

## **Hydrogeochemical Modelling System: A Case Study of Gümüşhacıköy (Amasya, TURKEY) Aquifer**

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### **Abstract**

Approximately 10 different systems of classification of natural water types were developed (Matthess, 1982). Stuyfzand Classification System combines excellent features of existing classifications with new, strongly diagnostic criteria for subdivision. And this classification plays very important role for determination of hydrogeochemical evolution of groundwater plain.

The location plain is important because of it has very huge amount of water in the Gümüşhacıköy Aquifer. This water is used for the industrial purposes and agricultural area in the plain. In this study hydrochemical evolution of Gümüşhacıköy Plain was determined using Stuyfzand Classification System and totally 79 well water, 37 well water analysis results between 1951 and 1972, and 42 well water analysis results between 2003 and 2004, were compared with each other considering this classification system. According to this classification system, the sequence concludes that freshening is going on from  $\text{NaHCO}_3+$  to  $\text{MgHCO}_3+$ . The south and southwest of the plain is formed  $\text{CaHCO}_3\phi$  water type according to the first analyses results but  $\text{CaHCO}_3+$  water type dominates the consequence of freshening to the second analyses results. Typical freshening is going on from west to east in time and the composition of the groundwater is turned into  $\text{CaHCO}_3+$  water type.

**Keywords:** *Stuyfzand Classification System, Hydrogeochemistry, Gümüşhacıköy Aquifer*

### **Özet**

Doğada, su tiplerini belirlemek amacıyla geliştirilen yaklaşık 10 farklı sınıflama sistemi bulunmaktadır (Matthess, 1982). Mevcut sınıflama sistemlerinin bir kombinasyonu olan Stuyfzand Sınıflama Sistemi, yeraltısuyu ortamının hidrojeokimyasal gelişimini belirlemede önemli bir rol oynamaktadır.

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Çalışma alanının önemi, Gümüşhacıköy Akiferi'nin yüksek miktarda yeraltısuyuna sahip olmasından dolayıdır. Bu yeraltısuyu çalışma alanında endüstriyel amaçlar için ve tarımda sulama amacı ile kullanılmaktadır. Merzifon-Gümüşhacıköy Havzası sınırları içerisinde yer alan Gümüşhacıköy Akiferi'nin hidrojeokimyasal evrimini belirlemek amacıyla akiferde bulunan toplam 79 sondaj kuyusunda yapılan su kimyası analiz sonuçları değerlendirilmiş ve yeraltısuyu kimyasal gelişimi ortaya konmuştur. Akiferde yapılan yeraltısuyu örnekleme 1951-1972 yılları arasını kapsayan 37 örnek ve 2003-2004 yıllarını kapsayan 42 örnekten oluşmaktadır. Çalışmanın sonucunda her iki örnekleme sonucunda geliştirilen hidrojeokimyasal model, Stuyfzand Sınıflama Sistemi'ne göre karşılaştırılarak yeraltısuyunun karakteristikleri ve hidrojeokimyasal gelişimi belirlenmiştir. Buna göre akiferde yıkanma  $\text{NaHCO}_3^+$ 'dan  $\text{MgHCO}_3^+$ 'ya doğru devam etmektedir. Gümüşhacıköy Akiferi'nin güney ve güneybatı kesimleri 1951-1972 yılları analiz sonuçlarına göre  $\text{CaHCO}_3\phi$  su tipinden oluşurken 2003-2004 yılları analiz sonuçlarına göre  $\text{CaHCO}_3+$  su tipindedir. Bir başka deyişle, ikinci analiz sonuçları yıkanma işleminin devam ettiğini göstermektedir. Stuyfzand Sınıflama Sistemi'nde açıklanan yıkanma işleminin Gümüşhacıköy Akiferi'nde batıdan doğuya doğru devam ettiği ve yeraltısuyu bileşiminin  $\text{CaHCO}_3+$  su tipine doğru değiştiği belirlenmiştir.

**Anahtar Sözcükler:** *Stuyfzand Sınıflama Sistemi, Hidrojeokimya, Gümüşhacıköy Akiferi.*

## Introduction

Classification systems are common tools within resources management and are used in a wide range of roles. This is also true for groundwater, as a review of groundwater classification systems developed or in use in Turkey jurisdictions revealed. There is currently no generic groundwater classification model that can be followed, hence classification systems are developed specific either to the objectives and needs of the jurisdiction or to characterize the technical aspects of the resource [1]. In developing the classification system a number of factors had to be considered. It need to be efficient and cost-effective and take advantage of existing water well and water chemistry data sources without requiring expensive drilling and sampling programs [1]. One need of the groundwater quality research as applied to groundwater is to have a clear understanding of the groundwater background quality reference, or baseline, in order for it to be compared to the current situation [2].

Although the history of geologic and hydrogeologic investigations in the Gümüşhacıköy Plain dates back to 1893, the first detailed report named "Hydrogeologic Report of the Artesian Wells in the Merzifon-Gümüşhacıköy Plain" was prepared by Dr. Recep Egemen in 1955 [3].

According to the study named “Brief Information about the Merzifon-Gümüşhacıköy Groundwater” carried out by Tufan Subaşı in 1967, discharge of the artesian wells was calculated as  $5,2 \times 10^6$  m<sup>3</sup>/year and detailed hydro geologic studies were suggested [4].

The report named “Irrigation from groundwater of the Merzifon-Gümüşhacıköy Plain” was prepared by the State Hydraulic Works in 1973 (Altuğ and Ertuğrul 1973) [5]. According to this report groundwater reservoir was calculated as  $25 \times 10^6$  m<sup>3</sup>/year and the report indicates that 4600 hectares with 15 l/sec - 160 wells could be irrigated.

### **General Properties of the Study Area**

Gümüşhacıköy Plain is located in the western part of the Amasya City. The plain is about 35 km far from Amasya City. The plain covers an area of about 300 km<sup>2</sup>, and recharge area of the Gümüşhacıköy Plain is 1060 km<sup>2</sup>. The plain is a generally flat area with low rolling hills in the eastern part of Gümüşhacıköy. Groundwater is supplied to wells and springs by two principal aquifers. The tuff, tuffite, agglomerate and volcanic lava differ from sand, clay and gravel in topographical shape. The neogene field was eroded by the river and flood waters and as a result it turned out to have a wavy structure. The volcanic field has a more flat shape with respect to neogene (Figure 1).

The drainage system in the plain is affected by the tectonically structure. The main rivers in the plain are Gümüşsuyu River, Köseler River and İmirler River. Dry climate conditions are dominant in the plain. Based on the data of the Merzifon Meteorological Station for the period of 1965-2005, the average annual precipitation is 417 mm, while the average temperature is 11,33 °C [6].

The main industries in the region are sugar-beet processing, sunflower processing, textile, wood products. Agricultural activities in the town are quite intensive. The crops grown in the plain are grains, sugar-beet, sunflower, onion, potato, poppy, maize, vegetable and fruit. Totally 167 wells are situated in the Gümüşhacıköy Aquifer at the present time. These wells have been used for domestic and industrial purposes in the villages of the Gümüşhacıköy, irrigation water in the aquifer [7].

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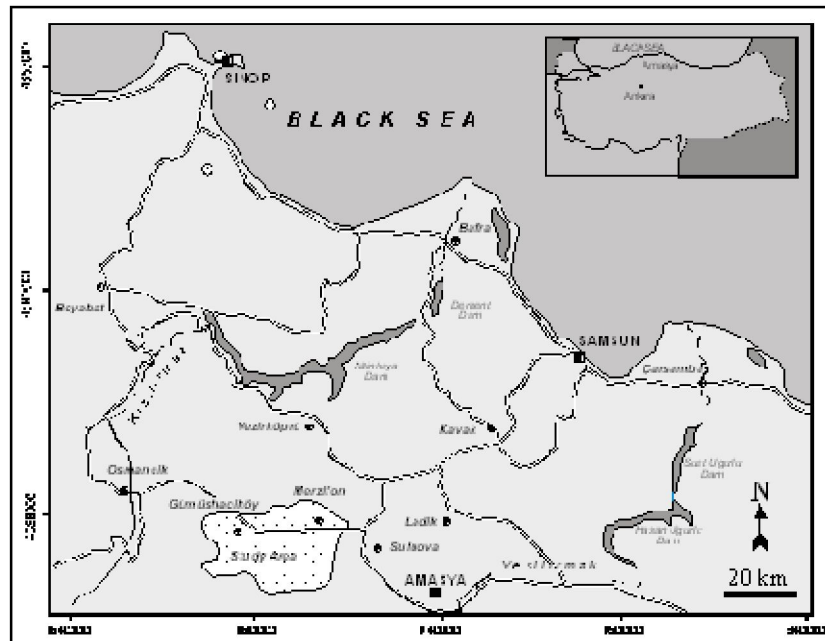


Figure 1. Location map of studied area

### Geologic Setting

In the area studied, the Paleozoic metamorphic suit is the oldest formation. This unit consists of clayey schist, chlorite schist, and green schist, marble and recrystallized limestone. The Jurassic limestone, with fossils which are generally compact and overlies uncomformably metamorphic suit in the plain are situated in the area. Lower Cretaceous limestone, pinky colored, very hard, recrystallized and much fissured, overlies Jurassic limestone. Upper Cretaceous limestone outcrops on the high altitudes in the plain. This series with mixed volcanic material composed of conglomerate, green and black sandstone, shale, marl, limestone, andesite, tuff and tuffite are deposited in the Upper Cretaceous. Senozoic started with the Middle Eocene flysch in the study area. Flysch consists of sandstone, shale, sandy limestone, marl, locally conglomerate, tuff and agglomerate. Catchments area was filled with continental material of 1000-1500 m thickness affected by east-west elongated faults in the Neogene. These thick series consist of Miocene blue clay and marl on the lower part; Pliocene sand, clay, gravel and a mixture of these on the upper part. The layer thickness ranges from 10 to 50 cm in these series. The Quaternary is characterized by the alluvium and the alluvium cone consisting of detrital material that comes from north and south with the flood waters. Alluvium and cone, of 10-60 m thickness and take form gravel, sand, clay and

mixture of these, form along the Gümüşsuyu River, Köselers River, İmirler River and Salhan River. Geological map of the study area is shown in Figure2.

### **Hydrogeology**

The most important units for groundwater transport in Gümüşhacıköy Plain are Quaternary alluvium and Pliocene clay, sand, gravel and mixture of these. It is seen that the distinguishing of Pliocene series and Quaternary alluvium are very challenging when the drilling cores in the plain are observed for these two units have same lithologic features. The plio-quaternary aquifer is unconfined at high altitudes in the north and west, but confined at low altitudes. Because the area between north and west of the area has not contained impervious layer Gümüşhacıköy Aquifer is determinate as unconfined aquifer in this area. But in the east part of the plain it is observed that an impermeable clay layer 2-10 m in thickness situated on the plio-quaternary aquifer. Thickness of this clay layer is increased from middle to west part of the plain.

The thickness of Plio-Quaternary loose material ranges from 20 to 150 m in this area. The aquifer around Gümüşhacıköy consists of gravel of great size, clay and clayey gravel and its thickness ranges from 50 to 350 m. Groundwater flow direction is from northwest to southeast in the İmirler Valley, from southwest to northeast in the Köselers Valley and from west to east in the Gümüşsuyu Valley.

Groundwater recharge in the Gümüşhacıköy Plain is through the infiltration of precipitation and influent surface water (Gümüş River and Köselers River) and irrigation channels. Domestic wastewaters of the town infiltrate into the aquifer and contaminate the groundwater.

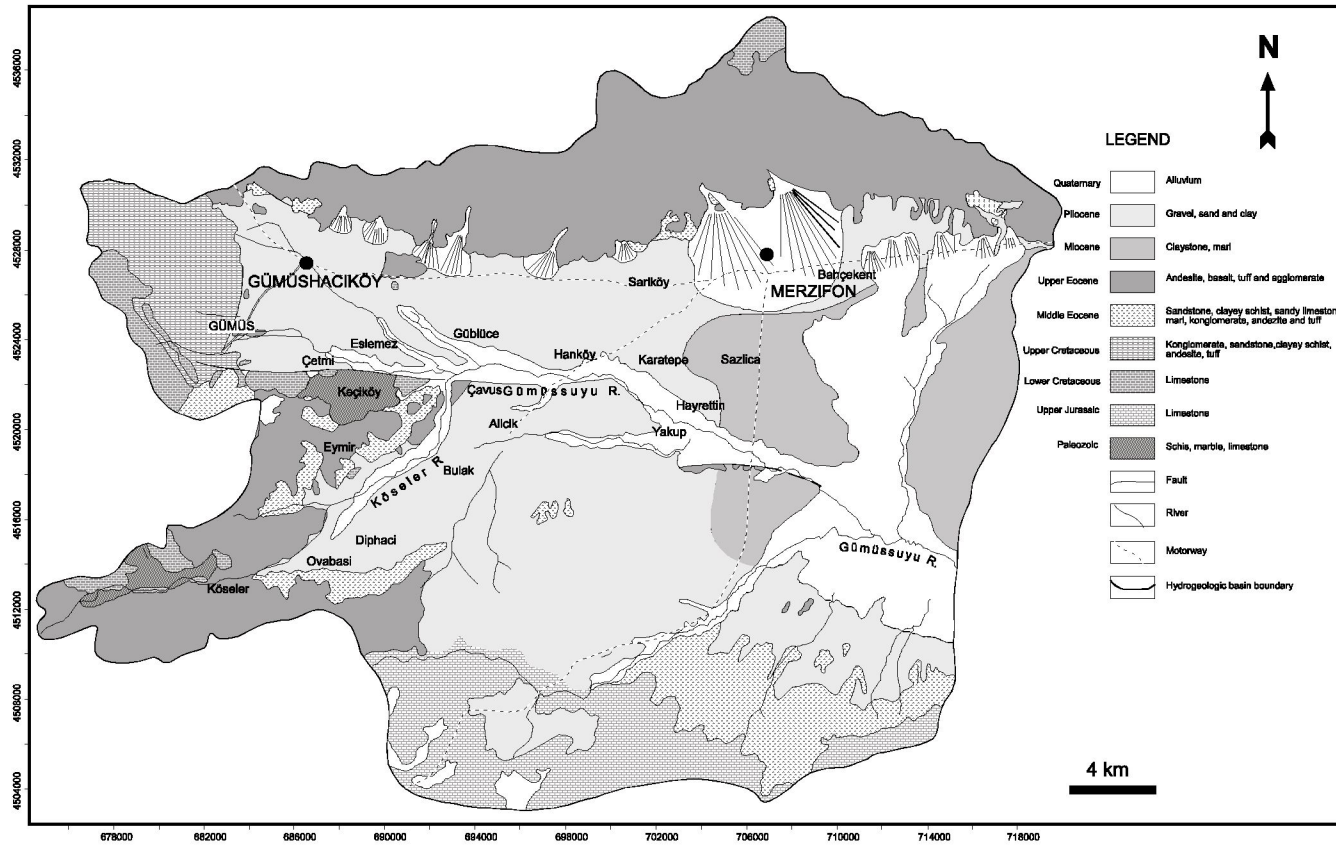


Figure 2. Geological of the studied area

## Hydrogeochemistry

The first hydrogeologic studies were begun by the State Hydraulic Works in 1951 in Merzifon-Gümüşhacıköy plain and have continued today. The well waters of the Gümüşhacıköy Plain have been used for municipal, industrial and irrigation purposes. Totally 167 water wells have been drilled in the Gümüşhacıköy Plain. 154 wells of these wells have been used for irrigation and industrial purposes, 13 of these have been employed for drinking water. During the first phase of the study, in July 2003, 37 wells have been drilled between 1951-1972 were identified and hydrogeologic and hydrogeochemical data were collected. 42 wells have been drilled after 1972 were studied in August 2004 in the second phase and same analyses were repeated. Stuyfzand Classification System was operated using with first hydrogeochemical analysis results and hydrochemical evolution of the Gümüşhacıköy Aquifer System was determined. Make use of the second analysis results Stuyfzand Classification System was defined again and two classification results relating to the hydrogeochemical evolution of the aquifer was performed.

The depth of the wells range between 50 m (minimum) and 290 m (maximum), discharge rates between 5 and 60 l/sec. Presently, new wells are still being drilled and operated by the State Hydraulic Works, as the water requirements of the city constantly increase. Moreover, private owners around the city also operate a number of groundwater wells.

The pH values of all samples are range between 6,8 and 9,9. EC values are change between 439-1276  $\mu\text{S}/\text{cm}$ . Total hardness values of the samples are range between 2,5-57,75 according to the French Hardness and change between “very soft” and “very hard” water types. pH, EC and TH values are shown in Table 1 chemical analysis results are shown in Table 2.

**Table 1.** pH, EC and Total Hardness value of the samples

|                            |       |       |       |       |       |       |       |       |       |       |       |       |       |
|----------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Well number                | 22013 | 17156 | 53060 | 52990 | 53055 | 20099 | 22191 | 23    | 53806 | 20175 | 4     | 14581 | 14583 |
| Ph                         | 6,9   | 8     | 7,9   | 8     | 7,3   | 7,2   | 6,9   | 7,4   | 7,2   | 7,6   | 7,4   | 7,4   | 7     |
| EC*10 <sup>6</sup> (25 °C) | 724   | 729   | 601   | 546   | 596   | 617   | 979   | 723   | 659   | 509   | 638   | 587   | 1276  |
| TH                         | 36,75 | 23,25 | 26,5  | 22    | 28,75 | 29,5  | 47,25 | 31,25 | 28,5  | 22,5  | 30,75 | 28    | 57,75 |
|                            | 14584 | 2     | 19308 | 28798 | 30714 | 52424 | 52425 | 22160 | 22163 | 20852 | 20850 | 53030 | 32    |
| Ph                         | 7,1   | 6,8   | 6,9   | 7     | 9,9   | 8,7   | 7,9   | 8,2   | 8,2   | 8     | 8,2   | 7,7   | 7,4   |
| EC*10 <sup>6</sup> (25 °C) | 915   | 646   | 745   | 646   | 551   | 653   | 1224  | 950   | 755   | 560   | 540   | 640   | 918   |
| TH                         | 38,75 | 30,75 | 35,5  | 31,5  | 2,5   | 20,9  | 35,55 | 32,75 | 29,15 | 21,9  | 19,35 | 25,4  | 41,2  |
|                            | 33995 | 66    | 18743 | 50362 | 53054 | 52989 | 45472 | 57919 | 7216  | 47    | 25    | 39    | 100   |
| Ph                         | 7,4   | 7,3   | 7,2   | 6,9   | 7     | 6,9   | 7,2   | 7     | 7,3   | 8,2   | 8,1   | 7,4   | 7,3   |
| EC*10 <sup>6</sup> (25 °C) | 632   | 704   | 796   | 755   | 612   | 827   | 551   | 816   | 571   | 1122  | 714   | 694   | 643   |
| TH                         | 32,9  | 35,2  | 37,15 | 41,4  | 33,85 | 42,7  | 29,15 | 41,95 | 27,65 | 35,05 | 27,45 | 34,95 | 32,4  |
|                            | 101   | 102   | 103   | 27    | 64    | 28    | 14    | 16    | 5     | 17    |       |       |       |
| Ph                         | 7,2   | 7,4   | 7,1   | 7,4   | 7,5   | 7,1   | 6,9   | 7,3   | 7,1   | 7,3   |       |       |       |
| EC*10 <sup>6</sup> (25 °C) | 665   | 620   | 714   |       | 598   | 612   | 673   | 476   | 683   | 479   |       |       |       |
| TH                         | 34,95 | 32,45 | 38,95 | 37,45 | 32,4  | 33,9  | 36,65 | 24,9  | 37,15 | 25,1  |       |       |       |

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**Table 2.** Chemical analysis results of the water samples

|                               |       |       |       |       |       |       |        |       |       |        |       |       |       |
|-------------------------------|-------|-------|-------|-------|-------|-------|--------|-------|-------|--------|-------|-------|-------|
| Well number                   | 22013 | 17156 | 53060 | 52990 | 53055 | 20099 | 22191  | 23    | 53806 | 20175  | 4     | 14581 | 14583 |
| Ca <sup>2+</sup>              | 91,2  | 58,1  | 69,1  | 58,1  | 77,2  | 82,2  | 133,3  | 79,2  | 73,1  | 63,1   | 83,2  | 84,2  | 147,3 |
| Mg <sup>2+</sup>              | 34    | 21,3  | 22,5  | 18,2  | 23,1  | 21,9  | 34     | 28    | 24,9  | 16,4   | 24,3  | 17    | 51,1  |
| Na <sup>+</sup>               | 29,9  | 69,9  | 29,9  | 26,91 | 16,1  | 17,04 | 28,98  | 34,96 | 28,98 | 23     | 11,96 | 14,03 | 42,09 |
| K <sup>+</sup>                | 1,95  | 2,34  | 1,56  | 1,56  | 0,78  | 1,56  | 3,12   | 1,56  | 1,17  | 1,17   | 1,56  | 1,17  | 5,07  |
| HCO <sub>3</sub> <sup>-</sup> | 373   | 247,5 | 225   | 320   | 245   | 245   | 385    | 270   | 275   | 220    | 282,5 | 220   | 445   |
| Cl <sup>-</sup>               | 11,4  | 19,9  | 21,3  | 15,6  | 19,9  | 12,8  | 44     | 9,9   | 18,5  | 11,4   | 9,94  | 9,9   | 60,4  |
| SO <sub>4</sub> <sup>2-</sup> | 109,4 | 107,5 | 73,9  | 39,4  | 48,5  | 68,2  | 88,8   | 102,2 | 46,6  | 38,9   | 37,4  | 74,9  | 139,7 |
| NH <sub>4</sub> <sup>+</sup>  | 0     | 0     | 0     | 0     | 0     | 0     | 0,05   | 0,1   | 0,15  | 0,15   | 0,05  | 0,4   | 0,05  |
| NO <sub>2</sub> <sup>-</sup>  | 0     | 0     | 0     | 0     | 0     | 0     | 0      | 0     | 0     | 0      | 0     | 0     | 0     |
| NO <sub>3</sub> <sup>-</sup>  | 4,63  | 3,03  | 5,36  | 2,93  | 5,07  | 4,96  | 1,313  | 5,54  | 3,23  | 5,17   | 2,62  | 5,88  | 15,61 |
| Ca <sup>2+</sup>              | 14584 | 2     | 19308 | 28798 | 30714 | 52424 | 52425  | 22160 | 22163 | 20852  | 20850 | 53030 | 32    |
| Mg <sup>2+</sup>              | 89,2  | 92,8  | 104,2 | 88,2  | 4     | 36    | 57     | 50    | 75    | 54     | 47    | 55    | 100   |
| Na <sup>+</sup>               | 40,1  | 19,5  | 23,1  | 23,1  | 3,6   | 28,6  | 51,1   | 48,6  | 24,9  | 20,1   | 18,2  | 28    | 38,9  |
| K <sup>+</sup>                | 42,09 | 13,11 | 19,09 | 11,04 | 106,3 | 59,11 | 126,04 | 69,92 | 41,86 | 29,9   | 37,3  | 31,05 | 49,91 |
| HCO <sub>3</sub> <sup>-</sup> | 3,12  | 6,24  | 2,34  | 6,63  | 0,78  | 1,95  | 3,51   | 1,17  | 1,95  | 1,56   | 3,51  | 1,95  | 1,56  |
| Cl <sup>-</sup>               | 320   | 275   | 297,5 | 307,5 | 21,5  | 275   | 340    | 352,5 | 257,5 | 245    | 250   | 227,5 | 337,5 |
| SO <sub>4</sub> <sup>2-</sup> | 32,7  | 12,8  | 21,3  | 11,4  | 18,5  | 14,2  | 35,5   | 48,3  | 15,6  | 18,5   | 14,2  | 11,4  | 14,2  |
| NH <sub>4</sub> <sup>+</sup>  | 112,3 | 49    | 69,2  | 23    | 14,9  | 41,8  | 231,4  | 55,7  | 99,8  | 13     | 7,2   | 75,8  | 156,5 |
| NO <sub>2</sub> <sup>-</sup>  | 0     | 0     | 0     | 0     | 0,3   | 0,1   | 0,1    | 0,1   | 0,05  | 0,05   | 0,05  | 0,2   | 0,05  |
| NO <sub>3</sub> <sup>-</sup>  | 0     | 0     | 0     | 0     | 0     | 0,001 | 0,001  | 0,004 | 0,004 | 0      | 0     | 0     | 0     |
| NO <sub>3</sub> <sup>-</sup>  | 10,69 | 4,05  | 7,74  | 3,85  | 0     | 0,1   | 7,3    | 6,75  | 3,35  | 3,05   | 3,35  | 3,4   | 4,55  |
| Ca <sup>2+</sup>              | 33995 | 66    | 18743 | 30362 | 53054 | 52989 | 45472  | 27919 | 2216  | 47     | 25    | 39    | 100   |
| Mg <sup>2+</sup>              | 86    | 78    | 97    | 112   | 104   | 110   | 84     | 89    | 73    | 55     | 48    | 81    | 77    |
| Na <sup>+</sup>               | 27,4  | 37,7  | 31    | 32,2  | 18,8  | 36,5  | 19,5   | 41,3  | 22,5  | 51,1   | 37,1  | 35,3  | 31,6  |
| K <sup>+</sup>                | 17,94 | 23,92 | 41,86 | 23    | 13,11 | 39,1  | 13,11  | 22,08 | 17,94 | 101,89 | 49,91 | 23,92 | 28,98 |
| HCO <sub>3</sub> <sup>-</sup> | 1,56  | 1,95  | 1,95  | 1,17  | 0,78  | 1,17  | 1,17   | 1,95  | 1,17  | 1,95   | 1,95  | 2,73  | 5,46  |
| Cl <sup>-</sup>               | 307,5 | 345   | 302,5 | 377,5 | 257,5 | 310   | 232,5  | 325   | 235   | 385    | 250   | 320   | 375   |
| SO <sub>4</sub> <sup>2-</sup> | 11,4  | 9,9   | 14,2  | 7,1   | 18,5  | 17    | 24,1   | 15,6  | 25,6  | 53,3   | 21,3  | 9,9   | 9,9   |
| NH <sub>4</sub> <sup>+</sup>  | 43,2  | 43,7  | 135,4 | 73,4  | 80,2  | 170,4 | 51,4   | 116,2 | 42,7  | 107    | 99,4  | 66,2  | 3,4   |
| NO <sub>2</sub> <sup>-</sup>  | 0     | 0     | 0     | 0,05  | 0     | 0     | 0      | 0,05  | 0,05  | 0,5    | 0,05  | 0,2   | 0     |
| NO <sub>3</sub> <sup>-</sup>  | 0     | 0     | 0,03  | 0,001 | 0,002 | 0     | 0      | 0     | 0,002 | 0      | 0,002 | 0     | 0     |
| NO <sub>3</sub> <sup>-</sup>  | 2,7   | 4,75  | 6,7   | 4,95  | 9,3   | 6,25  | 9      | 8     | 7,35  | 6,35   | 4,65  | 1,8   | 1,05  |
| Ca <sup>2+</sup>              | 101   | 102   | 103   | 27    | 64    | 28    | 14     | 16    | 5     | 17     |       |       |       |
| Mg <sup>2+</sup>              | 71    | 62    | 93    | 88    | 80    | 90    | 101    | 64    | 92    | 73     |       |       |       |
| Na <sup>+</sup>               | 41,3  | 40,7  | 37,7  | 37,1  | 29,8  | 27,4  | 21,3   | 34    | 16,4  |        |       |       |       |
| K <sup>+</sup>                | 14,95 | 13,1  | 19,09 | 11,96 | 13,11 | 14,03 | 23     | 14,03 | 16,1  | 13,11  |       |       |       |
| HCO <sub>3</sub> <sup>-</sup> | 5,07  | 5,46  | 3,12  | 0,78  | 1,17  | 1,56  | 0,78   | 0,78  | 1,17  | 0,78   |       |       |       |
| Cl <sup>-</sup>               | 372,5 | 340   | 400   | 372,5 | 337,5 | 310   | 307,5  | 195   | 320   | 225    |       |       |       |
| SO <sub>4</sub> <sup>2-</sup> | 7,1   | 8,5   | 8,5   | 7,1   | 8,5   | 21,3  | 11,4   | 8,5   | 8,5   | 11,4   |       |       |       |
| NH <sub>4</sub> <sup>+</sup>  | 3,8   | 5,8   | 20,2  | 16,3  | 2,9   | 28,8  | 88,8   | 69,1  | 71,5  | 37     |       |       |       |
| NO <sub>2</sub> <sup>-</sup>  | 0     | 0     | 0     | 0     | 0,1   | 0     | 0      | 0,05  | 0     | 0      |       |       |       |
| NO <sub>3</sub> <sup>-</sup>  | 0     | 0     | 0     | 0     | 0     | 0,004 | 0,001  | 0,001 | 0     | 0,001  |       |       |       |
| NO <sub>3</sub> <sup>-</sup>  | 0,95  | 3,25  | 0,05  | 2,3   | 0,65  | 2,3   | 5,9    | 4     | 5,5   | 5,1    |       |       |       |

### Stuyfzand Classification System

The hydrochemical classification system combines the superior features of existing classifications with the new. The first version [8] had been improved specifically for groundwater in coastal, calcareous sand aquifer systems with cat ion exchange phenomena due to fresh or salt water intrusion. The second version [9] has been enlarged for non-calcareous systems. Therefore, this classification can be applied to water in any hydro geologic systems.

Determination of a water type depends upon the determination of the main type, subtype and class of the water sample. This hierarchical structure is shown in Table 3.

**Table 3.** The hierarchical structure of the classification system, with four levels of subdivision. The number of subdivisions within types, subtypes and classes is merely a theoretical maximum, because many combinations do not occur in nature (Stuyfzand,1986)

| Name      | Subdivisions | Criteria                    | Codes  |
|-----------|--------------|-----------------------------|--|
| Main Type | 6            | Cl                          | F, F <sub>b</sub> , B, B <sub>s</sub> , S, H   |
| Type      | 11           | Total Hardness              | x, 0, 1, 2, 3, 4, 5, 6, 7, 8, 9  |
| Subtype   | 16           | Most important anion-cation | NaCl, NaSO <sub>4</sub> , NaHCO <sub>3</sub> , NaMix, KNO <sub>3</sub> , NH <sub>4</sub> SO <sub>4</sub> , CaCl, CaSO <sub>4</sub> , CaNO <sub>3</sub> , CaHCO <sub>3</sub> , CaMix, MgCl, MgHCO <sub>3</sub> , MgMix, AlSO <sub>4</sub> , FeSO <sub>4</sub> |
| Class     | 3            | (Na+K+Mg) corrected         | -, φ, +  |

Each of four levels of subdivision contributes to the total code of the water type, as indicated in Table 3. Chloride content indicates the main type. There are 6 different main types; fresh (F), fresh-brackish (F<sub>b</sub>), brackish (B), brackish-salt (B<sub>s</sub>), salt (S) and hyperhaline (H) (Table 4).

**Table 4.** Determination of the first symbol for water type according to the Cl—content (Stuyfzand, 1986)

| Major Type     | Code           | Cl (mg/l)     |
|----------------|----------------|---------------|
| Fresh          | F              | <150          |
| Fresh-brackish | F <sub>b</sub> | 150-300       |
| Brackish       | B              | 300-1000      |
| Brackish-salt  | B <sub>s</sub> | 1000-10.000   |
| Salt           | S              | 10.000-20.000 |
| Hyperhaline    | H              | >20.000       |

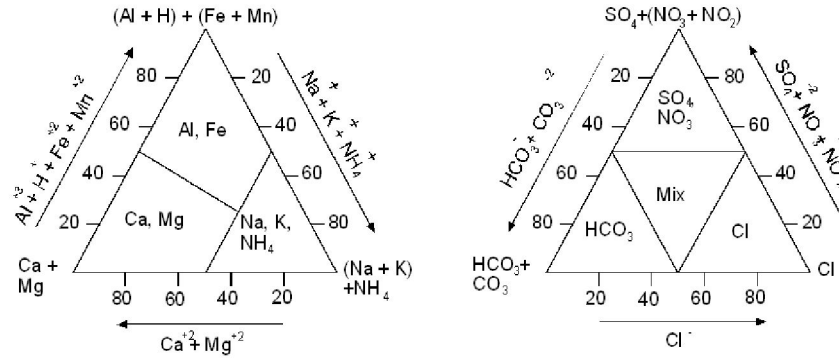
Total hardness of water determines the type. Hardness of waters changes between very soft (x) and extremely hard (9) (Table 5).

**Table 5.** Determination of the second symbol for water type according to the total hardness (TH) (Stuyfzand, 1986)

| Name            | Code | TH (°F)   |
|-----------------|------|-----------|
| Very soft       | X    | <5        |
| Soft            | 0    | 5-10      |
| Moderately hard | 1    | 10-20     |
| Hard            | 2    | 20-40     |
| Very hard       | 3    | 40-80     |
| Extremely hard  | 4    | 80-160    |
| Extremely hard  | 5    | 160-320   |
| Extremely hard  | 6    | 320-640   |
| Extremely hard  | 7    | 640-1280  |
| Extremely hard  | 8    | 1280-2560 |
| Extremely hard  | 9    | >2560     |

Combination of cation and anion predominate in the ion balance indicates the name of the subtype. First the strongest hydrogeochemical family is determined both for cations and anions, (Al + H + Fe + Mn) and (SO<sub>4</sub> + NO<sub>3</sub> + NO<sub>2</sub>) family. Then the strongest member of both families is chosen to form the combination. This phenomenon is shown in Figure 3.

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**Figure 3.** Subdivision of types on the basis of the proportional share of main constituents in the sum of cations (left) and anions (right) in meq/l. (Stuyfzand, 1986)

Each class is divided into 3 classes according to total amount of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{+2}$  in meq/l corrected for a contribution of sea salt;

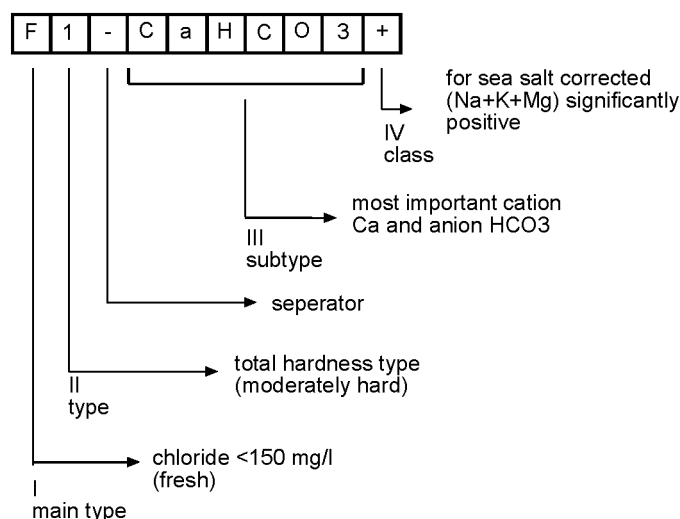
$$(\text{Na} + \text{K} + \text{Mg})_{\text{corrected}} = (\text{Na} + \text{K} + \text{Mg})_{\text{measured}} - 1,061 \text{ Cl}$$

3 classes are found out,  $(\text{Na} + \text{K} + \text{Mg})_{\text{deficit}} (-)$ ,  $(\text{Na} + \text{K} + \text{Mg})_{\text{equilibrium}} (\phi)$  and  $(\text{Na} + \text{K} + \text{Mg})_{\text{surplus}} (+)$ . (-) sign indicates a salt water intrusion and (+) sign indicates fresh water encroachment (Table 6). Upon fresh water encroachment, Ca expels the formerly adsorbed Na, K and Mg ions from the exchanger. With salt water intrusion the reverse takes place.

**Table 6.** Determination of cation exchange code (Stuyfzand, 1986)

| Name                  | Code   | Condition  |
|-----------------------|--------|--|
| (Na+K+Mg)-deficit     | -      | $(\text{Na}+\text{K}+\text{Mg})_{\text{corrected}} < -(1/2 \text{ Cl})^{1/2}$                                |
| (Na+K+Mg)-equilibrium | $\phi$ | $-(1/2 \text{ Cl})^{1/2} \leq (\text{Na}+\text{K}+\text{Mg})_{\text{corrected}} \leq (1/2 \text{ Cl})^{1/2}$ |
| (Na+K+Mg)-surplus     | +      | $(\text{Na}+\text{K}+\text{Mg})_{\text{corrected}} > (1/2 \text{ Cl})^{1/2}$                                 |

Final determination after the defining four classification parameters has been seen on Figure 4.



**Figure 4.** Coding and explaining of a water type in 10 positions. The example is called “a fresh, moderately hard calciumcarbonate water with a (Na + K + Mg)<sub>surplus</sub>” (Stuyfzand, 1986)

## Material and Methods

During the studies the water samples were collected from new wells and then the samples was analyzed. Water samples were collected from the wells in polyethylene bottles, and filtered through ash-free filter paper and spilt in one parts. This part was acidified with 5% nitric acid for analysis. pH and electric conductivity (EC) and were measured in the laboratory, and temperature of the waters were measured in-situ.

Major cations ( $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ), anions ( $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{-2}$ ),  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$  analyses of the groundwater samples were determined by titration in State Hydraulic Works Quality Control Laboratory.

The evolution of the groundwater of the plain is renewed by employing Stuyfzand Classification System. The evolution of the groundwater was determined by employing the results of the two classification systems.

## Experimental Procedure and Results

### Stuyfzand Classification System According to 1951-1972 Analysis Results

1951 and 1972 anylsls were carried out by the State Hydraulic Works in Samsun City. These results are taken from the State Hydraulic Works for this study. The evolution of the Gümüşhacıköy groundwater is determined by using Stuyfzand Classification System prepared with the analyses results between 1951 and 1972. Main type, type, subtype and class are identified for each

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water sample analyses with 37 wells. According to the Cl content put as the first symbol in the classification system, the waters are classified as “fresh” main type. The second symbol in the classification is; on the other hand, “total hardness”. The groundwater changes between “soft” and “very hard” to total hardness. The water composed of  $\text{CaHCO}_3$ , NaMix and CaMix is classified into the third symbol of dominant anion-cation pairs. The groundwater is  $(\text{Na} + \text{K} + \text{Mg})_{\text{surplus}}$  and  $(\text{Na} + \text{K} + \text{Mg})_{\text{equilibrium}}$  generally,  $(\text{Na} + \text{K} + \text{Mg})_{\text{deficit}}$  rarely to fourth symbol cation exchange code. Stuyfzand Classification System table and map is designed for Gümüşhacıköy groundwater by gathering these four components (Table 7) (Figure 5).

**Table 7.** Stuyfzand classification system of Gümüşhacıköy well waters according to 1951-1972 analyses results

| Well Number | Class of Water           | Well Number | Class of Water           |
|-------------|--------------------------|-------------|--------------------------|
| 486         | F2- $\text{CaHCO}_3+$    | 6802        | F1- $\text{CaHCO}_3+$    |
| 487         | F1- $\text{NaSO}_4+$     | 6803        | F0- $\text{NaHCO}_3+$    |
| 488         | F2- $\text{CaHCO}_3\phi$ | 6804        | F1- $\text{CaHCO}_3+$    |
| 1291        | F1- $\text{NaHCO}_3+$    | 6805        | F0- $\text{NaHCO}_3+$    |
| 1701        | F2- $\text{CaHCO}_3-$    | 6806        | F0- $\text{NaHCO}_3+$    |
| 1702        | F1- $\text{CaHCO}_3\phi$ | 14579       | F2- $\text{CaHCO}_3+$    |
| 1703        | F1- $\text{CaHCO}_3+$    | 14580       | F1- $\text{CaHCO}_3+$    |
| 1704        | F2- $\text{CaHCO}_3+$    | 14581       | F2- $\text{CaHCO}_3+$    |
| 1706        | F1- $\text{CaHCO}_3\phi$ | 14582       | F2- $\text{CaHCO}_3+$    |
| 1707        | F1- $\text{CaHCO}_3\phi$ | 14583       | F2- $\text{CaHCO}_3\phi$ |
| 1708        | F1- $\text{CaHCO}_3+$    | 14584       | F3- $\text{CaHCO}_3\phi$ |
| 1709        | F1- $\text{CaHCO}_3+$    | 15213       | F2- $\text{CaHCO}_3+$    |
| 1710        | F1- $\text{CaHCO}_3+$    | 15214       | F2- $\text{CaHCO}_3+$    |
| 1711        | F1- $\text{CaHCO}_3+$    | 15215       | F2- $\text{CaHCO}_3\phi$ |
| 1712        | F1- $\text{CaHCO}_3+$    | 16046       | F2- $\text{CaHCO}_3+$    |
| 1713        | Fx- $\text{NaHCO}_3+$    | 16047       | F2- $\text{CaHCO}_3+$    |
| 1714        | Fx- $\text{NaHCO}_3+$    | 16048       | F2- $\text{CaMix}+$      |
| 1715        | F0- $\text{NaHCO}_3+$    | 16694       | F1- $\text{CaHCO}_3+$    |
| 1716        | Fx- $\text{NaHCO}_3+$    |             |                          |

It is clear from the table that there is a number of water classes in the study area.  $\text{CaHCO}_3+$  and  $\text{CaHCO}_3\phi$  water types are accepted as two different types; 1 and 2 hardness codes are admitted as one water class in practice. X and 0 hardness codes in  $\text{NaHCO}_3+$  waters are accepted as one water class. Therefore, the classification is more general in practice. As a result of these FX,F0- $\text{NaHCO}_3+$ , F1,F2- $\text{CaHCO}_3+$  and F1,F2,F3- $\text{CaHCO}_3\phi$  water types form the whole plain.

In the north and northwest of the plain the type of the groundwater is F2- $\text{CaHCO}_3+$  as shown in Figure 5. The cation exchange occurs through the entering of fresh water to the media,. The middle of the plain is composed of F1- $\text{CaHCO}_3+$ , west F2- $\text{CaHCO}_3+$  and south and southwest F2- $\text{CaHCO}_3\phi$ . When thinking of the groundwater flow direction has occurred from northwest and southwest to east it has been seen that the freshening in groundwater with groundwater flow direction is became harmoniously. The groundwater is FX,F0- $\text{NaHCO}_3+$  water type in the east and southeast of the study area.

According to the results of Stuyfzand Classification System conducted groundwater sampling represent between 1951 and 1972 years, a typical freshening starting from west and keep going to east dominates in the Gümüşhacıköy plain.

Marine conditions absorbed by the clay surfaces are exchanged against fresh water cations from the infiltrating water. The  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{+2}$  cations from the clay surface are replaced by  $\text{Ca}^{+2}$  cation. This occurred rise to the genesis of the  $\text{Na}^+\text{HCO}_3^-$  and  $\text{Ca}^{+2}\text{HCO}_3^-$  water types. After the clay has been leached out completely the  $\text{CaHCO}_3\phi$  water type originates.

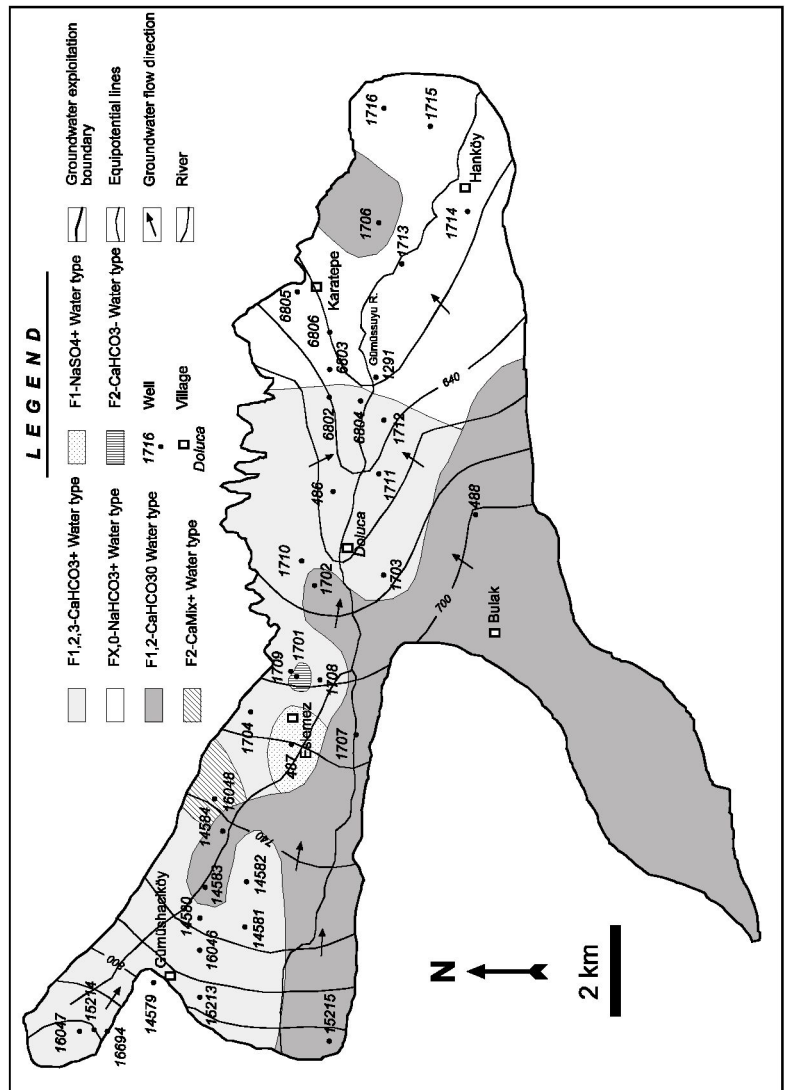


Figure 5. Stuyfzand classification system map designed according to 1951-1972 analyses results

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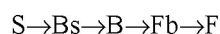
There are two main groundwater types in the plain;  $\text{NaHCO}_3+$  and  $\text{CaHCO}_3+$ ,  $\phi$  types. From the preceding discussion it is evident that dilution is increased towards the east and the freshening is going on. Groundwater composition is changed as a result of stages of cation exchange. Fresh water is originating from precipitation in which  $\text{CaHCO}_3^+$  has been dissolved.

In the plain in the west, cation exchange is in the final stage, and water is  $\text{CaHCO}_3+$ ,  $\phi$  type. In the south-east and east of the plain, cation exchange is in important stage and the water is  $\text{NaHCO}_3+$  type. The reason is that the clay cover is much thinner in the east.

A typical freshening process is seen below;

Initial sea water conditions ( $\text{SNaCl}\phi$ ) dominated in the beginning of the process. Original sea water diluted gradually due to the recharge phenomena and then sea water conditions coming from S ended up F.

Dilution of sea water is;



The second stage is cation exchange. Dilution stage is taken place in the solid matrix of clay minerals. Clay surfaces play exchanger role and pore water started to dilute. Typical marine cations Na, K, Mg are diluted and Ca concentration is increased. Na exchanges with Ca and Na decreases, Ca increases.

Cation exchange process is;



$\text{NaHCO}_3+$ ,  $\text{MgHCO}_3+$  and  $\text{CaHCO}_3+$  water types indicate typical freshening.

#### **Stuyfzand Classification System According to 2003-2004 Analysis Results**

From 1972 on the wells which have been drilled up so far has been used as drinking and irrigation water. Due to the increase in the number of wells the groundwater level is declined rapidly and the revision study has been started in 2002. The water samples have been collected from the new and old wells and analyzed during the revision study. 42 water analyses results are used and Stuyfzand Classification System is prepared for the plain.

All water samples are “fresh” main type according to the Cl content. The hardness of the groundwater changes between “very soft” and “very hard” with respect to the total hardness.  $\text{NaHCO}_3$ ,  $\text{MgHCO}_3$  and  $\text{CaHCO}_3$  water subtypes are dominant in the plain as to dominate anion-cation pairs. All waters are (Na

+ K + Mg)<sub>surplus</sub> compared to the cation exchange code. Finally, Stuyfzand Classification System was prepared in the form of tables and maps as shown in Table 8 and Figure 6.

**Table 8.** Stuyfzand classification system of Gümüşhacıköy well waters according to 2003-2004 analyses results

| Well Number | Class of Water                     | Well Number | Class of Water                     |
|-------------|------------------------------------|-------------|------------------------------------|
| 22013       | F2-CaHCO <sub>3</sub> <sup>+</sup> | 22163       | F2-CaHCO <sub>3</sub> <sup>+</sup> |
| 17156       | F2-CaHCO <sub>3</sub> <sup>+</sup> | 20852       | F2-CaHCO <sub>3</sub> <sup>+</sup> |
| 53060       | F2-CaHCO <sub>3</sub> <sup>+</sup> | 20850       | F1-CaHCO <sub>3</sub> <sup>+</sup> |
| 52990       | F2-CaHCO <sub>3</sub> <sup>+</sup> | 53030       | F2-CaHCO <sub>3</sub> <sup>+</sup> |
| 53055       | F2-CaHCO <sub>3</sub> <sup>+</sup> | BC2         | F3-CaHCO <sub>3</sub> <sup>+</sup> |
| 20099       | F2-CaHCO <sub>3</sub> <sup>+</sup> | 33995       | F2-CaHCO <sub>3</sub> <sup>+</sup> |
| 22191       | F3-CaHCO <sub>3</sub> <sup>+</sup> | SY          | F2-CaHCO <sub>3</sub> <sup>+</sup> |
| ST          | F2-CaHCO <sub>3</sub> <sup>+</sup> | 18743       | F2-CaHCO <sub>3</sub> <sup>+</sup> |
| 53806       | F2-CaHCO <sub>3</sub> <sup>+</sup> | 50362       | F3-CaHCO <sub>3</sub> <sup>+</sup> |
| 20175       | F2-CaHCO <sub>3</sub> <sup>+</sup> | 53054       | F2-CaHCO <sub>3</sub> <sup>+</sup> |
| BK          | F2-CaHCO <sub>3</sub> <sup>+</sup> | 52989       | F3-CaHCO <sub>3</sub> <sup>+</sup> |
| 14581       | F2-CaHCO <sub>3</sub> <sup>+</sup> | 45472       | F2-CaHCO <sub>3</sub> <sup>+</sup> |
| 14583       | F3-CaHCO <sub>3</sub> <sup>+</sup> | 57919       | F3-CaHCO <sub>3</sub> <sup>+</sup> |
| 14584       | F2-CaHCO <sub>3</sub> <sup>+</sup> | 7216B       | F2-CaHCO <sub>3</sub> <sup>+</sup> |
| AT          | F2-CaHCO <sub>3</sub> <sup>+</sup> | HD          | F2-MgHCO <sub>3</sub> <sup>+</sup> |
| 19308       | F2-CaHCO <sub>3</sub> <sup>+</sup> | BD          | F2-CaHCO <sub>3</sub> <sup>+</sup> |
| 28798       | F2-CaHCO <sub>3</sub> <sup>+</sup> | DD          | F2-CaHCO <sub>3</sub> <sup>+</sup> |
| 30714       | FX-NaHCO <sub>3</sub> <sup>+</sup> | OD          | F2-CaHCO <sub>3</sub> <sup>+</sup> |
| 52424       | F2-MgHCO <sub>3</sub> <sup>+</sup> | ED          | F2-CaHCO <sub>3</sub> <sup>+</sup> |
| 52425       | F2-MgHCO <sub>3</sub> <sup>+</sup> | CD          | F2-CaHCO <sub>3</sub> <sup>+</sup> |
| 22160       | F2-MgHCO <sub>3</sub> <sup>+</sup> | GD          | F2-CaHCO <sub>3</sub> <sup>+</sup> |

According to these results as seen on Figure 6 the dominating water types of the west of the plain are composed of F1, F2, F3-CaHCO<sub>3</sub><sup>+</sup> and east of the aquifer are consisted of FX,0-NaHCO<sub>3</sub><sup>+</sup> water type.

## Discussion And Conclusions

Stuyfzand Classification System is prepared from the results of the first analyses produced between 1951 and 1972 years. Therefore a hydrogeochemical evolution model belonging to the Gümüşhacıköy Aquifer has been determined. According to these results F2-CaHCO<sub>3</sub><sup>+</sup> water types are dominant in the north of the plain, F1-CaHCO<sub>3</sub><sup>+</sup> water types are dominant in the middle of the plain, F2-CaHCO<sub>3</sub><sup>+</sup> water types are dominant in the west of the plain, F2-CaHCO<sub>3</sub><sup>+</sup> types are dominant in the southwest. Groundwater flow direction has been occurred from northwest and southwest towards east in the Gümüşhacıköy Aquifer. Concluding the groundwater has took placed the FX, F0-NaHCO<sub>3</sub><sup>+</sup> water type in the east and southeast of the plain, freshening in the aquifer is harmonious with the groundwater flow.

The revision study started in 2002 after groundwater level is decreased in Gümüşhacıköy plain. The water samples were gathered and analyzed during the revision study and Stuyfzand Classification System is prepared again. According to second analysis results F1, F2, F3-CaHCO<sub>3</sub><sup>+</sup> water types are dominant in the west and FX, F0-NaHCO<sub>3</sub><sup>+</sup> water type are dominant in the east of the plain.

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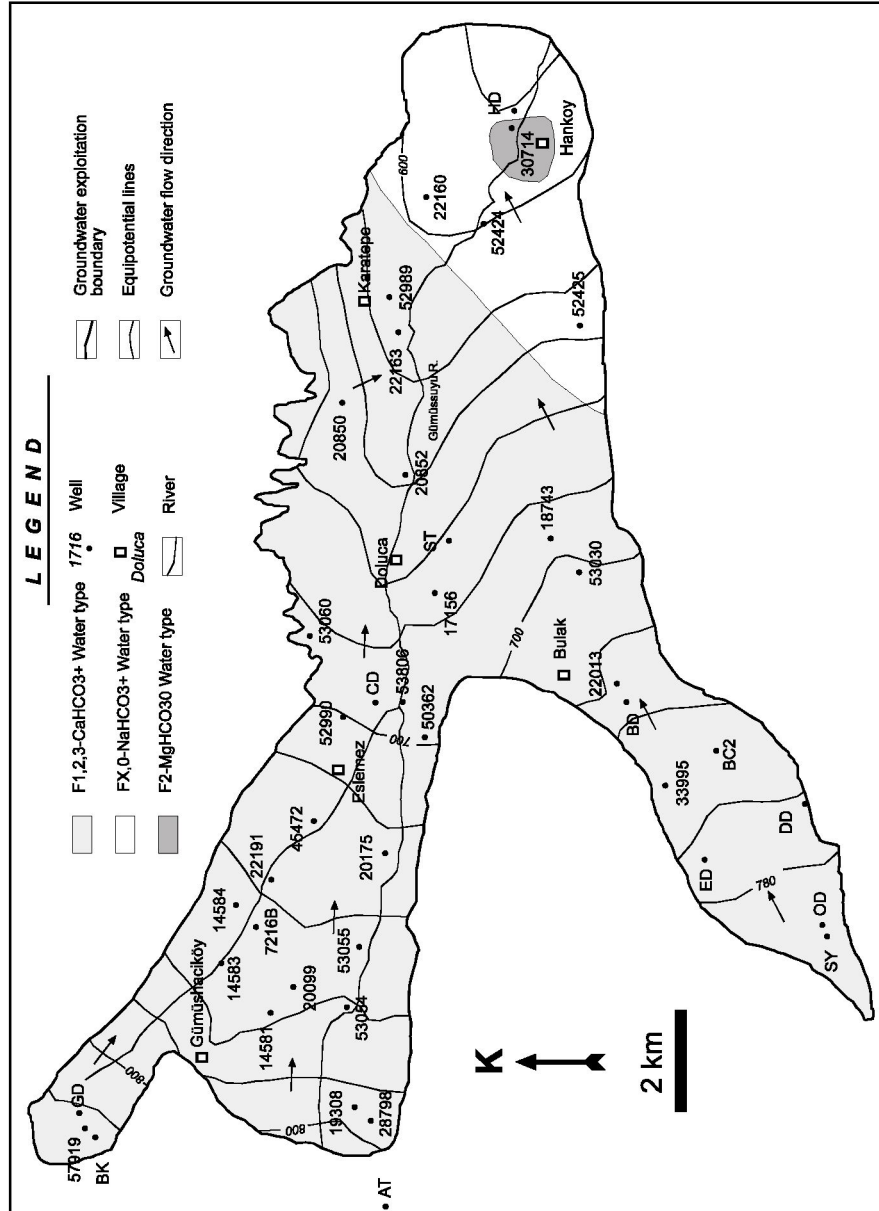


Figure 6. Stuyfzand classification system map designed according to 2003-2004 analyses results

When these two maps are compared it seems clear that the zone in  $\text{NaHCO}_3+$  water type with respect to the first analyses results is in  $\text{MgHCO}_3+$  water type according to the second analyses results. This sequence concludes that freshening is going on from  $\text{NaHCO}_3+$  to  $\text{MgHCO}_3+$ . The south and southwest of the plain is formed  $\text{CaHCO}_3\phi$  water type according to the first analyses results but  $\text{CaHCO}_3+$  water type dominates the consequence of freshening to the second analyses results. Typical freshening is going on from west to east in time and the composition of the groundwater is turned into  $\text{CaHCO}_3+$  water type.

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