# Source of aluminum in Pleistocene aquifer in Ben Cat and Thuan An Binh Duong province

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# ABSTRACT:

In the study area, the Pleistocene aquifer has small depth. From 2009, pH was discovered with high depletion and suddent increase of aluminum in groundwater. However, in 2013, the aluminum concentratin seems to be stable. The analyzed results of mineral composition, soil, sludge, groundwater, and waste water samples showed that sources of aluminum is mainly from the local soil material, and the other is from the industrial activities. Hydrolysis of alumosilicat is the main process that put aluminum into groundwater. Factors supports the dissolution of aluminum in groundwater are hydrogeological structure, soil materials, over groundwater pumping activities, irregular casing of wells, agriculture activites, etc.

Keywords: Aluminum source, mineral composition, hydrolysis.

#### **1. INTRODUCTION**

The socio-economic development entails the increase of groundwater demand in Binh Duong province. According to the analysed data and recent researches show groundwater is being contaminated by heavy metal such Al, Cr and nitrogen and organic compound. In particular in the Pleistocene aquifer (with depth of about 25-40 m), there is an increase of contaminant. This aquifer is used primarily serve domestic demand and industrial activities in the area. The research is attempt to find the sources and present of aluminum in Pleistocene aquifer in Ben Cat and Thuan An districts, Binh Duong Province. Our research concentrated to evaluate contamination potential due to industrial activities with 21,1 km<sup>2</sup> area.

The early Pleistocene (qp1) presents in both districts. However, in Ben Cat district, there are two aquifer with Pleistocen age (qp2-3 overlays on qp1) (Figure 1). Popular types of groundwater are Cl-HCO3-Na-(Ca), HCO3-Cl-Na-(Ca), somewhere has HCO3-Cl-

Ca. In attention, nitrogen compounds is quite high, particularly, NH4+ present in many samples. The highest groundwater extractrion is in Thuan An with 45,442 m3/day while in Ben Cat with 19,665 m3/day.

## 2. STUDY METHODS

To study the existence of any ion, we need to consider three main problems: 1) Sources of that ion, 2) physical-chemical processes that lead the ion into environment, 3) conditions allow the ion react in those processes. To clear these problems, we collected the secondary data in order to understand what happened in the area. The we collect samples and analyse those samples with Fe, Al, pH, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>. Besides, we develop groundwater flow model by using GMS software with Modflow and MT3DMS modules to evalute the potential of aluminum transport in the study area. We drilled 7 boreholes in Thuan An - Di An districts, 5 boreholes in Ben Cat district and collect core samples for mineral composition analysis. 112 water samples were collected with different periods in 2012 and 2013.



Figure 1. Hydrogeological cross - section in Thuan An and Ben Cat districts

#### **3.RESULTATES AND DISCUSSION**

# 3.4.pH and Al concentration in 2011-2013

#### 3.1.Groundwater flow model in the study area

The groundwater direction in qp<sub>2-3</sub> in Ben Cat flows to Saigon river and Thi Tinh river. Groundwater direction in qp1 flow to the east - south and to Saigon river (Fig.2)

# **3.2.Base value of aluminum and pH in Pleistocene** aquifer in Binh Duong province

We used the results of 3 national monitoring stations from 1991 to 1997 as base value of aluminum and pH. At this time, there is rare industrial activities and less of human activities. These data were considered as the natural condition of the Pleistocene aquifer in the study area. The Q22504T station is in Phuoc Hoa, Tan Uyen in n2<sup>2</sup>. The Q225060 station is in Phuoc Hoa, Tan Uyen in mz. The other Q224020 station is in qp<sub>2-3</sub> in Thoi Hoa, Ben Cat. The samples were collected in dry and rainy season. According to those data, base value of pHs is from 6.4-6.5 were acceptable for groundwater quality. Al3+ at these stations is from 0.0-0.01 mg/l was also acceptable. The sources of aluminum should be from nature.

# 3.3. Changing of aluminum and other environmental indexes in 2009-2010 in Pleistocene aquifer

Our studied results show that pH in the study area is very low from 3.3-6.4. pH in rainy reason is higher than in dry season. Comparison with pH in 2009, pH in 2010 is low 1.2-1.58 time (figure 3). Together with low pH, aluminum concentration is changing respectively. Highest aluminum concentration in 2010 is 12.47 mg/l in An Phu at -40 m depth in early Pleistotence aquifer. Lowes aluminum concentration is 0.011 mg/l in Ben Cat district at -60 m depth (figure 4).

According to our research in 2011-2013 in Ben Cat and Thuan districts, averages of pHs in 2009, 2010, 2012, 2013 are 4.64, 3.66, 5.78, 4.43 respectively, lower than the national standard (pH is from 5.5-8.5). This is very good condition to support the solution of aluminum into groundwater. pH of groundwater is changed according to depth. Figure 5 shows that the deeper aquifer, the higher pH is. It explains that aluminum concentration in deeper aquifer is lower (figure 7). At depth 30-45 m, groundwater environment is acidic with pH below 3 in many samples. pH of water sample in 2013 is less than 5.5, mostly ranges from 3.5-4.5. pH and aluminum concentration have very good agreement (figure 6). Figure 6 shows that when pH is less than 4.7, aluminum concentration in groundwarer tends to higher because of solution of aluminum. Even when the environment is more ankaline, aluminum is also increasing. When environment is neutral, aluminum concentration is acceptable. The analyzed results also present high aluminium concentration ranges 25-45 m depth. verage aluminum concentration in 2010 is higher than 2009, 2012, and 2013. Aluminum concentration is found at 70 m depth in Pliocene aquifer (Natural Geography Institute, 2009). It may due to percolation of aluminum from the upper aquifer through hydrogeolical windows.

Figure 8 shows the large difference of aluminum between 2012 and 2013 at HK03, HK05, HK10 and HK12.These locations are maybe near the contamination sources. Only HK11shows aluminum concentration is higher in 2012. It may due to the incomplete dilution at low permeable layers.



Figure 2. Groundwater contour in  $qp_{2-3}(a_1)$  and  $qp_1(a_2)$  in Ben Cat and  $qp_1$  in Thuan An – Di An (b)







## 4.CHANGING OF ALUMINUM IN SPACE

#### In Ben Cat district

In the drilled locations, aluminum is higher than drinking water standard (0.2mg/l) except in HK11 (in October 2012). These boreholes are near the industrial zone in Ben Cat district. pH values are neutral (except HK08 and HK09 – in July 2013). The reason is maybe



■pH - Al 2009 ◆pH - Al 2010 ▲pH - Al 10/2012 ●pH - Al 7/2013

Figure 6. Relation of pH and aluminum

from industrial activities discharges high acidic waste water (may be including aluminum) and percolates to the aquifer. Figure 9 shows that high aluminum concentration is located at low pH. In Thuan An, at almost monitoring borehole, aluminum in groundwater is over the standard, particularly in dry season. It is not much difference at the sampling locaions (from 0.12 -2.2 mg/l). The aluminum distribution in Thuan An is quite similar in space. Therefore, it is very difficult to find the sources of aluminum. It may from the sources existing in the past and this source may stop in the present. Figure 10 shows the distribution of Al and pH in Thuan An (October 2013). The area is with low pH and lower Al concentration if compare with Ben Cat district.



Figure 7. Relationship between thedepth and aluminum content



Figure 8. Changing of Al in 2012 – 2013



Figure 9. Aluminum and pH distribion in Ben Cat district



Figure 10. Aluminum and pH distribution in Thuan An (October 2013)

#### 4.1.Source of aluminum

### Natural source

Natural source is from soil composition. The analyzed results of mineral composition with 14

samples show that minerals contain Al is from 35-40% of samples even though dissolved Al from soil materials is not so high. Sample UD3-HK2 show highest dissolved Al is 1,649 mg/kg and in the other samples were not find Al.

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The total Al in soil samples is quite high, highest is 22,854 mg/kg, the lowest is 3956 mg/kg. In some advance condition, Al may dissolve to the groundwater.

#### Human source

Human source is maybe from waste water from industrial zones, slugde, agricultural activities. The waste water samples was analyzed at Ba Bo chanel with 0.224 mg/l of aluminum and in the output of waste water discharge in Viet Huong II industrial zone is 0.567 mg/l. the high Al concentration may percolate to groundwater with long time.

# 4.2.Physical – chemical process to induce al to groundwater

The reaction of aluminosilicate minerals have low dissolution. The popular of chemical reactions are hydrolysis reaction as described below:

$$Na_{2}Al_{2}SiO_{16} + CO_{2} + H_{2}O = H_{2}Al_{2}Si_{2}O_{8} + 2Na + CO_{3}^{22} + 4SiO_{2}$$
(1)

 $2Na_{2}Al_{2}Si_{6}O_{16} + 5H_{2}O = 2Na_{2}SiO_{3} + 5H_{2}SiO_{3} + 2Al_{2}O_{3} + 5SiO_{2}$ (2)

Reaction (1) happens in oxidation zone or in where aquifer presents in or near ground surface. Reaction (2) happens in reduction zone without oxygen.

To continue the hydrolysis, the reaction (2) is

$$Na_2SiO_3 + 2H_2O = 2Na^+ + 2OH^- + H_2SiO_3$$
 (3)

 $H_2SiO_3 = H^+ + HSiO_3^-$ (4)

Because  $H_2SiO_3$  weak acids dissociate at very low levels should gradually lower the amount of H<sup>+</sup> ions than OH<sup>-</sup> ions and water will be available at a pH greater than 6.5. When the temperature increases, the solubility of silica also gradually increases, which explains the significant presence of  $H_2SiO_3$  in hot water. Moreover, fine grains contain significant of Fe and Al sulfate. In the reduction condition, Al sulfate has reaction as below:

$Al_2(SO_4)_3 + 6H_2O = AlOH)_3 + 3H_2SO_4$	(5)
In neutral pH:	
$\mathrm{Al}(\mathrm{OH})_3 = \mathrm{Al}(\mathrm{OH}_2^+ + (\mathrm{OH})^-)$	(6)
In low pH	

$$Al(OH)_{2^{+}} + OH^{-} = Al^{3_{+}} + 3 OH^{-}$$
 (7)

It means Al(OH)<sub>3</sub> can dissolve in acidic environment and if pH increase

In alkaline environemt:

 $Al(OH)_3 = Al(OH)_2O^- + H^+$ (8)

If pH is high, then:

 $Al(OH)_2O^- + H^+ = AlO_2^- + H^+ + H_2O$  (9)

Thus, Al can go to water as reaction (5) to (9). This may be acceptable to know that most of the sediments from the Pleistocene age are sourced from rivers, seas or mixture and alkaline soils are common in the southern delta. When the aluminum content increased sharply (up to > 14 mg/l, at which aluminum is derived exotic - entirely possible due to the impact of industrial activities.

# 4.3.Factors affect the inducement of aluminum to groundwater

#### Natural factors

Im portance factors are natural mineral composition and geochemistry of the rocks topsoil and in the aquifers. Soil compositions in vadoze zone and other layers are the sources of metal elements in groundwater. Aquifer is not deep , much thicker zone aeration , permeability of the layers are not small self- protection is not high ... However, because agriculture is so atmospheric conditions to penetrate quite easily , with the presence of oxygen and carbon dioxide freedom creates localized oxidizing environment.

#### **Human factors**

Through the analysis of changes in pH, concentrations of aluminum, manganese and some of them correlated with time and with depth, we can say that the sudden change in pH, aluminum content of the water for a while short term impact of artificial elements. Can outlined the following basic element: The exploitation of underground water strong focus on aquifer depth is not as big as aquifers and aquifer qp2-3 qp1 lead to lower water levels significant, since it has changed the fundamental geochemical conditions of the aquifer to create conditions for a number of chemical and physical processes occurring in the interaction

between ground water and soil, which penetrates the aluminum -containing layers water.

Drilling operations, the well is not properly structure is also one of the factors causing the current equivalent of aluminum contamination in groundwater. The population growth and the development of residential areas led to increasing amounts of domestic wastewater and sewage sludge, thereby improving the flexibility of aluminum in the soil. The sudden change in the pH of the water also allows us to recognize the possibility of discharge sources that discharge directly into the aquifer area recorded as the change is quite large, almost covering 2 whole study area. The use of chemical fertilizers in agricultural activities such as inorganic fertilizers under acidic groups such as potassium sulfate physiological (K<sub>2</sub>SO<sub>4</sub>), potassium chloride (KCl), super phosphate acid residues are also facilitated to accumulate aluminum in the soil.

### **5.CONCLUSION**

The study area has geological conditions are not too complicated. Ben Cat area aquifers exist two qp<sub>2-3</sub> and qp<sub>1</sub>, whereas in areas Thuan An - Di exists only qp<sub>1</sub> aquifer. The Pleistocene aquifer exposed to ground surface and quite sensitive to pollution factors. Pleistocene aquifers often discharge to Saigon river, Thi Tinh River and Dong Nai river, depending on the research area.

Groundwater monitoring data in Binh Duong in 1991 – 1997 was used as base value for this research. During this period, the average pH value of about 6.4, and the background levels of aluminum in ground water in the range from 0 to 0,01 mg/l.

Aluminum concentration in Pleistocene aquifer is with high fluctuations and tend to clear in season, time, in depth, and in space. Aluminum concentration in water has a strong correlation with pH. Very small concentrations of aluminum in neutral water, whereas the higher concentration of acidic or alkaline water. The pHs of the groundwater study area abrupt change from neutral to acid - which in difficult conditions occur naturally, it confirms the impact of human activities.

Sources of aluminum in groundwater include nature and human sources. In addition, waste water with low pH is make geochemistry environment change in groundwater and promotes the physical – chemical process of Al dissolution.

The hydrolysis of alumosilicat is the main process that induces high Al concentration in groudwater, some dissolved in the acidic conditions in the presence of organic matter, nitrogen compounds. The advance environment conditions are created primarily by natural factors and human actions, in which the artificial factors play a major role reduced pH environment.

Along with the presence of aluminum in groundwater, some metals such as copper, manganese are also signs of increasing. Therefore, the additional studies on other metals in groundwater are necessary to do to make clearer about contaminanted aquifer picture in the study area.

# Nguồn gốc nhôm trong nước dưới đất tầng Pleistocen tại khu vực Bến Cát, Thuận An, tỉnh Bình Dương

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# TÓM TẮT:

Bài báo trình bày những kết quả nghiên cứu do chính nhóm tác giả thực hiện tại khu vực Bến cát, Thuận An – Dĩ An, tỉnh Bình Dương. Ở các khu vực nghiên cứu tồn tại các tầng chứa nước tuổi Pleiostocen với độ sâu phân bố không lớn. Từ năm 2009 tại đây đã phát hiện sự suy giảm đột ngột giá trị pH và hàm lượng nhôm tăng đột biến trong nước dước đất. Những biến động này kéo dài tới năm 2013 song tương đối ổn định hơn, biên độ giao động giảm dần. Kết quả phân tích thành phần khoáng vật, hóa học các mẫu đất, mẫu nước triết, mẫu nước thải các khu công nghiệp cho thấy nguồn cung cấp nhôm cho nước dưới đất chủ yếu từ thành phần đất đá, một phần từ nước thải các khu công nghiệp, bùn thải sinh hoạt. Các quá trình hóa lý đưa nhôm vào nước dưới đất chủ yếu là quá trình thủy phân các alumosilicat khi có điều kiện địa hóa phù hợp, quá trình hòa tan một số muối sulfat nhôm phân tán trong đất hạt mịn. Các nhân tố tạo điều kiện để nhôm thâm nhập vào nước dưới đất chủ yếu là cấu trúc địa chất thủy văn, thành phần đất đá, các hoạt động khai thác nước dưới đất quá mức làm suy giảm mực nước, kết cấu các giếng khai thác nước không đúng quy cách, các hoạt động nông nghiệp, sự gia tăng dân số.

Từ khóa: nguồn ô nhiễm nhôm, thành phần khoáng vật, sự thủy phân.

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