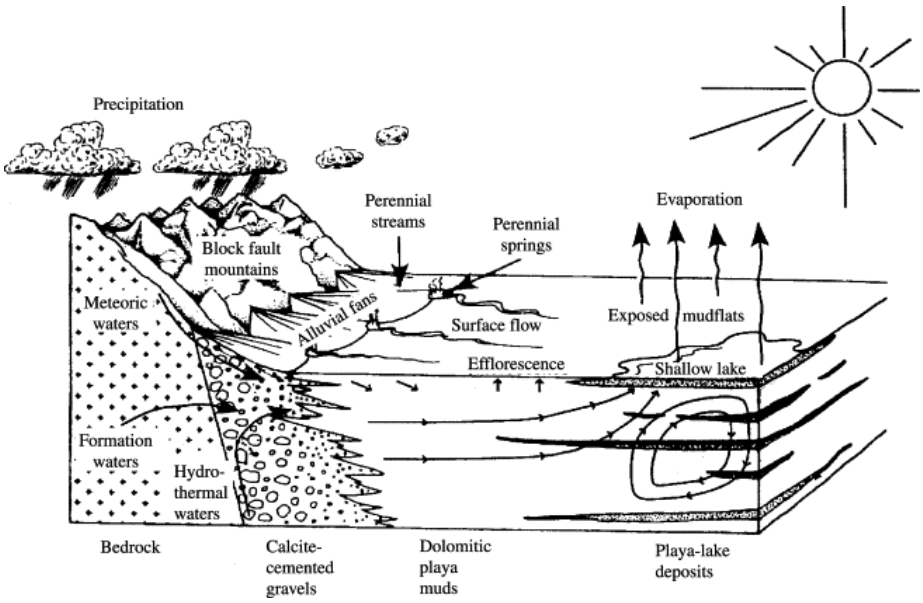
Annotated Bibliography on

Geochemistry and Hydrochemistry of Groundwater



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February 2023

National Scientific & Technical Information Center
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Introduction:

Groundwater contains a wide variety of dissolved inorganic constituents as a result of chemical interactions with geological materials and to lesser extent contributions from the atmosphere. The study of hydrochemistry is of prime importance in deciding about the quality of groundwater supply. Hydrochemistry helps to evaluate hydrogeochemical processes responsible for temporal and spatial changes in the chemistry of groundwater (ScienceDirect).

This annotated bibliography contains article abstracts from 2020-2022.

This benefits WRC researchers.

E-resources used: Scopus.

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Articles Abstract:

1- Kadam, A., Wagh, V., Jacobs, J., Patil, S., Pawar, N., Umrikar, B., Sankhua, R., & Kumar, S. (2022). Integrated approach for the evaluation of groundwater quality through hydro geochemistry and human health risk from Shivganga river basin, Pune, Maharashtra, India. *Environmental Science and Pollution Research, 29*(3), 4311-4333. 10.1007/s11356-021-15554-2

Abstract: The present study is focused on seasonal variation in groundwater quality, hydrochemistry, and associated human health risk in the Shivganga river basin, Western Maharashtra, India, to promote sustainable development of groundwater resources of this semi-arid region. The qualitative geochemical analysis, contamination levels, and human health risk assessment (HHRA) of groundwater are integral steps in groundwater management in the Deccan Plateau basalt flow region of India. Representative groundwater samples (n = 68) collected from the Shivganga River basin area of Pune district, Maharashtra, during pre-monsoon (PRM) and post-monsoon (POM) seasons in 2015 were analyzed for major cations and anions. According to the World Health Organization (WHO, 2017) drinking standards, EC, total dissolved solids, hardness, bicarbonate, calcium, and magnesium surpassed the desirable limit. Boron and fluoride content exceeded the prescribed desirable limit of the WHO. The pollution and drinking suitability were assessed by computing pollution index of groundwater (PIG), groundwater quality index (GWQI), and HHRA particularly for boron and fluoride toxicity. PIG values inferred that about 6% of groundwater samples has moderate, 24% has low, and 70% has insignificant pollution in the PRM season, while only 1 sample (3%) showed high pollution, 6% showed low, and 91% showed insignificant pollution in the POM season. GWQI classification demonstrated that 27% and 15% samples are within the poor category, and only 15% and 18% of the samples fall into excellent water category in the PRM and the POM seasons, respectively. Total hazard index (THI) revealed that 88% of children, 59% of adults, and about 38% of infants are exposed to non-carcinogenic risk, as THI values (>1) were noted for the PRM season, while 62% of children, 47% of adults, and 24% of infants are vulnerable to non-carcinogenic health hazard during the POM period.

2- Huang, L., Sun, Z., Zhou, A., Bi, J., & Liu, Y. (2022). Source and enrichment mechanism of fluoride in groundwater of the Hotan Oasis within the Tarim Basin, Northwestem China. *Environmental Pollution, 300*10.1016/j.envpol.2022.118962

Abstract: In arid inland irrigated areas, the role of human activities on fluoride enrichment in groundwater is not fully understood. There is an extremely arid climate, high-intensity irrigation, and severe soil salinization in the Hotan Oasis within the Tarim Basin, Northwestern China. In this study, hydrogeochemistry and environmental isotope methods were combined to explore the distribution characteristics and controlling processes of fluoride enrichment in groundwater. The F− concentration in groundwater had a range of 1.12–9.4 mg/L. F− concentrations of all the groundwater samples were higher than 1.0 mg/L (Chinese Standards for Drinking Water Quality), and about 89% were higher than 1.5 mg/L (WHO Guidelines for Drinking Water Quality). High fluoride groundwater was mainly distributed downstream of the river and in the middle of the interfluvial zone. Vertically, the fluoride concentration was higher when the sampling depth was less than 15 m. There was a significant positive correlation between F− concentration and salinity in groundwater. F− in groundwater was mainly derived from river water fluoride, which could be imported to groundwater with infiltration of rivers and irrigation canals as well as irrigation return flow. Anthropogenic inputs may be partly responsible for fluoride enrichment in groundwater. Fluoride accumulated in the vadose zone by strong evapotranspiration and then leached into groundwater with irrigation return flow was the main mechanism of F− enrichment in groundwater in the study area. This work is a clear example of how human activities together with natural processes can affect the chemical quality of groundwater, which is essential to safeguard the sustainable management of water and soil resources inland arid oasis areas. © 2022 Elsevier Ltd

3- Natasha, Bibi, I., Shahid, M., Niazi, N. K., Younas, F., Naqvi, S. R., Shaheen, S. M., Imran, M., Wang, H., Hussaini, K. M., Zhang, H., & Rinklebe, J. (2021). Hydrogeochemical and health risk evaluation of arsenic in shallow and deep aquifers along the different floodplains of Punjab, Pakistan. *Journal of Hazardous Materials, 402*10.1016/j.jhazmat.2020.124074

Abstract: The current study delineated the distribution, (hydro)geochemical behavior and health risk of arsenic (As) in shallow (depth 35 m; tube wells) aquifers in five areas along the Indus River

(Bhakar, Kallur Kot), Jhelum River (Jhelum) and Chenab River (Hafizabad, Gujranwala) floodplains of Punjab, Pakistan. Relatively, greater As concentration was observed in deep wells (mean: 24.3 μg L−1) compared to shallow wells (19.4 μg L−1), with groundwater As spanning 0.1–121.7 μg L−1 (n = 133) in three floodplains. Groundwater from Hafizabad (Chenab River floodplain) possessed the highest As (121.7 μg L−1), Na+ (180 mg L−1), Ca2+ (95 mg L−1), Cl− (101 mg L−1) and SO42− (1353 mg L−1) concentrations. Arsenic health risk modeling indicated the potential carcinogenic (value > 10−4) and non-carcinogenic (hazard quotient > 1.0) risks for groundwater of all areas, with the utmost risk estimated for Chenab floodplain and deep aquifers. Positive saturation index values for Fe oxide mineral phases may suggest their potential role in As mobilization/release in these aquifer environments. This study provides critically-important and baseline knowledge for a widespread groundwater As examination along these three floodplains, which is vital for launching suitable As mitigation and remediation programs to reduce the potential health risk. © 2020 Elsevier B.V.

4- Zhang, J., Chen, L., Hou, X., Lin, M., Ren, X., Li, J., Zhang, M., & Zheng, X. (2021). Multi-isotopes and hydrochemistry combined to reveal the major factors affecting Carboniferous groundwater evolution in the Huaibei coalfield, North China. *Science of the Total Environment, 791*10.1016/j.scitotenv.2021.148420

Abstract: Both natural processes and anthropogenic activities have significant effects on groundwater evolution in coal mining regions. In this study, the primary controlling mechanism of the groundwater chemistry evolution for the Carboniferous groundwater in the Huaibei coalfield, North China was proposed based on the hydrogeochemical indicators combining with multiple isotope tracers. The diversity of hydrochemical types indicates the complexity of the hydrogeochemical environment in the groundwater, which is recharged by precipitation infiltration with minimal evaporation according to the distributions of δD and δ18O. Additionally, ion correlation analysis suggests that minerals dissolution and cation exchange between Na+ and Ca2+ are the dominant processes within that groundwater. The hydrochemical and δ13CDIC characteristics of the groundwater demonstrate that HCO3− is mainly controlled by the dissolution of carbonate minerals and soil CO2, and the proportion of the latter is believed to be dominated by the hydrogeologic conditions. Similarly, the values of SO42− and δ34SSO4 indicate that a small

portion of SO42− in the groundwater in the northern part originates from the meteoric precipitation, while it is mainly derived from the dissolution of gypsum in the southern part. Furthermore, mining activities also alter the groundwater level and flow conditions through pumping and drainage, which enhances the interaction between groundwater and aquifer lithologies, thereby affects the hydrogeochemical processes. The findings of this work are of great significance for promoting the safe exploitation of deep coal resources and the sustainable utilization of groundwater in the Huaibei coalfield, as well as the most of other coalfields in North China.

5- Ligate, F., Ijumulana, J., Ahmad, A., Kimambo, V., Irunde, R., Mtamba, J. O., Mtalo, F., & Bhattacharya, P. (2021). Groundwater resources in the East African Rift Valley: Understanding the geogenic contamination and water quality challenges in Tanzania. *Scientific African, 13*10.1016/j.sciaf.2021.e00831

Abstract: Over the years, groundwater has been used as a means of adaptation to the seasonal and perennial scarcity of surface water. Groundwater provides water for households, livestock, and irrigation in semi-arid areas of Tanzania. It is acknowledged that groundwater is susceptible to chemical and other mineral contamination which not only poses a threat to the health of human beings and livestock but also agriculture. However, the potential of groundwater in terms of its viability and quality has not received adequate scrutiny from scholars. This paper provides a review of water quality and highlights the geogenic contamination of groundwater resources in Tanzania. The literature reviewed focused on the water resource sector in the major drainage basins of Tanzania, the information about drinking water quality with respect to geogenic contamination were sought. This paper has established that fluoride is the main and well-known groundwater contaminant. This is attributed to the existence of fluoride-rich minerals such as fluorite (CaF2), fluorapatite (Ca5(PO4)3F), cryolite (Na3AlF6), sellaite (MgF2), villiaumite (NaF), and topaz ((Al2(SiO4)F2), bastnaesite ((Ca, La, Nd)CO3F), and their ash deposits peeling from the granite and alkaline volcanic rocks, dominant in the region. The presence of fluoride in water sources in northern Tanzannia, part of the EARV contributes to the serious health effects on humans such as dental, skeletal, and crippling fluorosis. In addition, some literature indicated arsenic as a serious drinking water geogenic pollutant in the north-west parts of Tanzania. They pointed out that

oxidation of arsenopyrite minerals is responsible for the dissolution and release of arsenic into groundwater. From this review we conclude that information on geochemistry/hydro-geochemistry of fluoride and arsenic in the aquifers is far inadequate and recommends that more research and development (R&D) efforts from scholars, researchers, and government institutions should be invested for further investigations and solutions. The focus should be creating awareness about the danger of using arsenic and fluoride contaminated water and development of affordable and environmental friendly water purification technologies. © 2021 The Author(s)

6- Wang, J., Liang, X., Ma, B., Liu, Y., Jin, M., Knappett, P. S. K., & Liu, Y. (2021). Using isotopes and hydrogeochemistry to characterize groundwater flow systems within intensively pumped aquifers in an arid inland basin, Northwest China. *Journal of Hydrology, 595*10.1016/j.jhydrol.2021.126048

Abstract: The impacts of long-term pumping on groundwater flow patterns and groundwater chemistry are unclear in the Manas River Basin, an arid inland basin in Northwest China. In this study, hydraulic heads, hydrochemistry and environmental isotopic tracers were analyzed to reveal groundwater flow patterns, recharge sources and deduce hydrogeochemical processes in this highly exploited aquifer system. Spatial trends in the isotopic ratios δ18O and δ2H indicate that groundwater originates from glacial melting and precipitation in the mountainous area. In the piedmont plains, dissolution of calcite, gypsum and dolomite yields a groundwater type dominated by Ca-HCO3-SO4 with TDS of 300 mg/L. In this area, high 3H concentrations demarcate local flow systems and imply modern precipitation recharge. Downgradient in the lowlands, irrigation return flow recharges shallow groundwater through local flow paths. Groundwater pumping has intensified vertical hydraulic gradients causing vertical mixing between aquifers. Generally, across the basin, regional flow systems contain groundwater with 14C ages ranging from modern to 33,000 years, with the oldest waters found in wells with depths greater than 200 m. From high to low elevation groundwater chemistry transitions from Ca-HCO3-SO4 to Na-Cl-SO4 type as concentrations of Cl− and overall TDS increase. The replacement of Ca2+ with Na+ as the dominant cation suggests reverse ion exchange and carbonate precipitation occur along the intermediate and regional flow paths. Anthropogenic activities (i.e. pumping, irrigation return flow, application of fertilizers) impact shallow groundwater chemistry (<60 m). This research

reveals the impacts of natural and human-induced hydrogeochemical processes impacting groundwater chemistry in this basin with implications for similar semi-arid to arid, inter-montane basins around the world. © 2021 Elsevier B.V.

7- Kumar, M., Goswami, R., Patel, A. K., Srivastava, M., & Das, N. (2020). Scenario, perspectives and mechanism of arsenic and fluoride Co-occurrence in the groundwater: A review. *Chemosphere, 24*910.1016/j.chemosphere.2020.126126

Abstract: Arsenic (As) and fluoride (F−) are the two most conspicuous contaminants, in terms of distribution and menace, in aquifers around the world. While the majority of studies focus on the individual accounts of their hydro-geochemistry, the current work is an effort to bring together the past and contemporary works on As and F− co-occurrence. Co-occurrence in the context of As and F− is a broad umbrella term and necessarily does not imply a positive correlation between the two contaminants. In arid oxidized aquifers, healthy relationships between As and F− is reported owing desorption based release from the positively charged (hydr)oxides of metals like iron (Fe) under alkaline pH. In many instances, multiple pathways of release led to little or no correlation between the two, yet there were high concentrations of both at the same time. The key influencer of the strength of the co-occurrence is seasonality, environment, and climatic conditions. Besides, the existing primary ion and dissolved organic matter also affect the release and enrichment of As–F- in the aquifer system. Anthropogenic forcing in the form of mining, irrigation return flow, extraction, recharge, and agrochemicals remains the most significant contributing factor in the co-occurrence. The epidemiological indicate that the interface of these two interacting elements concerning public health is considerably complicated and can be affected by some uncertain factors. The existing explanations of interactions between As–F are indecisive, especially their antagonistic interactions that need further investigation. “Multi-contamination perspectives of groundwater” is an essential consideration for the overarching question of freshwater sustainability. © 2020 Elsevier Ltd

8- Zhang, Q., Xu, P., Qian, H., & Yang, F. (2020). Hydrogeochemistry and fluoride contamination in Jiaokou Irrigation District, Central China: Assessment based on multivariate statistical approach and human health risk. Science of the Total Environment, 74110.1016/j.scitotenv.2020.140460

Abstract: Too little and too much fluorine are potentially hazardous for human health. In the Jiaokou Irrigation District, ionic concentrations, hydrogeochemistry, and fluoride contaminations were analyzed using correlation matrices, principal component analysis (PCA), and health risk assessment. The patterns for the average cation and anion concentrations were Na+ > Mg2+ > Ca2+ > K+ and SO42− > HCO3− > Cl− > NO3− > CO32−. The fluoride concentrations ranged between 0.29 and 8.92 mg/L (mean = 2.4 mg/L). 5% of the samples displayed lower than the recommended limit of 0.5 mg/L fluoride content, while 69% exceeded the allowable limits of 1.5 mg/L for drinking. The low F− content is distributed in a small part of the southeast, while elevated F− mainly in the central area of the study region. The PCA results indicated three principal components (PC), PC1 having the greatest variance (45.83%) and affected by positive loadings of TDS, Cl−, SO42−, Na+, and Mg2+, PC2 accounting for 17.03% and dominated by Ca2+, pH, HCO3−, and K+, and PC3 representing 12.17% and mainly comprising of CO32−. High fluoride groundwater is of the SO4-Cl-Na type, followed by HCO3-Na type. Evaporation and ion exchange play important roles in producing high fluoride groundwater. Furthermore, saturation index and anthropogenic activities also promote the high fluoride concentrations. The values of the total hazard quotient of 93% groundwater samples were greater than 1 for infants, followed by 85% for children, 68% for teenagers, and 57% for adults. Non-carcinogenic health risks to infants may occur over the entire study area, while for adults, health risks are mainly found in Weinan and Pucheng. High fluorine may have a potential negative influence on neurodevelopment, especially for infants and children. Adults in this region have serious dental fluorosis and skeletal fluorosis because of long-term drinking of high fluoride groundwater. Therefore, measures, including using organic fertilizers, strengthening defluoridation process, and optimizing water supply strategies, are necessary in this area. © 2020 Elsevier B.V.

9- Stopelli, E., Duyen, V. T., Mai, T. T., Trang, P. T. K., Viet, P. H., Lightfoot, A., Kipfer, R., Schneider, M., Eiche, E., Kontny, A., Neumann, T., Glodowska, M., Patzner, M., Kappler, A., Kleindienst, S., Rathi, B., Cirpka, O., Bostick, B., Prommer, H., . . . Berg, M. (2020). Spatial and temporal evolution of groundwater arsenic contamination in the Red River delta, Vietnam: Interplay of mobilisation and retardation processes. *Science of the Total Environment, 717*10.1016/j.scitotenv.2020.137143

Abstract: Geogenic arsenic (As) contamination of groundwater poses a major threat to global health, particularly in Asia. To mitigate this exposure, groundwater is increasingly extracted from low-As Pleistocene aquifers. This, however, disturbs groundwater flow and potentially draws high-As groundwater into low-As aquifers. Here we report a detailed characterisation of the Van Phuc aquifer in the Red River Delta region, Vietnam, where high-As groundwater from a Holocene aquifer is being drawn into a low-As Pleistocene aquifer. This study includes data from eight years (2010–2017) of groundwater observations to develop an understanding of the spatial and temporal evolution of the redox status and groundwater hydrochemistry. Arsenic concentrations were highly variable (0.5–510 μg/L) over spatial scales of <200 m. Five hydro(geo)chemical zones (indicated as A to E) were identified in the aquifer, each associated with specific As mobilisation and retardation processes. At the riverbank (zone A), As is mobilised from freshly deposited sediments where Fe(III)-reducing conditions occur. Arsenic is then transported across the Holocene aquifer (zone B), where the vertical intrusion of evaporative water, likely enriched in dissolved organic matter, promotes methanogenic conditions and further release of As (zone C). In the redox transition zone at the boundary of the two aquifers (zone D), groundwater arsenic concentrations decrease by sorption and incorporations onto Fe(II) carbonates and Fe(II)/Fe(III) (oxyhydr)oxides under reducing conditions. The sorption/incorporation of As onto Fe(III) minerals at the redox transition and in the Mn(IV)-reducing Pleistocene aquifer (zone E) has consistently kept As concentrations below 10 μg/L for the studied period of 2010–2017, and the location of the redox transition zone does not appear to have propagated significantly. Yet, the largest temporal hydrochemical changes were found in the Pleistocene aquifer caused by groundwater advection from the Holocene aquifer. This is critical and calls for detailed investigations. © 2020 The Authors

10- B Patil, V. B., Pinto, S. M., Govindaraju, T., Hebbalu, V. S., Bhat, V., & Kannanur, L. N. (2020). Multivariate statistics and water quality index (WQI) approach for geochemical assessment of groundwater quality—a case study of Kanavi Halla Sub-Basin, Belagavi, India. *Environmental Geochemistry and Health, 42*(9), 2667-2684. 10.1007/s10653-019-00500-6

Abstract: Groundwater quality analysis has become essentially important in the present world scenario. In recent years, advanced technologies have replaced the traditional ones which are being helpful in simplifying the complex works. In this study, multivariate statistical analysis is carried out with the help of SPSS software for 45 groundwater samples of Kanavi Halla Sub-Basin (KHSB). The quality of groundwater is determined for various parameters which were analyzed and their concentration is correlated with other parameters using correlation matrix. The PCA technique is applied on water quality parameters, from which four components are extracted with 80.28% total variance. The extracted components suggest that the sources behind the higher loadings of each factor are by geological, agricultural, rainfall, domestic wastewater and industrial activities. Results of the Kaiser–Meyer–Olkin and Bartlett's test conducted have value of 0.659 which is greater than the standard value (0.5). Based on water quality index (WQI), it was noticeably depicted that 2/3rd of the KHSB groundwater quality falls under poor to very poor condition, and hardly 26% of groundwater available is portable. Thus, this study contributes the effective use of multivariate statistics and WQI analysis for groundwater quality. It helps in understanding the hydro-geochemistry of the groundwater and also aids in minimizing the larger set of data into smaller set with effective interpretation. © 2020, Springer Nature B.V.

11- Hossain, M., & Patra, P. K. (2020). Hydrogeochemical characterisation and health hazards of fluoride enriched groundwater in diverse aquifer types. *Environmental Pollution, 258*10.1016/j.envpol.2019.113646

Abstract: High concentration of fluoride (up to 20.9 mg/L) in groundwater with significant variation (p = 5.9E-128) among samples was reported from Birbhum district, an acknowledged fluoride endemic region in India. The groundwater samples (N = 368) were grouped based on their hydrochemical properties and aquifer geology for hydro-geochemical characterization. Friedman's

test showed p Granite-gneiss > Older alluvium ≥ Younger alluvium. Dissolution of minerals (such as fluorite, biotite) in laterite sheeted basalt, and granite-gneiss is the main source of groundwater fluoride in the region. Fluoride concentration is also influenced by depth of water table. Hydrochemical study indicated that fluoride concentration was higher in Na–HCO3 than in Ca–SO4 and Ca–HCO3 type of groundwater. The fluoride concentration were positively correlated with Na+ and pH and negatively correlated with the Ca2+ and Mg2+ signifying linkage with halite dissolution and calcite, dolomite precipitation. Geostatistical mapping of WQI through empirical bayesian kriging (EBK) with respect to regional optimal guideline value (0.73 mg/L) classified that groundwater in some parts of the district are unfit for drinking purpose. Health survey (N = 1767) based on Dean's criteria for dental fluorosis indicated presence of slight to moderate dental hazard. Besides, providing baseline data for management of groundwater quality in the study area, the study demonstrated the applicability of Bland-Altman analysis and empirical bayesian kriging (EBK) in delineation and interpolation of fluoride contaminated region. © 2019 Elsevier Ltd

12- Liu, J., & Han, G. (2020). Effects of chemical weathering and CO2 outgassing on δ13CDIC signals in a karst watershed. *Journal of Hydrology, 58*910.1016/j.jhydrol.2020.125192

Abstract: As the important part of carbon cycle research, riverine dissolved inorganic carbon (DIC) has attracted continuous attentions for its close relationship with global climate change. In order to investigate the dominant factors of dissolved inorganic carbon species and its stable carbon isotopic signals in large watershed under base flow condition, 81 river water samples were collected in the Xijiang River during the dry season in 2015. The elemental ratios in river water revealed the hydro-chemistry in Xijiang River were mainly controlled by the carbonate weathering. The characteristics of the most samples were the high DIC concentrations and narrow range of δ13CDIC, which can be interpreted as the result of chemical weathering under open system based on the simulated calculation of soil respiration and mineral dissolution. The relatively lower DIC concentrations and δ13CDIC values have been observed in tributaries draining silicate terrains, this result may be controlled both by the mineral dissolution and CO2 outgassing. Most samples had the over-saturated pCO2 levels compared to the atmosphere, the respiratory quotient (RQ) demonstrated that high pCO2 values were not from the biologic respiration, instead, the groundwater influx with the high soil pCO2 increased pCO2 level in river

waters. The CO2 concentration gradient between river water and atmosphere caused a violent CO2 outgassing accompanied isotope fractionation. The outgassing significantly dropped the pCO2 in river water and caused an enrichment of C13 in DIC. Based on the theoretical calculation and previous observation, the negative correlation between the δ13CDIC and pCO2 in river water was caused by the CO2 outgassing. Additionally, the isotope exchange between the DIC and atmosphere CO2 can also partially increase the riverine CO2. This study examined the impacts of soil respiration, minerals dissolution and CO2 outgassing on DIC and δ13CDIC, and found that the riverine δ13CDIC is probably not reflect the mixing of source signals such as soil CO2 and carbonate, instead, it is mainly controlled by the fractionation in minerals dissolution and CO2 outgassing. © 2020 Elsevier B.V.

13- Kim, K. -., Yun, S. -., Yu, S., Choi, B. -., Kim, M. -., & Lee, K. -. (2020). Geochemical pattern recognitions of deep thermal groundwater in South Korea using self-organizing map: Identified pathways of geochemical reaction and mixing. *Journal of Hydrology, 589*10.1016/j.jhydrol.2020.125202

Abstract: The hydrogeochemistry of deep groundwater needs to be characterized for geological CO2 storage or radioactive waste disposal. However, various origins and their interactions and complex hydrogeological conditions make it difficult to assess. Moreover, it is challenging to interpret a large national dataset of hydrochemical variables due to wide composition ranges. This study aimed to define the representative geochemical facies of deep groundwater (average well depth of 624 ± 262 m) obtained from spa areas over South Korea by applying both linear (principal component analysis; PCA) and non-linear (self-organizing map; SOM) dimensionality reduction methods to a large dataset (n = 355) with 16 hydrochemical variables. The SOM results combined with hierarchical cluster analysis showed that deep thermal groundwater in South Korea is classified into five major geochemical groups (G1 to G5) with four mixing groups (M1 to M4). G1 to G5 represent high-TDS saline (7% of the samples), acidic CO2-rich (4%), high-pH alkaline (14%), sulfate-rich (9%), and dilute freshwater (11%), respectively. More than half of the samples (56%) belonged to the four mixing groups. In particular, the SOM reduced the number of samples (n = 355) to 104 neurons, visualizing the cluster structure of samples and the relationship among hydrochemical variables in a 2D array of neurons, which made it possible to distinguish the facies

(G4 and G5 and M1 to M4) that could not be defined by PCA due to the extremely distinct geochemistry of G1 and G2. Based on the compositional changes of neurons between the geochemical (G1 to G5) and mixing (M1 to M4) groups, major reaction pathways were identified for each geochemical group. The hydrochemistry of each group mainly evolves through distinct water–rock interactions but is modified by varying degrees of mixing with dilute shallow groundwater during ascent. This study provides a state-of-the-art method to interpret a large and complex hydrogeochemical dataset; the SOM is expected to be a useful alternative to PCA. Besides, the results of this study can be useful to select a site suitable for geological CO2 storage or radioactive waste disposal. © 2020 Elsevier B.V.

14- Telahigue, F., Mejri, H., Mansouri, B., Souid, F., Agoubi, B., Chahlaoui, A., & Kharroubi, A. (2020). Assessing seawater intrusion in arid and semi-arid Mediterranean coastal aquifers using geochemical approaches. *Physics and Chemistry of the Earth, 115*10.1016/j.pce.2019.102811

Abstract: The Plio-Quaternary aquifer of Jerba Island (Tunisia), the Upper Miocene-Pliocene-Quaternary aquifer of Tripoli (Libya), the Plio-Quaternary aquifer of Nador plain (Algeria), the Bou Areg Plio-Quaternary aquifer (Morocco), the Miocene carbonate aquifer of Porto Torres (NW Sardinia, Italy) and the Pleistocene oolitic aquifer of the Baghoush area (Egypt), are essential contributor sources of drinking water and irrigation water for agricultural needs. They are increasingly being degraded by salinization processes, essentially allied with groundwater over-exploitation. In this study, a hydrogeochemical investigation, by interpretations of conservative dissolved ions was used to probe the main mechanisms controlling groundwater salinization and to characterize the associated hydrogeochemical processes occurring in Mediterranean coastal aquifers. Groundwaters of the different aquifers are of meteoric origin and they mostly flow toward the coast. Based on EC and ionic ratios, a hydro-chemical zonation of water types (ranging from Ca-HCO3, Na-HCO3, Ca-Mg-Cl-SO4, Ca-Cl to Na-Cl) from recharge areas toward the coast is revealed. This zonation is mainly controlled by migration and mixing of saline waters with regional groundwaters. The behaviour of the major ions, the adherence of the majority of ion/Cl ratios and molar ratios characterising salinity in function of [Cl−] indicate that besides mixture with seawater, groundwater chemistry of the six aquifers is also influenced by evaporation, weathering of

silicates, cation exchange and anthropogenic pollutants. The study provides insights into the hydrodynamic and geochemical relationships between freshwater and seawater at different Mediterranean coastal aquifers and provides regional authorities with a basic tools for sustainable water management aiming to limit seawater intrusion. © 2019 Elsevier Ltd

15- Li, X., Tang, C., Cao, Y., & Li, D. (2020). A multiple isotope (H, O, N, C and S) approach to elucidate the hydrochemical evolution of shallow groundwater in a rapidly urbanized area of the Pearl River Delta, China. *Science of the Total Environment, 724*10.1016/j.scitotenv.2020.137930

Abstract: A comprehensive understanding of the impacts of natural and human activities on groundwater evolution is critical for sustainable groundwater resource management, as groundwater quality degradation from urbanization has raised widespread concerns. However, conclusions based only on basic hydrochemical data would be fragmentary because complex processes occur with high concentrations of pollutants in rapidly urbanized areas. Thus, the hydrogeochemical and multi-isotope approaches were combined to elucidate the groundwater hydrogeochemical evolution in such an area. The results demonstrated that the major hydrochemical types of groundwater were Cl–Na and HCO3-Ca in 2018 and that the hydrochemical patterns had changed since 1980. The predominant controlling factors for groundwater hydrochemistry were rock weathering due to carbonic, sulfuric and nitric acids, while the cation exchange and evaporation processes acted as natural factors; redox reactions, including denitrification, sulfate reduction, and methanogenesis, also affected groundwater hydrochemistry. The impacts of anthropogenic activities on groundwater hydrochemistry consisted of direct impacts that referred to the infiltration of manure and septic waste responsible for the occurrence of high $NO3^-$ content and part of the $SO4^{2-}$ content in groundwater and indirect impacts that included the following issues: (1) acid rain accelerated water-rock interactions and resulted in the accumulation of $SO4^{2-}$; (2) sulfate reduction and methanogenesis increased the $HCO3^-$ content and expanded the distribution of HCO3-type water; (3) organic matter associated with manure and septic waste accelerated the development of a reducing environment in groundwater; and (4) the occurrence of a strong reducing environment promoted the release of Mn, aggravated heavy metal pollution and imposed adverse effects on the ecological system. © 2020 Elsevier B.V.

16- Hao, Q., Xiao, Y., Chen, K., Zhu, Y., & Li, J. (2020). Comprehensive understanding of groundwater geochemistry and suitability for sustainable drinking purposes in confined aquifers of the wuyi region, central north china plain. *Water (Switzerland), 12*(11), 1-25. 10.3390/w12113052

Abstract: Confined groundwater is important for the domestic water supply in arid and semiarid regions that have salty phreatic water. A systematic investigation was conducted in the Wuyi region, a typical central area of the North China Plain (NCP), regarding the confined groundwater geochemistry. A total of 59 samples were collected from confined aquifers across the region for in situ parameter determination and laboratory analysis. The results showed the confined groundwater was neutral to slightly alkaline, and dominantly soft fresh. The moderately hard brackish water and very hard brackish water accounted for 1.69% and 6.78% of the total samples, respectively. The hydro-chemical faces are mainly SO4·Cl–Na type with a few of the HCO3–Na type. The entropy-weighted water quality index assessment demonstrated that 21.3% of the groundwater samples came under the medium to extremely poor quality, and were unsuitable for drinking purposes due to the high content of major ions. Various populations are at a chronic health risk at some local sites by high levels of F- and Fe in groundwater, with susceptibility in the order of adult females < adult males < children < infants. The poor groundwater quality and health threats result from the natural water–rock interactions (including mineral dissolution and cation exchange) rather than anthropogenic inputs. This research can provide references for groundwater resource development and management in the NCP and other similar regions worldwide. © 2020 by the authors. Licensee MDPI, Basel, Switzerland.

17- Yan, J., Chen, J., Zhang, W., & Ma, F. (2020). Determining fluoride distribution and influencing factors in groundwater in Songyuan, Northeast China, using hydrochemical and isotopic methods. *Journal of Geochemical Exploration, 217*10.1016/j.gexplo.2020.106605

Abstract: Groundwater is the main source of drinking water for residents of the Songnen Plain, and its high fluoride content affects the health of residents. Previous studies have revealed hydro-geological conditions for fluoride enrichment, but relatively little research has been done on

hydrogeochemical processes. In this study, the analysis of the stable isotopes and the water chemistry of 444 groundwater samples showed that high-fluoride groundwater has the characteristics of high Na+ and high HCO3−, and the pH is neutral to weakly alkaline. Geochemical analysis revealed that fluorite in the sedimentary layer is the main source of fluoride in the groundwater. In addition, the concentration of F− is related to the alkaline environment, human activity, fluorite solubility, cation exchange, and silicate weathering. The relationship between δ18O and F− indicates that evaporation does not have a notable effect on F− enrichment. Hydrogen and oxygen isotope analysis, combined with previous survey results on the groundwater circulation in Songyuan, show that the increase of the F− concentration in the Quaternary confined aquifer is either related to submerged overflow or to the destruction of the aquifer structure, due to artificial abstraction, indicating the effects of water cycle on the diffusion of F− between different aquifers. © 2020 Elsevier B.V.

18- Hoffmann, J. J. L., Schneider von Deimling, J., Schröder, J. F., Schmidt, M., Held, P., Crutchley, G. J., Scholten, J., & Gorman, A. R. (2020). Complex Eyed Pockmarks and Submarine Groundwater Discharge Revealed by Acoustic Data and Sediment Cores in Eckernförde Bay, SW Baltic Sea. *Geochemistry, Geophysics, Geosystems, 21*(4)10.1029/2019GC008825

Abstract: Submarine groundwater discharge into coastal areas is a common global phenomenon and is rapidly gaining scientific interest due to its influence on marine ecology, the coastal sedimentary environment, and its potential as a future freshwater resource. We conducted an integrated study of hydroacoustic surveys combined with geochemical pore water and water column investigations at a well-known groundwater seep site in Eckernförde Bay (Germany). We aim to better constrain the effects of shallow gas and submarine groundwater discharge on high-frequency multibeam backscatter data and to present acoustic indications for submarine groundwater discharge. Our high-quality hydroacoustic data reveal hitherto unknown internal structures within the pockmarks in Eckernförde Bay. Using precisely positioned sediment core samples, our hydroacoustic-geochemical approach can differentiate intrapockmark regimes that were formerly assigned to pockmarks of a different nature. We demonstrate that high-frequency multibeam data, in particular the backscatter signals, can be used to detect shallow free gas in areas

of enhanced groundwater advection in muddy sediments. Intriguingly, our data reveal relatively small (typically <15 m across) pockmarks within the much larger, previously mapped pockmarks. The small pockmarks, which we refer to as "intrapockmarks," have formed due to the localized ascent of gas and groundwater; they manifest themselves as a new type of "eyed" pockmarks, revealed by their acoustic backscatter pattern. Our data suggest that, in organic-rich muddy sediments, morphological lows combined with a strong multibeam backscatter signal can be indicative of free shallow gas and subsequent advective groundwater flow.

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Abstract: Ground-based electrical geophysical data calibrated with borehole information are conveniently used to delineate subsurface strata because of their inherent capability to assess the lateral and vertical variations in the pore water. In this study, joined geophysical approach of vertical electrical sounding (VES) and electrical resistivity tomography (ERT) has been steered to define the strata in the hyporheic zone and in the water bearing caches in the Akwa Ibom State University's littoral shorefront. Four ERTs with each using Wenner array with 5 m electrode spacing were conducted along four profiles at the same locations that VES were conducted. Twelve surface VES soundings were performed with maximum current electrode separations of (AB/2 = 150 m). The integration of formation resistivity with six boreholes reveals motley topsoil/dry strata with resistivity value greater than 200 Ω - m above water table; saturated clay/saline water depository with resistivity value less than 30 Ω - m below water table; fine-grained sand/brackish water depository with resistivity range spanning between 70 and 200 Ω - m below water table; medium-grained sand/freshwater depository with resistivity ranging from 500 to 800 Ω - m below water table and gravelly sand/freshwater depository with resistivity value greater 800 Ω - m below water table were inferred from top to bottom within the maximum current electrode separations. These ranges of resistivity show lithological diversity in subsurface layer. Geochemical analysis was performed for main cations (magnesium, sodium, potassium, calcium, iron and manganese),

anions (bicarbonates, sulphates, chloride, and fluoride) and other physical parameters such as, pH, electrical conductivity, total dissolved solids, dissolved oxygen, biochemical oxygen demand and chemical oxygen demand. The results of the interpretation of hydrochemical species of the groundwater samples revealed that the groundwater in most locations within the study area is fresh, slightly alkaline to acidic based on the EC, pH and TDS values. The order of abundance for anions and cations is HCO3– > Cl– > SO42– > F– and Na+ > Ca2+ > Mg2+ > K+ > Fe2+ > Mn2+ respectively. The observation of elevated BOD with lower DO even in the muddy area suggests anoxic condition (DO 5 mg/L), based on the measured DO values (00.12–2.61 mg/L). The elevated ferric iron concentrations on the surface water, which later seeps into the groundwater systems, are due to excessive accumulation of dissolved organic matter (DOM) and the consequent reduction reaction within the DOM in surface water. © 2020, Springer Nature Switzerland AG.

20- Dong, S., Feng, H., Xia, M., Li, Y., Wang, C., & Wang, L. (2020). Spatial–temporal evolutions of groundwater environment in prairie opencast coal mine area: a case study of Yimin Coal Mine, China. *Environmental Geochemistry and Health, 42*(10), 3101-3118. 10.1007/s10653-020-00544-z

Abstract: The interactions between groundwater and its environment was investigated in prairie mining area in this study, through the groundwater system evolutions in mining area before and after the mining actions (from 1973 to 2016) of Yimin coal mine. The results showed that (1) the mining activities of the open-pit coal changed the original reduction environment into the oxidizing environment in the mining area. The pyrite and sulfur-bearing coal in the stratum oxidized, produced acid and triggered a series of subsequent reactions, resulting in the decrease in the pH value of the groundwater in the mining area. The concentration of SO42−, Fe2+, Fe3+, Ca2+ and Mg2+ and the total hardness increased. The regional hydrochemical type evolved from HCO3–Na·Ca·Mg type before mining to the type of HCO3·SO4–Na·Ca·Mg after mining. (2) Coal mining strongly draining underground water accelerated the regional groundwater circulation, and then made the groundwater desalination. The concentrations of TDS, COD and Na++K+ in the mining area all showed a decreasing trend. (3) The coal mining activities made the calcite and dolomite in saturated state under the natural condition of underground water to be unsaturated again. The

hydro-geochemical action evolves from double control (water–rock interaction and evaporation–concentration) to water–rock interaction control.

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