Hydrochemistry of shallow groundwater around Quesna industrial city, Egypt

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Abstract: Groundwater contamination has major implications for health and the environment in urban areas. The purpose of this work is to investigate the contamination process and to describe the hydrochemical processes that are taking place in the groundwater in the urban area of one of the Nile delta villages (Kfour Eraml) near Quesna industrial zone at El-Menoufia governorate. The saturation indices of some minerals in the groundwater were studied using the Visual Minteq geochemical model. The results show that minerals which exhibited oversaturation were; Kaolinite, Dolomite, Malachite, Calcite. Undersaturated mineral phases included the following; Anhydrite, Gypsum, Siderite, Rhodochrosite, Melanterite, Halite, and the vast species of the analyzed elements, These included carbonates, sulfates as well as chlorides. The waters were unsaturated or less supersaturated with respect to most of the minerals, reasons largely differences in physicochemical conditions. Groundwater chemical composition in the study area is mainly controlled by El Khadraweya agricultural drain which receives mixed sewage, industrial and domestic wastes.
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1. Introduction

Groundwater quality depends, to a large extent, on the quality of the recharge source, land use as well as the geological composition of the aquifer. In the floodplain, where the main recharge source is the percolating exess irrigation water, groundwater quality is reflecting the qulity of the Nile water as well as the impacts of landuse. . Similarly, in the north, towards the Mediterranean, seawater intrusion is the principal process controlling groundwater quality. In the urban and sub-urban areas, the majority of the pollution comes from domestic and industrial sources. (Abdel Rahman, 1999)

Population explosion, haphazard rapid urbanization, industrial and technological expansion, energy utilization and waste generation from domestic and industrial sources have rendered many waters hazardous to man and other living resources. There are laws guiding environmental pollution in Egypt but, many industries discharge untreated or inadequately treated wastewater into waterways (Amuda and Ibrahim; 2006).

Wastewater and septic system effluents contain high concentrations of dissolved organic carbon (DOC), ammonia, pathogens and organic micropollutants, as well as heavy metals and trace elements, particularly in the case of the release of industrial wastewater into sewer systems (Navarroa and Carbonell; 2007). The net result is large scale pollution of the water bodies which may act as a source of water supply for domestic use of the inhabitants of localities. This loss of water quality is causing health hazards and death of human, livestock and death of aquatic lives, crop failure and loss of aesthetics (Nasr *et al.,* 2006)

The purpose of this work is to determine the geochemical process that contaminants go through after reaching the groundwater in the urban area in Kfour Eraml village around Quesna industrial zone. In order to do so the main cations, anions evolution, electrical conductivity and the concentrations of metal polluting agents (Cu, Cr, Fe, Mn and Ni) were studied. The saturation indices of calcite, dolomite, ferrihydrite and siderite in the groundwater flow were studied using the Visual Minteq geochemical model. (Navarroa and Carbonell; 2007).

2. Materials and methods
Study area

Kfour Eraml village is located administratively in El-Menoufia governorate one of the Middle Delta governorates in Egypt Figure 1. It is one of hundreds of Egyptian villages where Potable water is available from a groundwater drinking scheme in the area, while the villagers use this water in domestic uses and depends on hand pumps for drinking purposes. It was clear from the discussion with residents in the study area they believe that the water pumped to consumers is not always treated and may therefore be polluted, especially in the view of disrupted pumping in the pipes which may result in adverse seepage from the drainage water (water table) to the water distribution pipelines.

Figure 1. Location map of the studied area

Shallow wells (<20m in depth) were dug near the household and groundwater was then pumped to the surface. In the absence of a sanitation system, villagers connected their toilets to excavate trenches (septic tanks) as a means of wastewater disposal. When these trenches, become full, special pumping trucks empty them. The contents are then disposed of randomly and inappropriately in El Khadraweya agricultural drain, Figure 2. Since the wastewater trenches have not been constructed with any sort of lining, pumped well water may be contaminated with wastewater seeping into the ground from the trenches, posing serious health threats to the local community.

Figure. 2, shows the discharge of untreated wastewater into El Khdraweya agricultural drain in the study area.

Kfour Eraml is the closest village to Quesna industrial zone. This zone is divided into four industrial zones each includes a number of factories with different industrial activities such as leather, foods, paper, coating, dyes and many other industries.

A number of factories through self-financed projects have constructed private sewer systems, no wastewater treatment plants are installed, and the collected/transmitted sewage is dumped as raw sewage into El Khadraweya agricultural drain Figure 3.

Figure 3, a private sewer system directly connected to El Khdraweya agricultural drain

Sampling

To investigate the state of shallow groundwater quality, the extent and type of pollution, samples from twelve hand pumps Figure 4 has been collected for three times in March, July and December 2012.

Urgent tests like Electric conductivity, temperature and pH values were obtained as a field data at the time of sampling. All the samples were filtered using cellulose nitrate films of 0.45 mm in diameter, transferred into pre-cleaned polyethylene container and stored at 4 ^{O}C till analyzed.

Figure 4, sampling sites in the studied area

Analytical Methods

The tests carried out and the testing methods followed using the standard procedures recommended by APHA (2005).

pH of the samples was recorded using a potentiometric method using pH meter already calibrated by using buffer solutions of known value before reading. Electrical conductivity (EC) was determined by a conductivity meter calibrated with KCl for each effluent sample. Gravimetric method was used for measuring total suspended solids (TSS) and total dissolved solids (TDS), and alkalinity was determined using standard titration techniques.

The collected samples were analyzed for major cations Ca^{2+}, Mg^{2+}, Na^+ and K^+ using Inductively Coupled Plasma (ICP-OES), and the concentrations of major anions Cl^- and SO_4^{2-} and NO_3^- were determined using ion chromatography (IC).

For the analysis of heavy metals Copper (Cu), Zinc (Zn), Iron (Fe), Manganese (Mn), Nickel (Ni), Cadmium (Cd), Lead (Pb), and Chromium (Cr), acidified samples (HNO_3, pH < 2) were analyzed using the inductively coupled plasma with mass spectroscopy (ICP-MS) method.

Charge balance errors in analytical results were calculated using the computer program *visual* MINTEQ and the accuracy of the IC, ICP and ICP-MS analyses were controlled using means of certified reference standards.

Geochemical Modeling

Calculations of solute speciation, and solid phase saturation indices were made using the computer program *visual* MINTEQ 3.0 (Gustafsson, 2011), beta software, developed for the USEPA. The model is used to perform the calculations necessary to simulate the contact of waste solutions with heterogeneous sediments or the interaction of groundwater with solidified wastes. The computer equilibrium model contains a thermodynamic database which contains equilibrium constants for aqueous simple and complex species as well as solubility product and redox potential, in addition to other equilibrium parameters (Jenne, E.,1979), (Melchior and Bassett, 1990), (Donald 1995), (Gustafsson *et al.,* 2003). Visual MINTEQ can calculate ion species/solubility, adsorption, oxidation-reduction, gas phase equilibrium, and precipitation/dissolution of solid phases (Ball *et al.,* 1980, Felmy *et al.,* 1984, Gustafsson *et al.,* 2009).

3. Results and discussion

All the represented data is an average result of three samples collected in March, July and December 2012. Concentrations of major chemical species are presented in Table 1, The analytical results show that groundwater in the study area is generally alkaline in nature with pH ranging from 7.31 to 7.94. The Electrical Conductivity (EC) which expresses the ionic strength of the solution, varied between 3140 to 596 μs/cm.

The major cations analyzed included calcium, magnesium, sodium and potassium. The concentrations exhibited the following order, $Na^+ > Ca^{2+} > Mg^{2+} > K^+$. Sodium ($Na^+$) is the important and most abundant alkali metal which is highly mobile and soluble in groundwater. Concentration of Na^+ ranged from 37 to 280 mg/l in the studied groundwater samples. Calcium (Ca^{2+}) was next in dominance with concentration ranged from 46.8 to 254 mg/l. This may reflect the process of chemical weathering of silicates and the common occurrence of calcium carbonate (Langmuir, 1997). The other cations, magnesium (Mg^{2+}) 14 to 74 mg/l and while, Potassium (K^+) exhibited the lowest concentration levels relative to other cations it ranged from 5 to 47 mg/L. This is common in natural waters due to its tendency to be fixed by clay minerals and precipitate in the formation of secondary minerals (Matheis, 1982).

Table 1: The chemical constituents in groundwater

Sample No.	pH	EC μs/cm	TDS mg/l		Ca	K	Mg	Na	Cl	NO3	SO4	HCO3
1	7.61	1220	785	mg/l	80	9	25	145	160	20	130	315
				meq/l	3.99	0.23	2.05	6.3	4.51	0.32	2.7	5.16
2	7.5	1360	864	mg/l	89.8	14	44.7	125	190	91.6	116	300
				meq/l	4.48	0.36	3.68	5.44	5.36	1.47	2.41	4.92
3	7.94	596	380	mg/l	46.8	3.2	25	37	55	31	60	170
				meq/l	2.33	0.082	2.06	1.61	1.55	0.5	1.25	2.79
4	7.47	3140	2009	mg/l	254	47	74.4	280	420	700	150	390
				meq/l	12.67	1.2	6.12	12.18	11.84	11.29	3.12	6.39
5	7.84	1380	523	mg/l	52	5	59.8	150	210	140	80	265
				meq/l	2.59	0.13	4.92	6.5	5.92	2.26	1.66	4.34
6	7.73	818	524	mg/l	81.8	5	25.8	54	71	51	61	273
				meq/l	4.08	0.13	2.12	2.35	2	0.82	1.27	4.47
7	7.75	815	521	mg/l	72	9	15.7	70	103	32	55	228
				meq/l	3.59	0.23	1.29	3.04	2.9	0.52	1.15	3.74
8	7.31	1170	749	mg/l	114	5	28	84	120	130	71	300
				meq/l	5.69	0.13	2.3	3.65	3.38	2.09	1.48	4.92
9	7.38	2160	1380	mg/l	145	39	39.3	230	255	65.2	100	670
				meq/l	7.23	0.99	3.23	10	7.19	1.05	2.08	10.98
10	7.35	794	508	mg/l	78	9	18	56	66	58	63	242
				meq/l	3.89	0.23	1.48	2.43	1.86	0.93	1.31	3.97
11	7.85	670	429	mg/l	70	8	20	40	60	42	48	220
				meq/l	3.49	0.2	1.64	1.73	1.69	0.67	1	3.6
12	7.81	622	398	mg/l	64	6.7	14	40	55	4.33	30	247
				meq/l	3.19	0.17	1.15	1.74	1.55	0.07	0.62	4.05

The major anions and nutrient analyzed were bicarbonate (HCO_3^-), chloride (Cl^-), sulphate (SO_4^{2-}) and nitrate (NO_3^-). Bicarbonate was the dominant anion with concentration ranged from 170 to 670 mg/l, Chloride was next in dominance with concentration ranged from 55 to 420 mg/l may be due to a potential input of sewage and waste water leakage from septic tanks. Concentration of sulphate (SO_4^{2-}) ranged from 30 to 150 mg/l this might be due to gypsum and anhydrite dissolution in the circulating waters.

The nitrate (NO_3^-) concentrations in the studied groundwater samples were between 4.33 and 700 mg/l, nitrate in groundwater is usually due to point source and nonpoint source pollution. Since nitrogenous materials are rare in the geological record, nitrate in groundwater is usually due to anthropogenic activity (Fathy and Traugott, 2012).

The source of nitrates contamination might be originated from fertilizer applied to the fields and orchard areas Also dairy lagoons may play an important role in nitrates contamination because sample No. 4 which is located in livestock farm contains highest nitrate concentration 700 mg/l.

Agricultural practices generally result in nonpoint source pollution of groundwater (Hall *et al.,* 2001; Delgado and Shaffer, 2002). With nonpoint sources, groundwater quality may be depleted over time due to the cumulative effects of several years of practices (Addiscott *et al.,* 1992; Schilling and Wolter, 2001). The wells are located in a rural area (Kfour Eraml village) where crops may be irrigated with sewage water from El-Khadraweya agricultural drain which receives mixed sewage, industrial, domestic wastes and agricultural wates. Increasing nitrate pollution is a relatively recent phenomenon and is correlated with the increasing use of nitrogen fertilizers over the last 30 to 40 years (Hallberg, 1989; Hallberg *et al.,* 1989). Baldwin's study showed a direct link between increasing nitrogen inputs on agricultural lands and water quality in the Thousand Springs, Snake River Watershed, (Baldwin, *et al.,* 2000).The major point sources include septic tanks and dairy lagoons. Many studies have shown high concentrations of nitrate in areas with septic tanks (Cantor and Knox, 1984; Keeney, 1986; Arnold 1999, Almasri, 2004)

Heavy metals:

Concentrations of trace metals (Fe, Mn, Ni, Cr, Cu and Zn) in the studied groundwater wells are presented in Table 2. Iron (Fe) concentration in groundwater ranged from 0.12 to 0.225 mg/L. The Known primary sources of iron are silicates and aluminosilicates (Deer *et al.,* 1992). Pyrite (FeS_2) and magnetite (Fe_2O_4) are other common minor minerals. Manganese (Mn) concentrations ranged from 0.016 to 0.241 mg/L. The concentration levels of Ni, Cr, Cu and Zn were also recorded. The ranges for these elements are; Ni (0.003 to 0.017), Cr (0.008 to 0.067), Cu (0.087 to 1.721), and Zn (0.088 to 0.87) with all values in mg/L. The presence heavy metals in the groundwater near industrial facilities may be caused by the infiltration of wastewater in which these metals are present.

Table 2: concentrations of some heavy metals in the studied ground water samples all values are in mg/l

Sample	Cr	Cu	Fe	Mn	Ni	Zn
1	0.014	0.16	0.13	0.05	0.005	0.1
2	0.013	0.27	0.15	0.055	0.014	0.214
3	0.011	0.17	0.12	0.083	0.003	0.3
4	0.014	0.37	0.14	0.19	0.003	0.208
5	0.01	0.13	0.185	0.06	0.008	0.4
6	0.017	0.19	0.12	0.1	0.006	0.3
7	0.013	0.112	0.112	0.106	0.01	0.52
8	0.023	1.691	0.19	0.079	0.008	0.87
9	0.008	1.721	0.225	0.241	0.017	0.142
10	0.01	0.812	0.141	0.038	0.005	0.28
11	0.067	0.242	0.173	0.168	0.003	0.35
12	0.011	0.087	0.19	0.016	0.007	0.088

Hydrochemical modeling

Mineral equilibrium calculations for groundwater are useful in predicting the presence of reactive minerals in groundwater system and estimating mineral activity; (Taylor *et al.*, 1996; Deutsch, 1997; Zhu *et al.*, 2008).The groundwater or solution is considered to be in equilibrium with regards to a particular mineral if the saturation index (SI) = 0. It is considered to be undersaturated if SI<0 and oversaturated if the SI>0.

Thermodynamic stability of a groundwater is characterized by the state of the saturation index (SI)

with respect to a particular mineral. Since most of the earth materials are alumino-silicates, the SI of water in contact with these minerals helps us to understand / predict the reaction pathways. The value of ionic activity product (IAP) for a mineral equilibrium reaction in a natural water may be compared with the value of, the solubility product (K_{sp}) of the mineral.

Mineral saturation states were calculated as part of the output from the modeling programs. They are useful for indicating what minerals might be dissolved or precipitating into or from groundwater, or controlling the groundwater composition. The calculations are based on an equilibrium model, so the results are only an indication, as kinetic factors may inhibit approach to equilibrium. The minerals which exhibited oversaturation (SI>0) were; Kaolinite, Dolomite, Malachite, Calcite. Undersaturated mineral phases included the following; anhydrite, Gypsum, siderite, rhodochrosite, melanterite, Halite, and the vast

species of the analyzed elements. These included carbonates, sulfates as well as chlorides. The waters were unsaturated or less supersaturated with respect to most of the minerals, reasons largely differences in physicochemical conditions.

Reactions of groundwater with, CO_3^- and SO_4^- minerals are often expected to reach equilibrium within years in the aquifer. This however depends on the abundance of such mineral phases within the porous media. The modeling indicates that groundwater compositions are controlled by a complex set of minerals and processes. Dissolution, precipitation and cation exchange are the dominant of the processes within groundwater systems. Some elements e.g., Fe, Mn are controlled by mineral solubilities and equilibrium processes, they can affect the precipitation or dissolution of other more toxic elements, e.g., Pb, Cu , Cr and Ni. (Ekwere and Edet 2012)
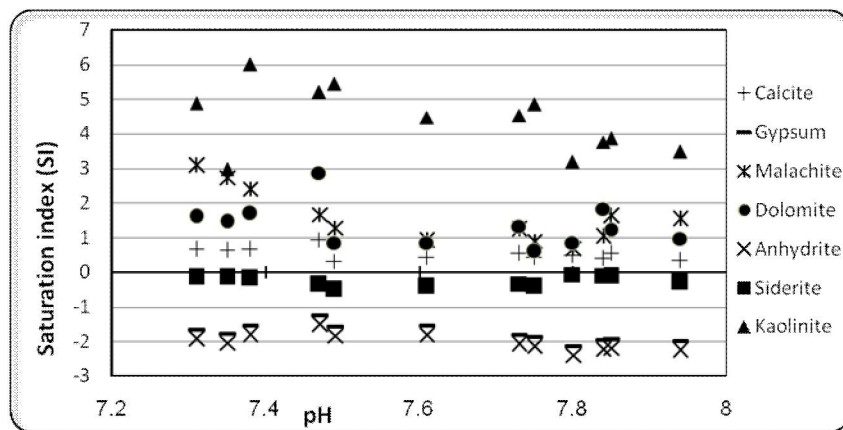

Figure 5, The relation between the SI of minerals in different samples and their respective pH

The clay minerals were grouped with respect to the range of saturation index as supersaturated including Kaolinite ($Al_2Si_2O_5(OH)_4$, Dlomite ($CaMg(CO3)_2$ and Malachite ($Cu_2CO_3(OH)_2$), near saturated to saturated including Calcite ($CaCO_3$), siderite ($FeCO_3$) and undersaturated including anhydrite ($CaSO_4$) and Gypsum ($CaSO_4 \cdot 2H_2O$).

The SI of the minerals in the supersaturated group are concentrated at pH above 7.5 and there is a decreasing trend with increase of pH Figure (5),This increase of pH reduces the availability of H^+ for ion exchange. Groundwater in all the water-wells in the area is supersaturated with respect to silica and carbonate minerals. The dominant geochemical process is the dissolution of carbonate minerals (e.g. calcite and dolomite), which contributes the Ca^{2+}, Mg^{2+}, and HCO_3^- to the groundwater. Gypsum dissolution contributes both Ca^{2+} and SO_2^{4-} to groundwater. The Ca^{2+} released by the dissolution of

gypsum leads to the precipitation of additional calcite, which leads to supersaturation or near equilibrium of groundwater with calcite. This phenomenon is referred to as common- ion driven precipitation or common ion effect (Back and Hanshaw, 1970; Langmuir, 1997). The common ion effect of gypsum dissolution and calcite precipitation is often accompanied by dolomite dissolution. (Sharif *et al.,* 2008).

HCO_3^- is always higher than equivalent Ca^{2+}, which is an indication that some HCO_3^- is also coming from processes other than calcite dissolution, or the Ca^{2+} is lost in the cation exchange reactions. Dissolution of silicate and oxidation of organic matter may have produced the excess HCO_3^- in the groundwater. The concentrations (meq/L) of Na^+ and Cl^- in the studied groundwater provide evidence that halite (NaCl) dissolution is not a major process controlling Na^+ and Cl^- in groundwater. Na^+ is higher

than Cl⁻ in all wells, shows the evidence of silicate dissolution and cation exchange, rather than dissolution of halite (Kresse and Fazio, 2002). The Cl⁻ concentrations in the groundwater are relatively high (up to 420 mg/L) in the study area, which may be the result of local recharge gained from surface contribution as recharge by El Khadraweya agricultural drain.

Ionic strength (IS) is a measure of total concentration of ions in solution which emphasizes the increased contribution of species with charges greater than one to solution non-ideality (Domenico and Schwartz 1990).

$$IS = 0.5\sum mz^2$$

where m is the concentration of a given ion in moles per liter and z is the charge on that ion. The terms in the summation include one for each ionic species present. The relationship of the IS of samples and SI of these minerals clearly shows a positive relationship to SI of most of studied minerals (Figure 6).
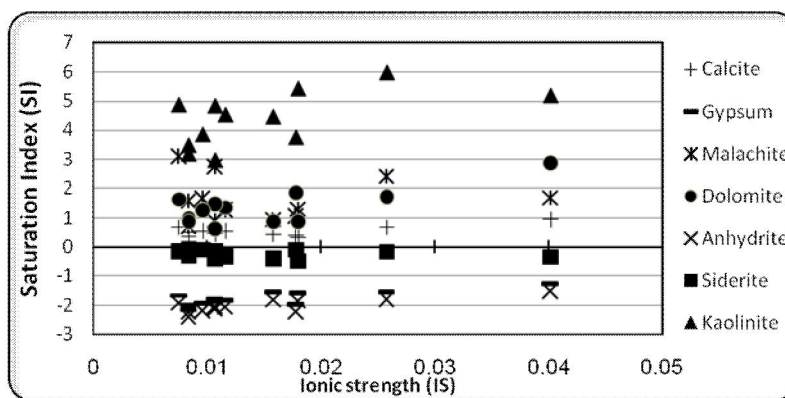

Figure 6, The relation between the saturation index (SI) of clay minerals in different samples and their respective ionic strength (IS)

4. Conclusion

The chemical composition of groundwater in Kfour Eraml village is strongly influenced by rock water interaction, dissolution and deposition of carbonate and silicate minerals, ion exchange and surface water interactions. Groundwater chemical composition in the study area is mainly controlled by El Khadraweya agricultural drain which receives mixed sewage, industrial and domestic wastes, which is explained by the mixing mechanism. Weathering of silicate minerals controls the major ions such as sodium, calcium, magnesium and potassium in groundwater in this area.

Groundwater in all the water-wells in the area is supersaturated with respect to silica and carbonate minerals. The dominant geochemical process is the dissolution of carbonate minerals (e.g. Calcite and dolomite), which contributes the Ca^{2+}, Mg^{2+}, and HCO_3^- to the groundwater. Gypsum dissolution contributes both Ca^{2+} and SO_4^{2-} to groundwater. The Ca^{2+} released by the dissolution of gypsum leads to the precipitation of additional calcite, which leads to supersaturation or near equilibrium of groundwater with calcite.

Therefore, in general, the groundwater chemistry of this area is principally controlled by the mixing of waters, evaporation, dissolution and deposition, and ion exchange processes.

References

1. Abdel Rahman, F., (1999) Water and Development in Greater Cairo (Egypt) Afers Internacionals, núm. 45-46, pp. 81-102.
2. Addiscott, T.M., Whitmore, A.P., Powlson, D.S., (1992) Farming, Fertilizers and the Nitrate Problem, CAB International, Wallingford.
3. Almasri, M.N., Kaluarachchi, J. J., (2004b) Assessment and management of long-term nitrate pollution of ground water in agriculture-dominated watersheds. Journal of Hydrology 295, 225–245.
4. Amuda, O.S., Ibrahim A.O.,(2006) Industrial wastewater treatment using natural material as adsorbent, African Journal of Biotechnology 5 (16), pp. 1483-1487.
5. Arnade, L.J., (1999) Seasonal correlation of well contamination and septic tank distance. Ground Water 37(6), 920–923.
6. Back, W., Hanshaw, B.B., (1970) Comparison of chemical hydrology of Florida and Yucatan. J. Hydrol. 10, 360–368.
7. Baldwin, Joe, D. Brandt, E. Hagan, B. Wicherski, 2000. *Cumulative Impacts Assessment, Thousand Springs Area of the Eastern Snake River Plain, Idaho*. groundwater Quality Technical Report No.14, pgs 28 – 32.
8. Ball, J. W., Nordstrom, D. K. and Jenne, E. A. (1980) Additional and Revised Thermochemical Data and Computer Code for WATEQ2-A Computerized Chemical Model for Trace and Major Element Speciation and Mineral Equilibria of Natural Waters,

U.S. Geological Survey, Water Resources Investigations WRI-78-116.

9. Cantor, L., Knox, R.C., (1984) Evaluation of Septic Tank Effects on Ground-water Quality, US Environmental Protection Agency, Washington, DC, EPA-600/2-284-107; 259 pp.

10. Deer, W. A., Howie, R. A., Zussman, J., (1992) An Introduction to the Rock Forming Minerals. John Wiley & Sons, New York.

11. Delgado, J. A., Shaffer, M.J., (2002) Essentials of a national nitrate leaching index assessment tool. Journal of Soil and Water Conservation 57, 327-335.

12. Deutsch, W. J., (1997) Groundwater Geochemistry, Fundamentals and Applications to contamination. Lewis Press, New York.

13. Domenico P. A., Schwartz, W. (1990) Physical and Chemical Hydrogeology (New York: John Wiley), p. 824.

14. Donald, L. S., (1995) Environmental Soil Chemistry, Academic Press, San Diego, California.

15. Ekwere, A. S., Edet, A., (2012) Distribution and Chemical Speciation of Some Elements in the Ground Waters of Oban Area (South-Eastern Nigeria), Research Journal of Environmental and Earth Sciences 4(3): 207-214.

16. Fathy A. , Traugott S., (2012) Hydrochemistry of surface water and groundwater from a fractured carbonate aquifer in the Helwan area, Egypt, J. Earth Syst. Sci. 121, (1) pp. 109–124.

17. Felmy, A. R., Girvin, D. C., and Jenne, E. A., (1984) MINTEQ A2 Computer Program for Calculating Aqueous Geochemical equilibrium, NTIS PB 84-157148. (EPA-600/3-84032) Nat. Tech. Inf. Ser. Springfield.

18. Gustafsson, J. P., 2011. Visual MINTEQ ver. 3.0. KTH, Department of Land and Water Resources Engineering. http://www2.lwr.kth.se/English/OurSoftware/vminteq

19. Gustafsson, J. P., Dässman, E. and Bäckström, M. (2009), Towards a consistent geochemical model for prediction of uranium (VI) removal from groundwater by ferrihydrite, Applied Geochemistry, 24 (3), 454 - 462.

20. Gustafsson, J. P., Pechová, P., Berggren, D. (2003), Modelling metal binding to soils: The role of organic matter. Environmental Science and Technology 37, 2767-2774

21. Hall, M. D., Shaffer, M. J., Waskom, R.M., Delgado, J.A., (2001). Regional nitrate leaching variability: what makes a difference in north-eastern Colorado, Journal of the American Water Resources Association 37(1), 139-408.

22. Hallberg, G.R. 1989. *Nitrate in Ground Water in the United States. IN: Nitrogen Management and Ground Water Protection.* Elsevier, Amsterdam, pp. 35-74.

23. Hallberg, G.R., R.D. Libra, D.J. Quade, J.P. Littke, and B.K. Nations, 1989. *Ground water Monitoring*

in the Big Springs Basin 1984-1987: Summary Review: Iowa Department of Natural Resources, Geological Survey Bureau, Technical Information Series 16. 68 p.

24. Jenne, E. D. ed.; (1979) Chemical Modeling in Aqueous Systems, ACS Symposium Series No. 93; American Chemical Society: Washington, DC,

25. Keeney, D.R., (1986), Sources of nitrate to ground water. Critical Reviews in Environmental Control 16 (3), 257–304.

26. Kresse, T. M., Fazio, J. A., (2002) Pesticides, Water quality and geochemical evolution of ground water in the alluvial aquifer, Bayou Bartholomew watershed, Arkansas. Arkansas Department of Environmental Quality. Water Quality Report WQ02-05-1, Little Rock, AR.

27. Langmuir, D., 1997. Aqueous Environmental Geochem. Prentice Hall, Inc. Upper Saddle River, New Jersey, pp: 07458.

28. Matheis, G., 1982. The Properties of Groundwater. Wiley, New York.

29. Melchior, D. C. and Bassett, R. L., eds. (1990), Chemical Modeling of Aqueous system II. ACS Symp. Ser. No. 416. Am. Chem. Soc., Washington DC.

30. Nasr, U., Rafia, N., Hamida B., Mudassar I., Ilyas D., (2006), pollution load in industrial effluent and groundwater of Gadoon Amazai Industrial Estate (GAIE) SWABI, NWFP, Journal of Agricultural and Biological Science, Vol. 1 (3) pp. 18-24.

31. Navarroa, A., Carbonell, M., (2007) Evaluation of groundwater contamination beneath an urban environment: The Beso's river basin (Barcelona, Spain), Journal of Environmental Management 85, 259–269.

32. Schilling, K.E., Wolter, C.F., (2001) Contribution of base flow to nonpoint source pollution loads in an agricultural watershed. Ground Water 39 (1), 49-58.

33. Sharif M., Davis R., Steele K., Kim B., Kresse T., Fazio J., (2008) Inverse geochemical modeling of groundwater evolution with emphasis on arsenic in the Mississippi River Valley alluvial aquifer, Arkansas (USA), Journal of Hydrology, 350, 41– 55.

34. Standard Methods for the Examination of Water and Wastewater (2005) American Public Health Association (APHA), 21st Edition.

35. Taylor, J.R., Weaver T.R., McPhail D.C. and Murphy N.C., (1996) Characterization and impact assessment of mine tailings in the King River System and delta, Western Tasmania. Final report: Project No. 5 Mt. Lyell Remediation Res. and Demonst. Program.

36. Zhu, G. F., Su, Y. H. and Feng, Q., (2008) The hydrochemical characteristics and evolution of groundwater and surface water in the Heihe River Basin, northwest China. Hydrogeology J., 16:167-182.

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