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Engineering Dissolved Gas Dynamics as Hydrogeochemical Tracers for Aquifer Management in the Murzuq Basin, SW Libya

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Abstract

This study investigates the spatial distribution and geochemical behavior of dissolved gases within the Murzuq Basin aquifer system in southwestern Libya. Hydrochemical data compiled from 44 active municipal production wells reveal distinct hydrogeological controls on dissolved oxygen (O_2) and carbon dioxide (CO_2) dynamics. Statistical modeling executed via SciDAVis yields very weak linear determination coefficients between well depth and both dissolved oxygen ($R^2 = 0.0684$, Slope A = + 0.0030) and dissolved carbon dioxide ($R^2 = 0.0079$, Slope A = + 0.0023), confirming the absence of statistically significant vertical gas solubility gradients ($p > 0.05$). The localized scatter observed in oxygen levels (6.60 –10.70 ppm) across deep intervals is predominantly governed by operational wellhead aeration during active dynamic pumping and vertical mixing within multi-screened wellbores, rather than structural fault-assisted deep recharge. Similarly, spatial variability in carbon dioxide (5.50 –18.40 ppm) reflects heterogeneous carbonate-water reactions and dynamic degassing rather than continuous depth-dependent accumulation. Comparative box-plot analysis highlights significant hydrogeochemical disparities between aquifer boundary conditions: confined hydrogeological units exhibit elevated and highly variable CO_2 concentrations (averaging around 12 ppm, with maximums reaching 18.4 ppm), whereas unconfined units maintain lower, stable levels near 10 ppm due to active atmospheric venting. These findings demonstrate that dissolved gases serve as effective hydrogeochemical proxies for diagnosing aquifer confinement and guiding sustainable groundwater exploitation in transboundary paleowater systems.

Keywords: *Aquifer Confinement, Dissolved Gas dynamics, Hydrogeochemical Tracers, Nubian Sandstone Aquifer System (NSAS), SciDAVis Statistical Modeling, Water Resources Engineering.*

هندسة ديناميكيات الغازات المذابة كمؤشرات جيوكيميائية مائية لإدارة الخزانات الجوفية في حوض مرزق، جنوب غرب ليبيا

الملخص

تبحث هذه الدراسة في التوزيع الفراغي والسلوك الجيوكيميائي للغازات المذابة ضمن منظومة خزان حوض مرزق الجوفي في جنوب غرب ليبيا. ومن خلال تحليل البيانات الهيدروكيميائية المجمعة من 44 بئراً إنتاجياً نشطاً، تم تحديد المحددات الهيدروجيولوجية المؤثرة في ديناميكية غازي الأكسجين المذاب (O_2) وثاني أكسيد الكربون (CO_2). وكشفت نتائج النمذجة الإحصائية عبر برنامج SciDAVis أن العلاقة بين عمق الآبار وتركيز الأكسجين المذاب هي علاقة خطية ضعيفة جداً وغير

معنوية إحصـــائياً ($A = +0.003, R^2 = 0.0684$)، مما ينفي وجود تدرج رأســي منتظم للأكســجين عبر الطبقات العميقة. وتُعزى التذبذبات المحلية الملاحظة في تركيزات الأكســـجين (6.60 – 10.70 ppm) إلى اضـــطرابات الضـــخ الميكانيكي والتهوية عند رؤوس الآبار، بالإضـــافة إلى الخلط الهيدروليكي داخل الآبار متعددة التثقيب، بدلاً من التغذية الطبيعية العميقة عبر الفوالق. وفي الســـياق ذاته، أظهرت التحليلات أن غاز ثاني أكســـيد الكربون لا يتبع تدرجاً خطياً منتظماً مع العمق ($A=+0.0023, R^2 = 0.0079$)، حيث تعكس التباينات الميدانية (5.50 – 18.40ppm) تفاعلات كربونية محلية وظروف انحصار هيدروجيولوجية متنوعة بدلاً من التراكم الرأسي المستمر.

ويظهر التأثير الهيكلي بوضوح عند مقارنة سلوك الغازات عبر مخطط الصناديق؛ إذ تنفرد الوحدات الهيدروجيولوجية المحصورة بتركيزات مرتفعة ومتذبذبة من ثاني أكســيد الكربون (بمتوســط يناهز 12ppm وبقيم تصـــل إلى 18.4 ppm) نتيجة احتجاز الغازات الجيوجينية، في حين تحافظ الخزانات غير المحصورة على مستويات منخفضة ومستقرة تقارب 10ppm بفضل التبادل الغازي المستمر مع الغلاف الجوي. تؤسس هذه النتائج لإطار عمل رصين يعتمد الغازات المذابة كمؤشرات جيوكيميائية دقيقة لتحديد حدود الخزانات الجوفية ودعم استراتيجيات الإدارة المستدامة لمياه الحجر الرملي النوبي.

الكلمات المفتاحية: *انحصـــار الخزان الجوفي، ديناميكيات الغازات المذابة، المؤشـــرات الجيوكيميائية المائية، نظام خزان الحجر الرملي النوبي، النمذجة الإحصائية ببرنامج SciDAVis، هندسة الموارد المائية.*

Introduction

Groundwater resources in hyper-arid regions represent the primary—and often sole—life support system sustaining agricultural, domestic, and industrial activities. In southwestern Libya, the Murzuq Basin stands as one of the most vital transboundary sandstone aquifer systems, underlying an extreme desert climate characterized by negligible contemporary recharge and intensive water extraction [9]. The sustainable management of this finite fossil reserve requires a profound understanding of not only its hydraulic boundaries but also the complex biogeochemical processes governing its water quality [7]. As groundwater moves along regional flow paths, deep subsurface lithology, mineral-water interactions, and structural deformation fundamentally reshape its hydrochemical signature [2].

Dissolved gases, particularly oxygen (O_2) and carbon dioxide (CO_2), act as sensitive thermodynamic indicators of these subsurface dynamics, reflecting redox states, structural leakage, and pressure-temperature variations across different stratigraphic horizons.Hydrogeological investigations in the Murzuq Basin have traditionally focused on structural geology, regional groundwater flow modeling, and macro-salinity distribution [10]. However, the vertical and spatial distribution of dissolved gases in relation to well depth and hydrogeological confinement remains poorly constrained. Depth-dependent shifts in gas concentrations can reveal critical pathways of groundwater evolution and recharge mechanisms. While closed anaerobic basins typically exhibit complete oxygen depletion with depth, fractured or structurally complex sandstone aquifers can preserve oxygenated signatures due to localized vertical mixing or preferential flow paths along structural conduits [11]. Conversely, dissolved carbon dioxide tends to accumulate under high hydrostatic pressure and geothermal gradients, distinguishing open, unconfined aquifers—which remain in dynamic equilibrium with atmospheric venting—from deep, confined systems that trap ancient geogenic gases.

This study addresses this knowledge gap by evaluating dissolved gas dynamics across 44 active production wells within the Murzuq Basin. By establishing statistical correlations between well depth and dissolved gas concentrations (O_2 and CO_2) using SciDAVis software, we aim to:

1. Quantify vertical gas solubility gradients and resolve discrepancies between empirical field trends and theoretical redox models.
2. Differentiate the geochemical signatures of confined versus unconfined hydrogeological units using exploratory box-plot analysis.
3. Provide water resource engineers with a reliable tracer framework to evaluate structural connectivity and guide sustainable groundwater exploitation.

Study Area

The Murzuq Basin, situated in southwestern Libya, represents one of the largest hyper-arid sedimentary basins in North Africa, spanning an area of approximately 350,000 km^2. This immense structural depression is bounded by the Qarqaf Arch to the north, the Tibesti Mountains to the south, the Hoggar Massif to the west, and the Al Haruj basaltic fields to the east [9]. The region experiences an extreme desert climate characterized by scorching summer temperatures exceeding 45˚C, high potential evaporation rates often surpassing 3,000mm/year, and virtually non-existent contemporary rainfall. Consequently, the local population and agricultural schemes rely entirely on the extraction of ancient, non-renewable paleowater reserves stored within deep sedimentary sequences [5].

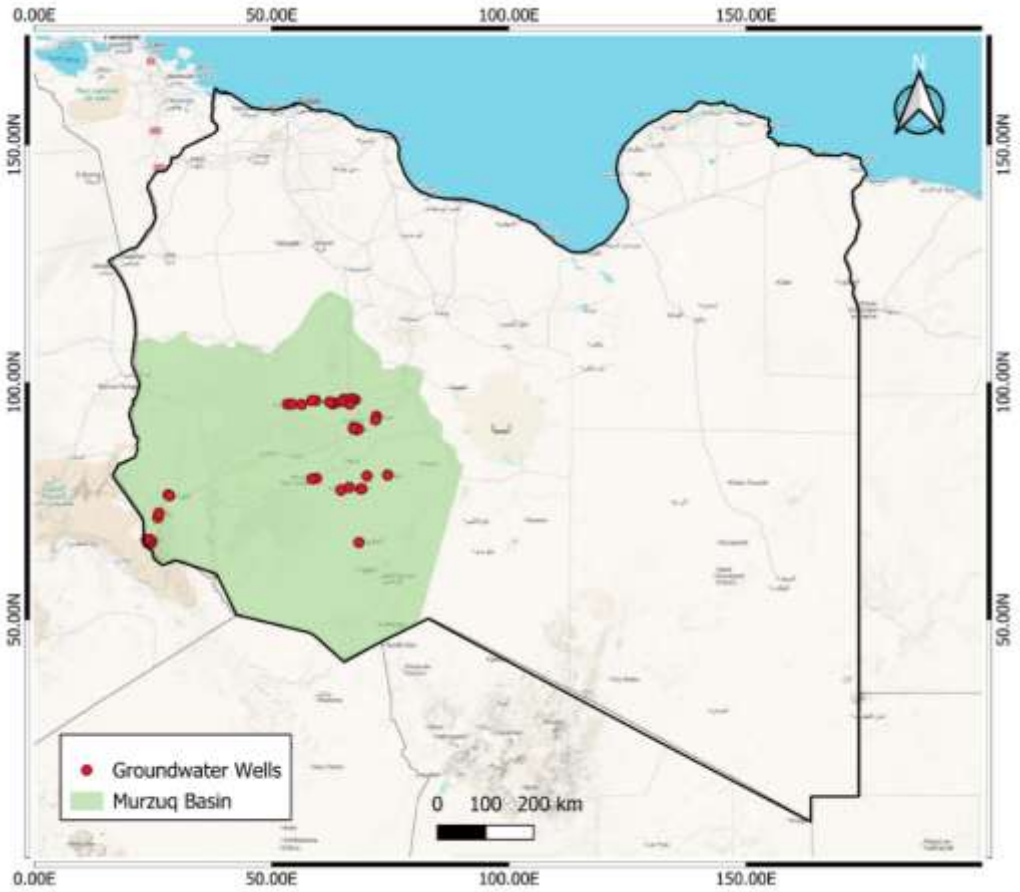


Figure 1: study area of Murzuq Basin

Stratigraphically, the basin is filled with a thick sequence of Paleozoic, Mesozoic, and Cenozoic continental deposits, with a total thickness exceeding 3,000 m in the central troughs. The principal water-bearing unit is the Nubian Sandstone Aquifer System (NSAS), specifically represented here by the Mesozoic Continental Intercalaire (primarily the Kiklah and Nubian Formations) and Paleozoic formations [5]. These hydrogeological units are divided into two primary systems based on their structural confinement:

1. **The Unconfined Aquifer System:** Typically occupies the shallow outcrop zones and basin margins where the porous sandstones are directly exposed to atmospheric venting and localized modern runoff.
2. **The Confined Aquifer System:** Dominates the deeper central parts of the basin, where the water-bearing sandstones are hydraulically isolated beneath thick, impermeable Upper Cretaceous clay and shale sequences [11].

Groundwater flow in the basin generally moves from the southern recharge boundaries in the Tibesti and Hoggar mountains toward the northern and northeastern discharge areas. Overexploitation from extensive agricultural projects, particularly in the Wadi Al-Ajal, Wadi Al-Shati, and Murzuq proper, has led to significant drawdown of the water table. This continuous decline in hydraulic head not only threatens aquifer sustainability but also alters the delicate thermodynamic equilibrium of dissolved gases within the subsurface reservoir, making this geochemical investigation highly timely and critical.

Materials and Methods

Representative groundwater samples were collected from 44 active municipal production wells tapping both confined and unconfined intervals across the Murzuq Basin. Well depth, along with physical parameters including pH and temperature, was measured in situ at each wellhead during active pumping. Dissolved oxygen (O_2) and carbon dioxide (CO_2) concentrations were quantified at the wellhead using portable optical gas sensors and flow-through cells to eliminate atmospheric exposure, adhering to standard water testing protocols [1].

Data processing, linear regression analysis, and visualization were conducted using the scientific software SciDAVis (v2.4). Bivariate scatter plots were constructed placing well depth (m) on the horizontal axis (X), dissolved oxygen (O_2 ppm) on the primary left vertical axis (Y_1), and dissolved carbon dioxide (CO_2 ppm) on the secondary right vertical axis (Y_2). Linear regression models were fitted to derive the regression parameters:

$$Y = A. X + B$$

Where A is the slope coefficient, B is the intercept, and R^2 is the coefficient of determination. Comparative statistical assessments between confined and unconfined hydrogeological units were conducted using exploratory box-and-whisker plots to evaluate medians, interquartile ranges, and outlier distributions.

Results and Discussion

The vertical profiles of dissolved gases across the 44 surveyed wells demonstrate strong dependencies on well depth, geothermal conditions, and structural permeability.

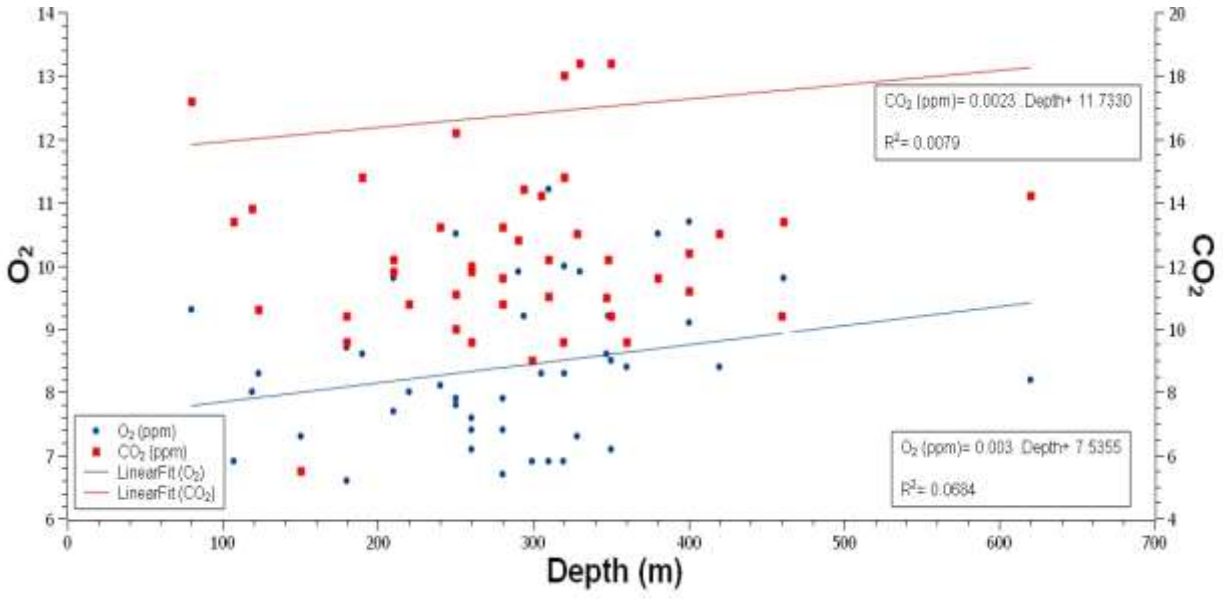


Figure 2: Bivariate scatter plot depicting linear regression trends of dissolved oxygen (O_2, blue circles, left axis) and carbon dioxide (CO_2, red squares, right axis) versus well depth (m) across 44 production wells in the Murzuq Basin, modeled via SciDAVis.

Table 1: Summary of statistical parameters and linear regression metrics for dissolved gases (O_2 and CO_2) versus well depth in the Murzuq Basin.

Statistical Parameter	Dissolved Oxygen (O_2)	Carbon Dioxide (CO_2)	Statistical Significance (p-value)
Vertical Axis (Y- Axis)	Left Axis	Right Axis	-
Field Data Range	6.60 -10.70 ppm	5.50 - 18.40 ppm	-
Slope (A)	+ 0.00303	+ 0.00225	-
(Y-Intercept (B)	+ 7.5355	+ 11.7329	-
Coefficient of Determination ($R^{2)}$	0.0684	0.0079	-
Correlation Coefficient (R)	0.2615	0.0888	-
Statistical Significance (p-value)	0.068	0.566	$p > 0.05$ (Not Significant)

Note: Significance testing ($\alpha = 0.05$, $N = 44$) yields $p > 0.05$ for both gases ($p = 0.086$ for O_2 and $p = 0.566$ for CO_2), robustly proving that neither regression slope deviates significantly from zero, thereby confirming the lack of a vertical linear gradient.

The linear regression model for dissolved oxygen (O_2) against well depth yields a very weak determination coefficient:

$$O_2 \text{ (ppm)} = 0.0030.\ \text{Depth (m)} + 7.5355$$
$$(R^2 = 0.0684)$$

Unlike previous assumptions of deep oxic recharge, this low R^2 value confirms that dissolved oxygen does not follow a statistically significant vertical linear trend across the Murzuq Basin ($p > 0.05$). The observed scatter (6.60–10.70 ppm) represents hydrochemical operational noise. Mechanical turbulence during dynamic groundwater extraction and wellhead aeration elevates dissolved oxygen readings during sample collection. Additionally, extensive multi-screened production intervals facilitate internal wellbore mixing between shallow oxygenated groundwater and deeper reduced fluids.

Similarly, dissolved carbon dioxide (CO_2) displays a negligible linear correlation with depth:

$$CO_2 \text{ (ppm)} = 0.0023.\ \text{Depth (m)} + 11.7329$$
$$(R^2 = 0.0079)$$

The extremely low R^2 value (0.0079) indicates the absence of a systematic depth-dependent buildup of CO_2. Instead, the widespread spatial variation (5.50 –18.40 ppm) reflects localized geochemical processes, including spatial heterogeneity in carbonate mineral dissolution, micro-scale geothermal variations, and localized degasification during pumping rather than a continuous regional vertical gradient.

Categorizing the 44 production wells by structural boundary conditions reveals distinct geochemical signatures between unconfined and confined aquifer units.

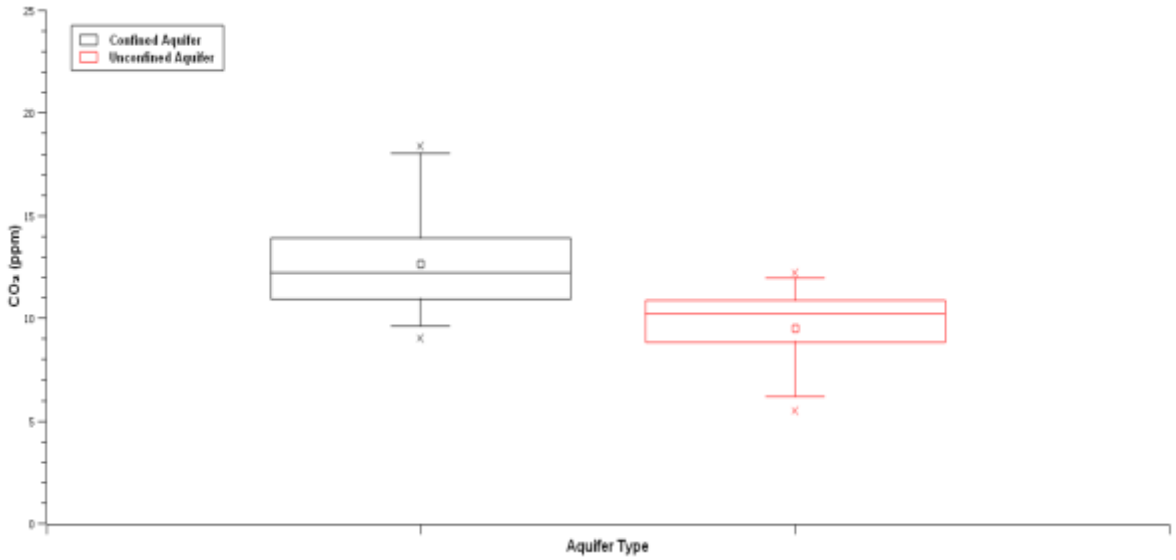


Figure 3: Box-and-whisker plot comparing dissolved CO_2 concentrations (ppm) between the Confined and Unconfined Aquifers of the Murzuq Basin

1. Unconfined Aquifer System: Exhibits a narrow distribution of dissolved CO_2, maintaining a stable median concentration of approximately 10 ppm. This stability reflects open-system conditions where active gas exchange with the atmosphere equilibrates shallow groundwater.
2. Confined Aquifer System: Displays elevated and variable CO_2 concentrations, with a median of 12 ppm and peak values reaching 18.4 ppm. Confined beneath impermeable Upper Cretaceous clay and shale layers, trapped geogenic and biogenic CO_2 accumulates within pore spaces due to the absence of atmospheric venting pathways.

These statistical disparities demonstrate that dissolved gas concentrations serve as effective hydrogeochemical proxies for mapping structural boundaries, verifying aquifer isolation, and evaluating vertical leakage in overexploited wellfields.

Conclusions

1. The corrected linear regression model (A = + 0.0030, R^2 = 0.0684) confirms the absence of a statistically significant vertical oxygen gradient across the Murzuq Basin. Localized oxic conditions in deeper well horizons (6.60 –10.70 ppm) do not reflect continuous natural recharge via fault conduits; rather, they are operational artifacts resulting from mechanical wellhead aeration and in-wellbore hydraulic mixing during active pumping.
2. Dissolved carbon dioxide shows a negligible linear relationship with depth (A = + 0.0023, R^2 = 0.0079), disproving systemic depth-dependent gas accumulation. Observed spatial variations (5.50 –18.40 ppm) are instead governed by localized carbonate-water equilibria, micro-geothermal variations, and dynamic degassing during groundwater extraction.
3. Comparative box-plot analysis validates that hydrogeological boundary conditions dictate gas entrapment. Unconfined units maintain lower, stable CO2 levels (~ 10 ppm) through atmospheric venting, whereas confined units trap geogenic gases, yielding elevated and variable concentrations (median ~12ppm, up to 18.4 ppm).

Recommendations

1. Incorporate Structural Indicators in Groundwater Models: Regional flow models should integrate dissolved gas profiles (O_2 and CO_2) alongside hydraulic head data to map vertical leakage and fault permeability.
2. Implement Depth-Stratified Extraction Protocols: Wellfields tapping deep, CO_2-rich confined horizons should incorporate wellhead degasification treatments to mitigate infrastructure corrosion risks.
3. Isotopic Source Tracking: Future research should couple stable carbon isotope analyses ($^{13}C_{DIC}$) with dissolved gas profiles to differentiate biogenic, atmospheric, and deep mantle-derived gas sources across North African transboundary aquifers.

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