At this study site, future research efforts should focus on quantifying the nitrate removal capacity of gravel pits. The ability to use a series of gravel pits to provide groundwater remediation services at a regional level can be evaluated by numerical groundwater modelling. Currently, it is questionable whether the small number of gravel pits in the study area can significantly affect nitrate concentrations in the aquifer, given the large volume of groundwater. From an economic perspective, the increase in the prices of gravel and sand as construction materials opens up the possibility of excavating new gravel pits, which is a likely scenario in the future as gravel and sand mining represents important industrial activity in Croatia. Our research showed that the monitoring of water quality in gravel pits is a prerequisite for understanding the processes within gravel pits and establishing appropriate protection measures, which can ultimately contribute to improving the quality of groundwater.

Author Contributions: I.K. conceptualization, methodology, data collection, writing—original draft preparation; T.M. methodology, data collection, writing—original draft preparation; A.C.S. analyses, writing—review and editing; K.M. analyses, writing—review and editing. All authors have read and agreed to the published version of the manuscript.
Funding: This research was financially supported by the Croatian Scientific Foundation (HRZZ) under grant number HRZZ-IP-2016-06-3565 and supported by the Young Researchers Career Development Project—Training of New Ph.Ds—HRZZ and ESF.

Data Availability Statement: The data presented in this study are available in this article. Additional data are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References


**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.