

Hydrochemical Impacts of Limestone Rock Mining

Ghinwa M. Naja · Rosanna Rivero ·
Stephen E. Davis III · Thomas Van Lent

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Abstract Hydrochemical impacts of shallow rock industrial-scale mining activities close to sensitive constructed and natural wetlands were investigated. The shallow surficial groundwater and surface water in the Everglades Agricultural Area (EAA) were characterized. The chemical composition of sulfate and chloride in groundwater increased with depth. The average concentration of chloride averaged 182 mgL^{-1} at 6 m deep and increased gradually to $1,010 \text{ mgL}^{-1}$ at 15 m deep, $1,550 \text{ mgL}^{-1}$ at 30 m deep to reach $7,800 \text{ mgL}^{-1}$ at 60 m deep. Comparatively, the surface water chemical composition in the surrounding areas showed much lower cationic and anionic charge. The specific conductivity and total dissolved solids of surface water in canals (close to the mining operations) are $<900 \text{ } \mu\text{Scm}^{-1}$ and $<600 \text{ mgL}^{-1}$, respectively, which should be compared to groundwater quality in wells from the EAA area ($>2,000 \text{ } \mu\text{Scm}^{-1}$ and $>1,000 \text{ mgL}^{-1}$, respectively). A steady-state groundwater fluid flow and transient solute transport modeling exercise was conducted to

estimate surface/groundwater interactions. The modeled solute in surface water was transported downgradient through groundwaters, migrated approximately 30 m from the source area (after 5 years of operation), and needed more than 116 years to dissipate. An upward transport was also identified whereby chloride and sulfate, naturally present in deeper groundwaters, migrated approximately 200 m (after 1 year of mining) into the pristine shallower aquifer and reached the surface water with a concentration equaling 80% of that in the rock mining pit.

Keywords Groundwater/surface water interactions · Everglades Agricultural Area · Chloride · Sulfate

1 Introduction

Worldwide, mining operations from prospecting to excavation are causing ecological problems from erosion, formation of sinkholes, biodiversity loss, and heavy metal and organic contamination of groundwater and surface water (Kraus and Wiegand 2006). High contaminant levels in the acid mine drainage originating from the coal and ore mining processes in general and open-pit mining in particular are well documented in the literature (Cherry et al. 2001; Skousen et al. 2002). Even though the environmental impacts of ore and coal mining have been adequately investigated, the impact of limestone rock mining has not been well studied.

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G. M. Naja (✉) · R. Rivero · S. E. Davis III · T. Van Lent
Everglades Foundation, Science Division,
18001 Old Cutler Road,
Palmetto Bay, FL 33157, USA
e-mail: mnaja@evergladesfoundation.org

Quarrying of limestone aggregate currently represents in the USA a \$7 billion per year activity (Lolcama et al. 2002). New data focusing on the surface and groundwater interactions are showing that the rock mining has a long-term and cumulative impact on stream water quality (Renken et al. 2008). Extraction of aggregates from below the natural water table in Northern Germany and the large volumes of mine water discharged into local rivers and channels caused the salinization of the streams (Iwanoff 1998). The effect of these mines is accentuated if the surrounding environment is already stressed by decades of agricultural farming, and it is particularly detrimental where water quality of the close-by areas is subject to high-quality standards.

In South Florida, the Everglades once extended from Lake Okeechobee southward to Florida Bay. Early assessments identified the peat soil south of the lake as ideal for agriculture (Jones 1948), thus establishing the Everglades Agricultural Area (EAA) that used to feature 2.7 m deep of excellent peat soil in 1912. After drainage and due to organic matter oxidation as well as because of extensive agricultural practices, the soil in this area oxidized and subsided to 1 m (Snyder 2004). On severely subsided soils, landowners are currently exploring other alternatives to traditional agriculture practices and rock mining appears as one lucrative option. Given the progress and importance of Everglades restoration and the sensitivity of the area, the impact of these mines (because of their location) should be carefully investigated.

The surface water/groundwater interactions are a relatively small (even though increasing since the Everglades drainage efforts) component of Everglades water budgets (Harvey and McCormick 2009). The inevitable consequence of surface mining activities in the EAA is the increase in direct groundwater/surface water interactions that keep altering the groundwater quality and the surface water quality. Indeed, the accumulated groundwater in the mining open pit is directly connected to surface water via discharge or seepage into canals. The purpose of this study is to examine the hydrochemical impacts of rock mines on the canal waters feeding the natural and constructed wetlands of the Everglades using monitored and simulated water quality data. To provide an indication of these surface water/groundwater interactions and the transport of solute due to mining operations (from

surface water to groundwater and vice versa), a numerical solute transport model was developed for an unconfined aquifer system.

2 Material and Methods

2.1 Everglades Agricultural Area

The EAA is located south of Lake Okeechobee and it is drained by four main north–south canals and one west–east canal. The EAA is bordered on the East by the Loxahatchee National Refuge (LNWR) and to the South by several constructed wetlands or stormwater treatment areas (STA) that convey water to water conservation areas (WCA) that feed the Everglades National Park (ENP) (Fig. 1). Water quality and ecology of the Greater Everglades (LNWR or WCA1, WCA2, WCA3, and ENP) are extensively monitored to prevent further degradation. The STAs are designed to reduce phosphorus levels in water pumped from the EAA into the WCAs. Several rock mines are currently operating in the EAA, and their locations are indicated in Fig. 1.

2.2 Groundwater Quality of the Surficial Aquifer in the Everglades Agricultural Area

Several studies investigated the regional quality of groundwater within the surficial aquifer system of the EAA. The first study (Parker et al. 1955) examined the groundwater in southeastern Florida by performing a complete inventory on the quantity and quality of water stored in the aquifers during two surveys. The second study (Scott 1977) investigated the groundwater conditions of the interior parts of Palm Beach county because of the general inadequacy of hydro-geologic information concerning the shallow aquifer inland from the coast. The latter report included a compilation of existing data on well depth, yield, and water quality of inland wells. The third report (Miller 1988) studied the surficial aquifer system in Palm Beach County in an attempt to determine the effects of increased urban and agricultural development on groundwater levels, flow directions, and quality.

An extensive inventory was assembled in the present study of data published regarding the groundwater and surface water quality in the EAA. Along with those cited above, the Florida Department of

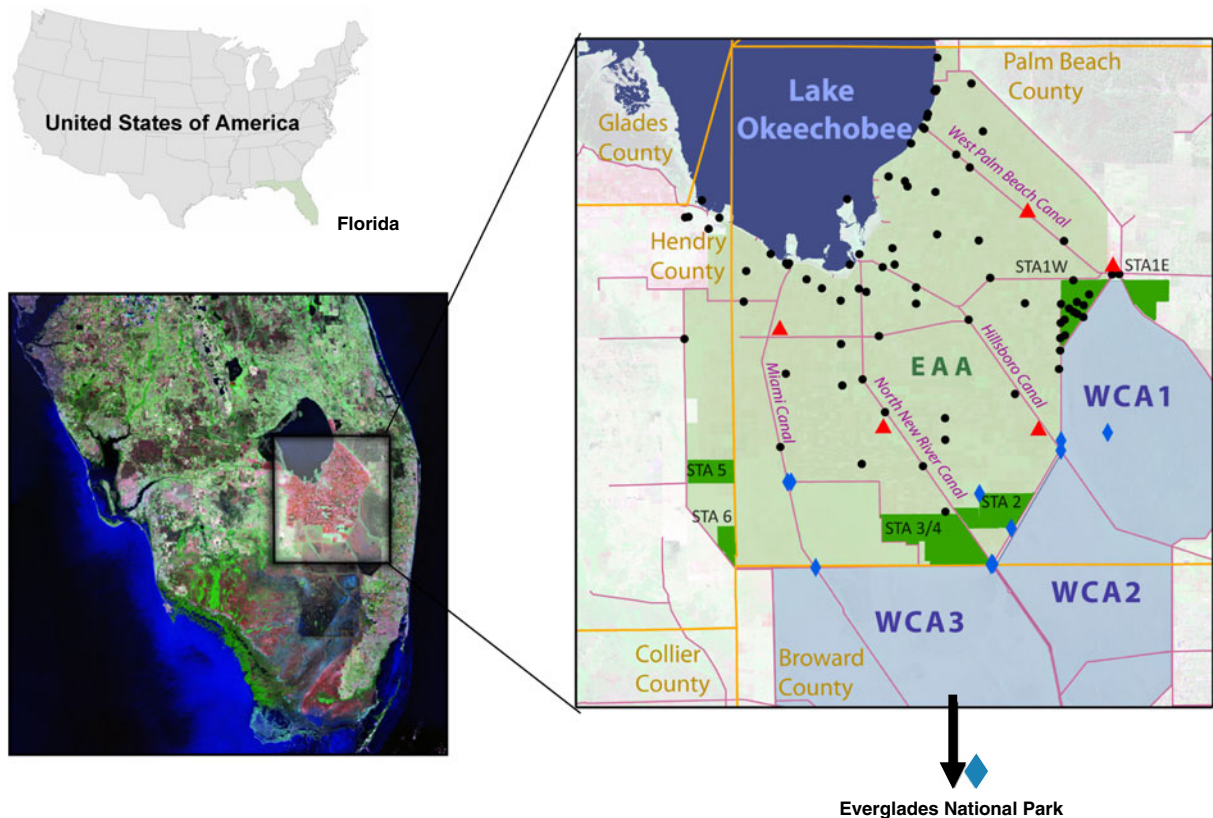


Fig. 1 Location of Florida, South Florida, and the study area (EAA Everglades Agricultural Area). WCA are the water conservation areas 1, 2, and 3. STA are the stormwater treatment areas (constructed wetlands). The Everglades National Park is

south of WCA3. The rock mine locations are indicated with the red triangles on the figure on the right. The blue diamonds indicate the surface water monitoring sites. The black circles indicate the location of the groundwater monitoring wells

Environmental Protection and the South Florida Water Management District have been monitoring several wells located in the EAA region or in the ENR (STA1W, East of the EAA) and those data were also considered (Fig. 1). The wells investigated in the present study are located in Fig. 1.

2.3 Modeling of Groundwater and Surface Water Interactions and Solute Transport

The rock mining sequence of operations is presented in the “[Supplementary Materials](#)” to aid in understanding the flow and solute transport in the rock mining pit. A steady-state groundwater fluid flow and transient solute transport modeling along a cross section in an unconfined aquifer was conducted. The model estimates solute transport subject to highly irregular flow conditions with strong anisotropic dispersion. The aquifer is composed of a first layer of

sand of hydraulic conductivity $K_1=2.893 \times 10^{-4} \text{ ms}^{-1}$ and a second layer of limestone of hydraulic conductivity $K_2=1.04 \times 10^{-3} \text{ ms}^{-1}$ (Harvey et al. 2004). The hydraulic conductivity of the gravel in the rock mining pit $K_3=2.893 \times 10^{-2} \text{ ms}^{-1}$.

The present modeling assumes that the peat layer would be removed before the rock mining operation starts for further reclamation purposes. The first layer of sand stretches from $y=0$ to $y=-4.5$ m and the limestone layer from $y=-4.5$ to -60 m. The rock mining pit is situated at $100 \text{ m} < x < 300 \text{ m}$ and is 15 m deep. Generally, groundwater moves from the upper surface to the outlet at $x=1,000$ m with a slope of 3.8 cm km^{-1} following the topography of the EAA. The depth of the surficial aquifer is approximately 60 m deep beneath the EAA. The regular vertical recharge, denoted R , is of $1.69 \times 10^{-8} \text{ ms}^{-1}$ (Harvey et al. 2005), and the water recharge in the opened rock mining pit is twice the regular value.

Two scenarios were considered:

1. The solute is reaching the aquifer from the surface table through the rock mining pit (the aquifer is considered initially pristine) and is stopped after 70 years of the mine operation, or
2. The solute (chloride or sulfate) is in the deep aquifer and reaching the pristine part of the aquifer and the surface water via the rock mining pit.

In both cases, the solute migrates within the aquifer via advection and dispersion. Throughout the domain, porosity (η) is 0.35 (sand), 0.4 (sand), and 0.5 (rock mining pit); the longitudinal dispersivity α_L and transverse vertical dispersivity α_T are 0.5 m and 0.005 m, respectively. The effective molecular diffusion coefficient D_m depends on the studied solute and the values of $20.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for chloride, $10.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for sulfate, and $8.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for phosphate were taken.

The modeling list of equations and boundary conditions used to simulate the solute transport are presented in the “Supplementary Materials”.

COMSOL-Femlab (www.comsol.com) computer software (Ramirez 1989) was employed in this work in order to solve the equations of the proposed mathematical model for the groundwater flow and solute transport. The same set of equations was also used to evaluate other flow and transport models including the three-dimensional multispecies transport model for simulation of advection, dispersion, and chemical reactions of contaminants in groundwater systems by Zheng and Wang (1998).

In the present case and once the equations were inputted through the software interface and the different constants specified (porosity, hydraulic conductivity, longitudinal, transverse vertical dispersivity, etc.), the computer process simulation was set to run. When solving the set of partial differential equations, the software runs the finite element analysis together with adaptive meshing and error control using a variety of numerical solvers (Wu et al. 2002). The flow field was divided into appropriately selected elements via different discretizations that were used for the solution procedure to ensure that the model solution and convergence were mesh independent. The *COMSOL-Femlab* output files were easily transformed to MS Excel files where the results could easily be graphed.

3 Results and Discussion

3.1 Groundwater Quality in the Everglades Agricultural Area in South Florida

Because of the heterogeneity of the groundwater quality, chloride, sulfate, and conductivity concentration changes depending on the location in the EAA and depth are presented in Figs. S-1, S-2, and S-3 (“Supplementary Materials”). These results, obtained from compiling the water quality data published for the EAA, are averaged in Fig. 2 along with calcium, sodium, total dissolved solids, and hardness levels. The concentration of chloride averaged 182 mgL^{-1} at 6 m deep and increased gradually to $1,011 \text{ mgL}^{-1}$ at 15 m deep, $1,548 \text{ mgL}^{-1}$ at 30 m deep to reach $7,800 \text{ mgL}^{-1}$ at 60 m deep. The other monitored chemical compounds followed the same trend. The effect of the groundwater recharge was noticeable for depth less than 15 m whereby the concentrations were not increasing as sharply as for the deeper groundwater levels.

The origin of sodium, calcium, carbonate, and chloride was explained by Renken et al. (2005) who studied the impact of anthropogenic development on groundwater hydrology in Southeastern Florida and concluded that at shallow depths the water contains mainly calcium bicarbonate, sodium bicarbonate, and sodium chloride. This combination was attributable to lower permeability and transmissivity within rocks that comprise the surficial aquifer system and the incomplete flushing of relict seawater by meteoric water (Reese and Wacker 2009).

The specific conductance can be used in Southeastern Florida to evaluate the relative quality of groundwater (Chen et al. 2006). The results are provided in Fig. 2c whereby the conductivity reached $25,000 \text{ } \mu\text{Scm}^{-1}$ at 60-m depth level. High specific conductance measurements are considered representative of relict seawater. The specific conductance has been mapped by Renken et al. (2005) at selected depths to determine where potable water and relict seawater exist. The present chloride and conductivity values correspond to the ones published in the literature. Indeed, based on the same report (Renken et al. 2005), the specific conductivity values of the surficial groundwater underneath the EAA are between 2,500 and $20,000 \text{ } \mu\text{Scm}^{-1}$ and the dissolved chloride concentrations are between 750 and $8,000 \text{ mgL}^{-1}$,

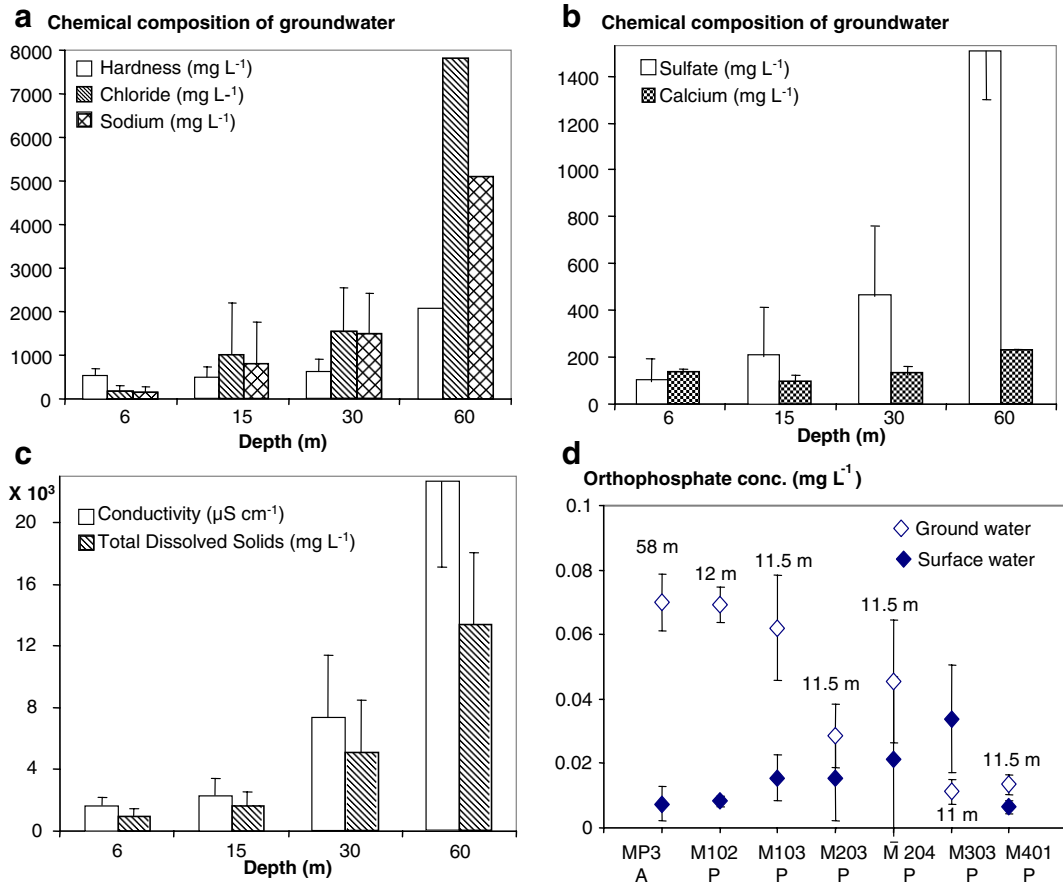


Fig. 2 Chemical composition and variation of the groundwater in the surficial aquifer beneath the Everglades Agricultural Area with depth (m). **a** Hardness (mg L⁻¹), chloride (mg L⁻¹), and sodium (mg L⁻¹), **b** sulfate (mg L⁻¹) and calcium (mg L⁻¹),

c conductivity (μS cm⁻¹) and the total dissolved solids (mg L⁻¹), **d** orthophosphate concentration (mg L⁻¹) at different locations and depth in ground and surface waters in the Everglades Agricultural Area (ENR site)

corresponding to a depth from 6 to 60 m, respectively. Comparatively, the average chloride concentration of the world's river waters is about 8 mg L⁻¹ (Wetzel 1983).

Sulfate is another chemical compound of concern in the groundwater in the EAA. Based on the monitored data (Fig. 2b), sulfate levels averaged 100 mg L⁻¹ at 6 m and reached 1,500 mg L⁻¹ at the depth of 60 m below the ground level. The sulfate in the surficial aquifer could originate from the relict seawater whereby seawater contains about 2,700 mg L⁻¹ (Hitchcock 1975). Sulfate in groundwater could also be derived chiefly from the oxidization of pyrite, leading also to the dissolution of arsenic. Comparatively, sulfate levels in lakes typically range from 3 to 30 mg L⁻¹ (Katz 1977).

Several studies indicated that concentrations of nitrate and phosphate are five to seven times higher in groundwater when compared to surface waters (Pionke and Urban 1985). Phosphorus monitoring data east of the EAA (STA1W) confirmed this (Fig. 2d). Pionke and Urban (1985) showed that nitrate and phosphate concentrations were much higher in groundwaters underlying cropland, even though these elements had to infiltrate through layers of peat and geological formations. Nitrate and phosphate fluctuations in shallow groundwater typically result from the cumulative effects of land use and associated concentration in the topsoil, net vertical recharge, local depth to groundwater, and lateral recharge from ground or surface water sources (Munoz-Carpena et al. 2005).

3.2 Surface Water Quality in South Florida

The surface water quality in South Florida is regularly monitored because of the surrounding constructed and natural wetland sensitivity. The water quality in the canals draining the EAA (Fig. 1) and feeding the constructed or natural wetlands south of EAA is presented in Figs. 3a–c. The inflow water quality into WCA2, WCA3, and ENP is also illustrated in the same figures, and it is to be compared to the groundwater quality data.

Figure 3a compares the specific conductivity and total dissolved solids of surface water in canals (<900 μScm^{-1} and <600 mgL^{-1} , respectively) close to the proposed mining operations that should be compared to groundwater quality in wells from the

EAA area (>2,000 μScm^{-1} and >1,000 mgL^{-1} , respectively). The surface water in the canals leading to STAs, WCA2, and WCA3 areas contains lower levels of cationic and anionic components (Figs. 3b, c). Surface water sulfate concentrations in marsh close to canal structures could reach 48 mgL^{-1} of sulfate, and the pristine areas far from agricultural runoffs have sulfate concentrations in surface water of 0.48 mgL^{-1} or less. Harvey and McCormick (2009) discussed canal water quality in the EAA and noted that the chemical content of water in the EAA canals can be attributed to flushing of peat oxidation products and fertilizer additives. The inflows to ENP and to LNWR are characterized by the lowest cationic and anionic charge as clearly illustrated in Fig. 3.

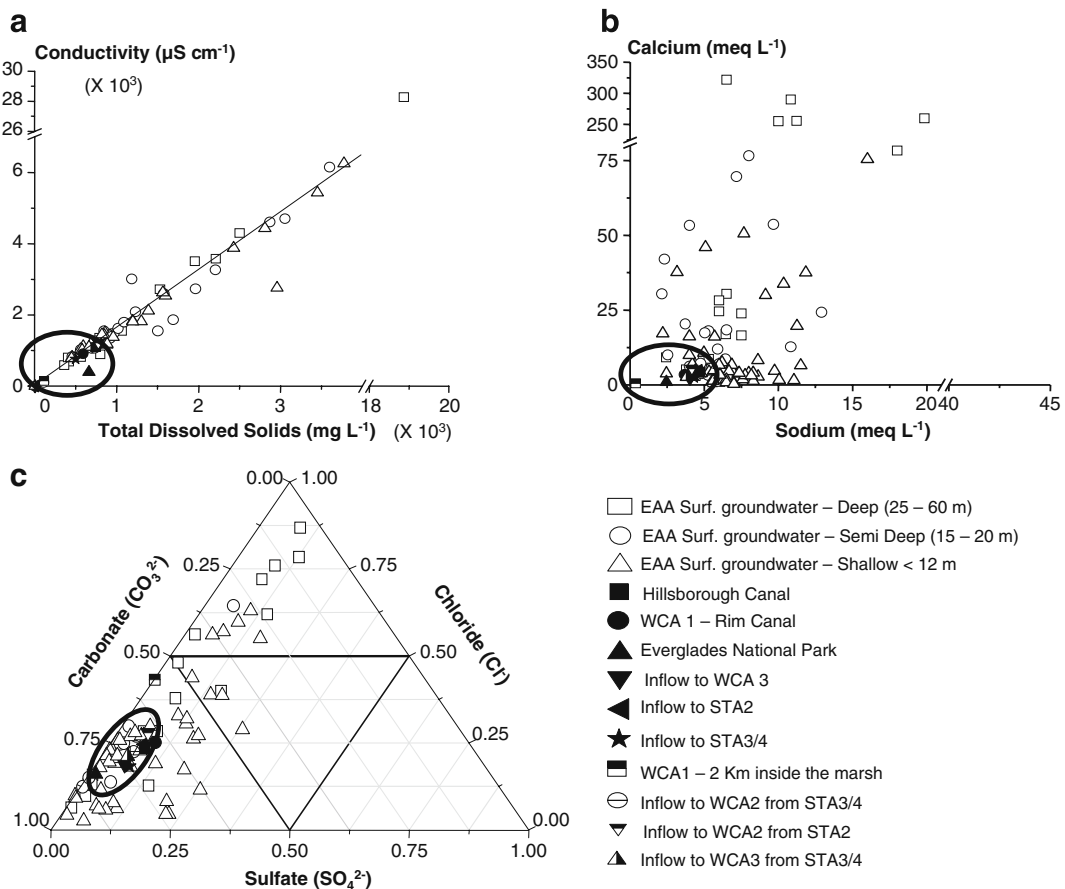


Fig. 3 Groundwater and surface water chemical correlations at different locations surrounding the rock mining sites indicated in Fig. 1. The surficial groundwater chemical composition was monitored at different depths (*triangles*, shallow (<12 m); *circles*, semideep (15–20 m); *squares*, deep (25–60 m)). The

surface water chemical composition was a 10-year average. **a** Conductivity ($\mu\text{S cm}^{-1}$) and the total dissolved solids (mgL^{-1}), **b** calcium (meqL^{-1}) and sodium (meqL^{-1}), **c** ternary plots representing the correlation between chloride, sulfate, and carbonate

3.3 Groundwater/Surface Water Interactions

The chloride, phosphate, and sulfate ion concentrations and the effects of dispersion on plume concentrations were investigated to provide an indication of the increased surface water/groundwater interactions. Within the simulated steady-state flow field, a constant concentration source term of one was assigned at the water table to represent the phosphorus ion loading (100–300 m). Similarly, chloride and sulfate loadings of one were assigned when studying the transport of these ions from the groundwater (100–300 m) to surface water. The migration of these three components was simulated for the period of 70 years (rock mining activity period), followed by the dissipation of the plume after removing the concentration source term (for phosphorus only).

3.3.1 Solute Transport Downgradient from Surface Water to Groundwater

The solute transport simulation results are presented in Fig. 4 after 22, 70, and 100 years of the rock mining operation. The examined solute could be a contaminant (chemical) or a pathogen (bacteria...) in the surface waters that could be transported downgradient from the open rock mining pits through groundwaters and reemerge as discharge to surface waters.

After a simulated time of 8 years, the solute concentration in the groundwater showed the formation of a typical “cigar-shaped” plume as defined by the contours. After 5 years of mine operation, the solute migrated approximately 30 m downgradient from the source area, with the highest concentration (=1) restricted to within approximately 15 m of the source area. After a period of approximately 16 years (Fig. 4a), the simulated plume reached a steady-state condition whereby the flux from the source area was balanced by the flux across the plume boundary. The contours under steady-state conditions are located approximately between 45 and 50 m downgradient from the source. After a simulation period of 70 years (i.e., the approximate life span of a rock mining operation), the solute source was removed to provide an indication of the time required for concentrations to dissipate (Fig. 4b). After 100 years, the solute concentration in the studied zone reached 70% of the initial concentration (Fig. 4c). After 116 years, no

simulated concentrations were above 25% of the initial concentration.

The above 2-D simulations indicate that the impacts associated with rock mining on groundwater quality depend on the groundwater flow, transport processes, and the aquifer properties. Based on the modeling results, wells and surface water features located within 1,000 m of the rock mining pit are at the greatest risk of contamination occurring because of the open pit. The modeling suggested that if rock mining activities were to be discontinued after 70 years of operation, the negative impact of contamination within the shallow aquifer would last for at least 30 more years.

3.3.2 Chloride and Sulfate Transport Upward from Groundwater

The solute transport simulation results are presented in Fig. 5 for periods of 1, 10, and 70 years of the rock mining operation. Because of the high water recharge and pressure, both elements migrated approximately 200 m (after 1 year of mining) in the pristine aquifer, with concentrations equaling 80% of the one in the rock mining pit (Fig. 5a). At a simulated time of 10 years, chloride and sulfate from groundwater source reached the pristine groundwater and the surface water via the outlet at 1,000 m through the rock mining pit (Fig. 5b). After 10 years (Fig. 5b), the plume reached a steady-state condition whereby the flux from the source area (deeper aquifer) is balanced by the water recharge. Concentrations ranged from 0% to 10% (of the initial concentration) in the upper layers (0 to 5 m deep) to 70–90% in the pristine aquifer and to 100% in the rock mining pit. The solutes (chloride and sulfate in our case) reached the surface water via the outlet at 1,000 m through the rock mining pit. The same concentration profile was found after 70 years of rock mining operation (Fig. 5b). Based on the modeling results, chloride will spread and the features (shallow water wells) located within 1,000 m of the rock mining pit are at the greatest risk of chloride or sulfate contamination because of the rock mining pits.

3.4 Water Quality Impacts and a Similar Case

Groundwater in the EAA region showed elevated concentrations of calcium, chloride, and sulfate

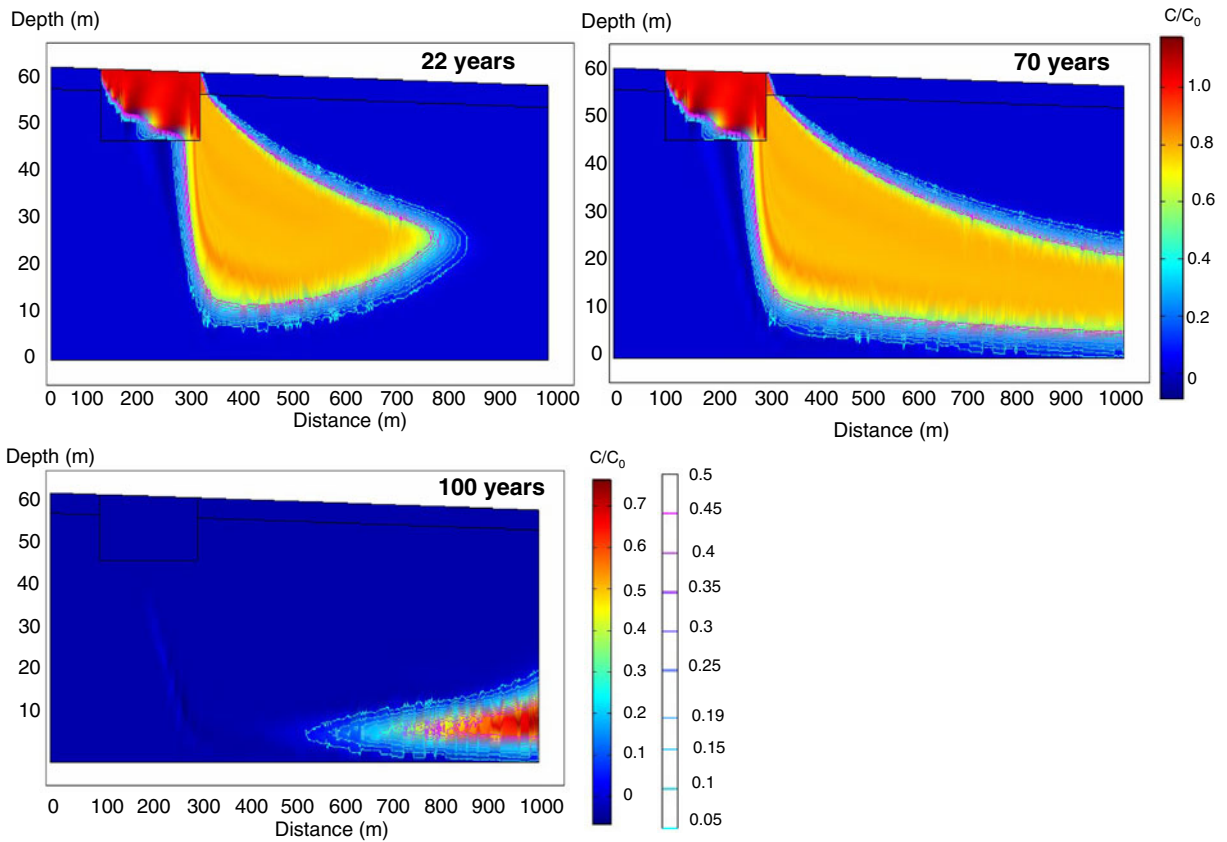
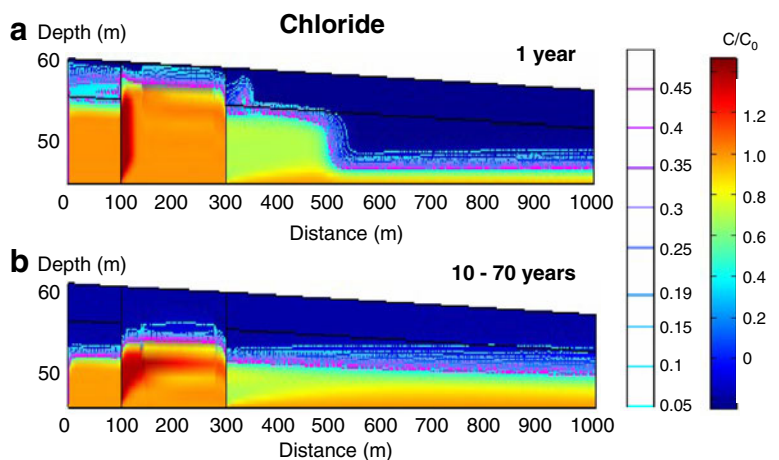


Fig. 4 Modeling results showing the surface water solute transport in the groundwater after 22, 70, and 100 years of rock mining

correlated with depth (Fig. 2). Combined with increased surface water/groundwater interactions (through the rock mining pit), higher chloride, specific conductivity, and sulfate and calcium levels in the surrounding surface waters are to be expected

in the long term. Through canal conveyance, these elements will reach WCAs and the ENP, a pristine area of South Florida, where anthropogenic impacts are minimal. Such impacts are of concern because pristine habitats are vulnerable to even relatively

Fig. 5 Modeling results showing chloride transport in the groundwater after 1, 10, and 70 years of rock mining



minor anthropogenic stresses. This is because the species assemblage of pristine environments is, in large measure, composed of taxa that are adapted to unperturbed environments; pollution-tolerant species generally are minor constituents of such assemblages. A bibliographic review and an extensive list of references detailing the possible environmental impacts of salt, sulfate, and calcium are presented in the “Supplementary Material” section.

A similar case has been investigated in the deep opencast mines for limestone in the northernmost state of Germany, Schleswig-Holstein, greatly impacting the local environment (Iwanoff 1998). The total amount of mine water pumped approaches $6 \times 10^6 \text{ m}^3 \text{ year}^{-1}$. The mine water is discharged at a rate of $3.5 \times 10^6 \text{ m}^3 \text{ year}^{-1}$, equal to approximately 114 L s^{-1} , containing chloride concentrations from approximately 1,000 to $1,200 \text{ mg L}^{-1}$, whereas the natural background concentration of chloride in the rivers and channels in the region does not exceed 100 mg L^{-1} . During dry periods, the volume of mine water exceeds the channel’s base flow, leading to significant increases in the salinity of channel water and impacting the environment. The models run by Iwanoff (1998) indicated that the mining operation would cause the salt content in the nearby river to increase to a maximum between 120 and 250 mg L^{-1} , depending on the river level.

4 Conclusions

The consequence of surface mining activities in the EAA is the increase in direct groundwater/surface water interactions, altering groundwater quality and surface water quality. Groundwater in this region showed elevated concentrations of calcium, chloride, and sulfate correlated with depth. Comparatively, the surface water chemical composition in the surrounding areas showed much lower cationic and anionic charge. The steady-state groundwater fluid flow and transient solute transport modeling exercise showed that solutes were transported downgradient through groundwaters. Furthermore, an upward transport was also identified whereby chloride and sulfate, naturally present in deeper groundwaters, migrated into the shallower pristine aquifer and reached the surface water. This increase of groundwater and surface water interactions caused by rock mining activities could impact the sensitive wet-

lands located downstream. Any changes introduced can have longer-term effects, perhaps not observable on a shorter time basis, mindful of the fact that the proposed mining operations are supposed to be active for more than 70 years.

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