HYDROCHEMICAL CHARACTERISTICS OF THE OROPOS COASTAL AQUIFERS, ATTICA, GREECE.

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Abstract

This article deals with the hydrochemistry of coastal aquifers of the Oropos plain, Attica, Greece. It is the first study which presents hydrochemical data of the Oropos plain groundwater. Groundwater samples from 34 wells were collected and analyzed for major and heavy metal constituents. Groundwater was differentiated between the Pleistocene confined aquifer and the group of the Holocene, the Miocene and the Mesozoic aquifers based on the electrical conductivity (EC) values and the chlorides content. Groundwater in the Pleistocene sediments presented EC values ranging between 766 and 971μS/cm and chlorides between 95-163mg/l. The group of the rest aquifers presented EC values up to 3770 μS/cm and chlorides up to 993mg/l. The Pleistocene aquifer seems to be protected from seawater intrusion, although, it is located adjacent to the shoreline. In addition, most of the heavy metal concentration exceeded the EU limits. Cd, Fe, Pb, Ni have been determined at 82, 2500, 817, 217 μg/lit respectively. Groundwater was, also, categorized into 2 main water types that of Ca-Mg-HCO3 type indicating recharge of fresh water and that of Ca-Mg-Cl type indicating reverse cation exchange of old Na-Cl waters.

Keywords: coastal aquifer, hydrochemistry, seawater intrusion, Oropos plain

Περίληπη

Αυτό το άρθρο ασχολείται με την υδροχημεία των παράκτιων υδροφορέων του Ωρωπού Αττικής. Για το σκοπό αυτό πραγματοποιήθηκαν χημικές αναλύσεις σε 34 δείγματα υπόγειων νερών και 1 επιφανειακό από τον Ασωπό ποταμό. Τα υπόγεια νερά διαφοροποιήθηκαν με βάση τις τιμές της ηλεκτρικής επιτροπής των πλειστοκαινικών, μειοκαινικών και μεσοζωικών ίζηματων με βάση τις τιμές της ηλεκτρικής παραγοντικής στην περιοχή της Ωρωπού. Επιπλέον, ανακαλύφθηκε ότι τα στοιχεία των υπόγειων νερών είναι σχετικά χαμηλά σε τιμές μέταλλων και είναι φυσικά καταλληλά για την χρήση για να μη δημιουργηθούν διαφορετικές παραγόντες από τα συμπεριληπτικά νερά Αττικής.
αγωγιμότητας (EC) και την περιεκτικότητα σε χλωριόντα. Τα υπόγεια νερά στα ιζήματα του Πλειστοκαινού παρουσίαζαν τιμές EC μέχρι 3770 μS/cm και χλωριόντα μέχρι 993 mg/l. Τα νερά των υπολοίπων υδροφορέων παρουσίασαν τιμές EC μέχρι 3770 μS/cm και χλωριόντα μέχρι 993 mg/l. Τμήμα του πλειστοκαινικού υδροφόρου ορίζεται, αν και βρίσκεται δίπλα στην ακτογραμμή, φαίνεται να προστατεύεται από τη διείσδυση θαλασσινού νερού. Επιπλέον, το μεγαλύτερο μέρος της συγκέντρωσης βαρέων μετάλλων υπερέβη τα όρια της ΕΕ. Τα Cd, Fe, Pb, Ni έχουν προσδιοριστεί στα 82, 2500, 817, 217 μg/l, αντίστοιχα. Τα υπόγεια ύδατα ταξινομήθηκαν επίσης σε 2 κύριους τύπους νερού. Ο πρώτος είναι του τύπου Ca-Mg-HCO3 που υποδηλώνει τροφοδοσία γλυκού νερού και ο δεύτερος του τύπου Ca-Mg-Cl που δείχνει αντίστροφη ανταλλαγή κατιόντων από παλαιότερα νερά Na-Cl.

Λέξεις κλειδιά: παράκτιος υδροφόρεας, υδροχημεία, θαλάσσια διείσδυση, Ωρωπός

1. Introduction

Coastal aquifers have been extensively studied over a century by many researchers (Post, 2004; Bear et al., 1999; Stigter et al., 1998; Stuyfzand, 1993; Todd, 1980; Freeze and Cherry, 1979; Stringfield et al., 1969; Henry, 1964; Herzberg, 1901; Ghyben, 1888). The main problem of coastal aquifers is seawater intrusion. This phenomenon takes place when coastal aquifers are hydraulically connected to the sea resulting in seawater intrudes inland due to natural and/or anthropogenic factors. However, in confined aquifers, which extend adjacent to the shoreline and which they are separated from seawater by thick confining clay layers, fresh groundwater can be preserved by salinisation (Hermides, 2018; Post et al., 2013; Post, 2004; Lloyd et al., 1985). This study presents the hydrochemistry of groundwater in part of the Pleistocene sediments located adjacent to the Oropos shoreline which is appeared to be preserved by salinisation. Chemical data from the Oropos groundwater are very few (Stamatis et al., 2011). The wide area has been hydrogeologically investigated the last decades by some researchers (Pagounis, 1994; Dounas et al., 1980). However, hydrogeology of the study area is not fully elucidated. The interaction of tectonic and stratigraphic factors (Katsikatsos, 2000; Mettos, 1992; Parginos et al., 1989; Perissoratis, 1989) combined with eustatic changes (Lambeck, 1996) established a complex hydrogeological regime where successive confined/leaky aquifers
have been formed. Groundwater in part of the Pleistocene sediments which are underlain the Holocene deposits, seems to retain its quality against the intrusion of seawater. The objective of this article is to highlight the occurrence of good quality groundwater which is hosted in the confined aquifer of the Pleistocene sediments located adjacent to the shoreline of the Oropos coastal area.

**Fig. 1:** Study area and sampling points (map projection GCS_GGRS_1987).

### 2. Study area

Oropos plain is located 40 km north of Athens (Fig. 1). Most of the plain which extends up to 50 km² is occupied by cultivated land. The surface topography of the plain is gently sloped from the elevation of 400 m in the south towards the Euboean Gulf to the north. Semi-arid climate prevails in the wide area with mean annual precipitation of 460 mm while the mean annual temperature is 16.2 °C. The plain is highly contaminated as a result of the heavy industry development.
Asopos River flows through the plain locally feeding the Quaternary sediments. Aquifers are tapped by hundreds of dug wells and boreholes.

Fig. 2: Geological map after Parginos et al., (1989); Katsikatsos, (2000) and sampling points (map projection GCS_GGRS_1987).
3. Geological setting

The geological structure of the study area (Fig. 2) is complex consisting of alpine and post-alpine sediments (Katsikatsos, 2000; Mettos, 1992; Parginos et al., 1989, Perissoratis, 1989). Alpine sediments comprise: (i) Permo-Triassic shales, sand, greywackes, phyllites and conglomerate with basic volcanic rocks intercalations of 400 m thick which consist of the basement of the study area; (ii) Triassic limestone, dolomitic limestone and dolomite 700 m in thickness; (iii) ophiolites which consist of the basement of the wide area; (iv) Cretaceous limestone 150 m thick; and (v) Cretaceous flysch of 150 m thick. Post-alpine sediments comprise: (i) lacustrine and lagoon Upper-Miocene marls, marly limestone at the base and torrential clay, sand and conglomerate at the top 200-300 m thick; (ii) torrential Pleistocene conglomerate/breccia and clay; and (iii) Holocene clay, sand and conglomerate.

The Oropos plain is a NE-SW oriented neotectonic depression. It has been affected by W-E, NE-SW and NW-SE striking tectonic and neotectonic faults that caused uplift or subsidence of the area during the Pleistocene (Papanikolaou et al., 1989; Perissoratis, 1989; Papanikolaou et al., 1988). It has been also affected by the Pleistocene sea level fluctuations (Lambeck, 1996). As a result the basin was filled with torrential, lacustrine and lagoon sediments depending on the actual sea level.

4. Hydrogeology

The interaction of tectonic and stratigraphic factors combined with eustatic changes established a complex hydrogeological regime where successive confined/leaky aquifers have been formed (Pagounis, 1994; Dounas et al., 1980). In total, four aquifers occur in the study area. The upper aquifer occurs in the Holocene sediments which is unconfined and locally confined. Many wells located in the topographic lows are ‘flowing artesian wells’. The second aquifer, which is confined, occurs in the Pleistocene sediments. Potentiometric surface stands 2-5 m below ground surface. The third aquifer occurs in the Miocene conglomerate and the last one in the Mesozoic carbonate. Many wells tap 2-3 aquifers standing up to 100 m in depth. The pumping rate ranges between
Wells located at the topographic highs tap the limestone from the depth of up to 220 m and the pumping rate ranges between 30-50 m³/h.

5. Methods and materials

The hydrochemistry of Oropos groundwater has been investigated using major and heavy metal constituents. Groundwater samples from 34 wells (Holocene aquifer samples 10; Pleistocene aquifer samples 11; Miocene aquifer samples 9; and carbonate aquifer 4 samples) and one sample from Asopos River surface water were collected during 2006. Chemical analyses were performed in the Mineralogy-Geology Laboratory of Agricultural University of Athens. Physico-chemical characteristics of Temperature T (°C), pH and Electrical Conductivity EC (µS/cm) were measured in situ. The method of titration was used for Ca²⁺, Mg²⁺, HCO₃⁻, and Cl⁻ determination. Hack Dr 3000 Spectrophotometer was used for NO₃⁻, PO₄³⁻, NH₄⁺ and SiO₂ determination. The concentration of Na⁺ and K⁺ was determined using the CORNING Flame Photometer 410. Heavy metals such as Sr, Cd, Cu, Fe, Mn, Ni, Pb, Cr VI και Zn were determined using AAS GBS 908 Atomic Absorption Spectrophotometer. Ion balance error which was better than 5% was calculated summing the ions concentration.

6. Results-Discussion

Statistics of physico-chemical characteristics of the groundwater are presented in Table 1 grouped by aquifer geology.

**Table 1: Statistics of physico/chemical parameters grouped based on the aquifer geology.**

| Parameters       | Units | Carbonate | Miocene | Pleistocene | Holocene | Asopos R. |
|------------------|-------|-----------|---------|-------------|----------|-----------|
|                  |       | range     | Median  | range       | Median   | range     | Median   | range     | Median   | range     | Median   | range     | Median   |
| Ph               |       | 7.2-7.8   | 7.4     | 7.2-8.0     | 7.48     | 7.5-8.0   | 7.71     | 7.4-7.9   | 7.62     | 8.38      |
| Temperature (T)  | °C    | 17.9-25.0 | 20.55   | 15-18.8     | 17.49    | 17-20     | 17.77    | 16.6-19   | 17.93    |           |
| Electrical       | µS/cm | 1120-2350 | 1605    | 845-2790    | 1455     | 766-971   | 854      | 526-3770  | 2097     | 14500     |
| Conductivity     |       |           |         |             |          |           |          |           |          |           |
| Hardness T/CaCO₃ | mg/l  | 23.6-63.5 | 39.63   | 19.1-60.0   | 35.16    | 19.2-26.4 | 22.26    | 5.73-67.41| 34.75    | 115       |
Hydrochemistry of groundwater in the Holocene, Miocene and Mesozoic sediments indicated seawater influence. Figure 3 shows the concentration of the major components. Electrical conductivity (EC) values ranged between 526 and 3770 μS/cm with a median at 2098 μS/cm. Chlorides ranged between 31 and 993 mg/l with a median at 260 mg/l. On the contrary, groundwater quality in part of the Pleistocene conglomerate, occurring below the Holocene sediments...
of about 10 m in thickness, was very good. Wells and pump depth that tap the Pleistocene aquifer are between 22-40 m. The EC values which ranged between 766 and 971 μS/cm with a median at 854 μS/cm and chlorides which ranged between 95 and 163 mg/l with a median 121 mg/l led to the conclusion that this coastal aquifer is protected from seawater intrusion, despite the fact that it is located adjacent to the shoreline. This happens because in many cases the torrential Pleistocene sediments are anisotropic and inhomogeneous due to occasional clay deposition. Clay plays determinant role in groundwater flow resulting in hydraulic differentiation through the formation extent. The value of 854 μS/cm would probably was lower if water from the upper layers did not insert in the borehole through the well screens. The rest part of the Pleistocene aquifer indicates seawater influence with chlorides ranging between 141-815 mg/l, although in 2-3 wells water quality is good with chlorides ranging around 100 mg/l but they are located far from the shoreline. Water quality degradation either occurs through the well screens coming from the contaminated Holocene strata or the recharge from the return of contaminated irrigation water coming from pumping of the underlain Miocene or Cretaceous strata.

The NO$_3^-$ and PO$_4^{3-}$ concentrations were increased in the agricultural area which is attributed to fertilizers. Most of the heavy metal concentration such as Cd, Fe, Pb and Ni exceeded the EU limits which they have been determined at 82, 2500, 817, 217 μg/lit, respectively. It is worth mentioning the occurrence of Cd in all the samples all over the Oropos plain (Fig. 4). It is probably attributed to fertilizers (Kabata-Pendas and Pendias, 1992). It is also worth highlighting that chromium VI concentration was not exceeded the EU limits. It is likely that it was adsorbed on the clay matrix of the aquifers.
Fig. 3: Chemical analyses graph showing the low chloride concentration of the Pleistocene sediments groundwater

The Na/Cl mass ratio in 12 samples ranged between 0.52-0.59 (0.79-0.90 meq ratio) indicating that seawater has influenced groundwaters; in 10 samples the ratio ranged between 0.28-0.50 (0.43-0.77 meq ratio) indicating reverse cation exchange; and in 11 samples the ratio ranged between 0.60-1.01 (0.93 -1.54 meq ratio) indicating cation exchange processes. The mass ratio values around 0.35 reveal strong reverse cation exchange which may indicate that groundwater is hosted in the aquifer for many years.

The Cl/SO\textsubscript{4} mass ratio in five samples ranged between 10.82-28.58 (29.4-77.4 meq ratio) indicating sulphates reduction processes and in the most samples the ratio ranged between 0.79-5.01 (2.0-13.8 meq ratio) indicating evaporites or fertilizes influence. The Cl/SO\textsubscript{4} mass ratio in five samples ranged from 5.08 to 8.58 (14-22 meq ratio) indicating influence of seawater. Evaporites occurrences may be possible in the Pliocene sediments that form the corresponding aquifer.

Based on the Piper diagram (Fig. 5) most of the samples showed Ca-Mg-Na-HCO\textsubscript{3} water type and some samples showed no dominant ion which means mixing processes are in progress.
Fig. 4: EC, Cl, Cd, Fe, Ni and Pb spatial distribution of in the Oropos plain groundwaters.
Fig. 5: Piper diagram shows i) earth alkaline with high alkali content bicarbonate (chloride) and ii) an ambiguous water type of Ca-Mg-Na-HCO3(-Cl) for the most groundwater samples.

This process could take place by pumping and through the well screens or through the clay layers due to the phenomenon of diffusion (Post, 2004). Groundwater was categorized into two (2) main water types based on the expanded Durov diagram (Lambrakis, 1991) which mainly presents the geochemical evolution of groundwater (Fig. 6): (i) the first group was mainly depicted on the field 2 with no dominant cation indicating fresh groundwater of Ca-Mg-HCO3 water type; and (ii) the second group was depicted on the field 8 that is Ca-Mg-Cl water type indicating reverse cation exchange of old Na-Cl waters (Lloyd et al., 1985). The Asopos River surface sample was projected on the field 9 indicating Na-Cl type contaminated by seawater because the sample was taken close to the shoreline. The expanded Durov diagram also gives a second view of the hydrogeological paths of groundwater flow. The fact that no
samples are depicted in 4, 6 and 7 fields could be explained that aquifers are not in hydraulic connection each other (Alam, 2010; Lloyd and Heathcote, 1985).

**Fig. 6:** Expanded Durov diagram shows Ca-Mg-HCO₃ water type for the most groundwaters samples

However, the Piper diagram shows mixing processes of different groundwater. The apparently divergence of the two diagrams could be explained by the fact that the mixing processes could take place through the screens of the wells during pumping and not through the aquifers. In addition, depending on the pressure of the aquifers maybe water is mixed through the screens in non-pumping conditions.
In Figure 7 is illustrated the area located adjacent to the shoreline of Oropos plain where groundwater quality was good. The aquifer which is formed in part of the Pleistocene sediments underlain the Holocene ones, seems to retain its good quality water protected from seawater due to very low hydraulic conductivity of clay.
7. Conclusions

A preliminary hydrochemical study on the Oropos plain groundwaters was carried out to investigate the extent of any contamination. Seawater intrusion possibly takes place through the Holocene, the Pliocene and the Carbonate aquifers. Heavy metals concentration of Cd, Fe, Pb, and Ni exceeded the EU limits while Cd concentration is attributed to fertilizers. The Pleistocene conglomerate seems to retain its good water quality against the seawater despite the fact that it is located adjacent to the shoreline and represent a reserve of good quality water which needs to be properly managed.

Groundwater was categorized into 2 main water types based on the expanded Durov diagram: (i) the first group was mainly depicted on the field 2 indicating fresh groundwater of Ca-Mg-HCO3 type; and (ii) the second group was depicted on the field 8 that is Ca-Mg-Cl type indicating reverse cation exchange of old Na-Cl waters. Based on the Piper diagram most of the samples showed Ca-HCO3 type and some samples showed no dominant type (ambiguous) which means mixing processes are in progress.

8. References

Alam, S.M.M., 2010. Hydrogeochemical evolution of groundwater of part of Ganges-Meghna Deltaic Plain AQUA mundi Am03029: 071 – 082

Dounas, A., Kallergis, G., Morfis, A., Pagounis, A., 1980. Hydrogeological research of brackish karstic springs at Ag. Apostoloi of Kalamos, Nr 31 IGME Athens.

Bear J.A., Cheng H.D., Sorek S., Ouuzar D, Herrera I., editors, 1999. Seawater intrusion in coastal aquifers -concepts, methods and practices Dordrecht, the Netherlands: Kluwer Academic Publishers; 625 pp

Freeze R.A., Cherry J.A., 1979. Groundwater, Prentice-Hall Inc., New Jersey
Ghyben W.B., 1888. Nota in verband met de voorgenomen putboring nabij Amsterdam (Memorandum concerning the proposed well drilling near Amsterdam) Tijdschrift van Let koninklijk Inst., Van Ing.

Henry H.R., 1964. Interface between salt water and fresh water in a coastal aquifer. In: Cooper Jr. HH, Kohout FA, Henry HR, Glover RE, editors Sea water in coastal aquifers (pp C35–C70) U.S. Geological Survey Water 691 Supply Paper, p. 1613-C.

Hermides D., 2018. Hydrogeological conditions of the Thriassion Plain basin with emphasis on the geohydraulic characteristics of the aquifers and the groundwater quality. PhD thesis, Agricultural University of Athens, pp 283.

Herzberg A., 1901. Die wasserversorgung einiger Nordseebader (Water supply to selected North Sea resorts) J. Gasbeleuchtung und Wasserversorgung (Munich), 44. 815–819, 842–844.

Kabata-Pendias, A. & Pendias, H., 1992. Trace Elements in Soils and Plants, 2nd Edition, CRC Press, Boca Ratón, Florida, 315pp

Katsikatsos, G., 2000. Geological map of Greece scale 1:50.000, “Eretria” sheet, IGME publication, Athens.

Lambeck, K., 1996. Sea Level change and shore-line evolution in Aegean Greece since Upper Palaeolithic time, Antiquity, 70/269, p 588-611

Lambrakis, N., 1991. Elaboration of the hydrochemical data by PC, Mineral Wealth Vol.74:53-60 (In Greek).

Lloyd, J.W., Heathcote, J.A., 1985. Natural inorganic hydrochemistry in relation to groundwater, Clarendon Press Oxford p. 294

Mettos, A., 1992. Geological and paleogeographic study of continental Neogene and Quaternary formation of NE Attica and SE Beotia Ph.D. Thesis University of Athens 270 p.
Pagounis, M., 1994. Hydrogeological research of Viotia Prefecture, IGME, Hydrological Hydrogeological research-water reserves determination, Volume I and II Athens.

Parginos, D., Bornovas, I., Mauridis, A., Mettos, A., 1989. Geological map of Greece scale 1:50.000, “Chalkida” sheet, IGME publication, Athens.

Papanikolaou, D., et al., 1989. Submarine tectonic map of S. Euboean Gulf, ed. OASP-HCMR-TDTEG.

Papanikolaou, D., Mariolakos, H., Lekkas, E., Lozios, S., 1988. Morphotectonic observations in Asopos basin and Oropos coastal zone, Contribution to Neotectonics of N. Attica. *Bulletin Geological Society Greece*, 20, 251-267.

Perissoratis, K., Mettos, A., Van Andel, T., 1989. Stratigraphy and Tectonics of S. Euboean Gulf and the wide Neogene basin, *Bulletin Geological Society Greece*, 23, p. 209-221.

Post V.E.A., Asmuth J., 2013. Review: Hydraulic head measurements – new technologies, classic pitfalls, *Hydrogeology Journal*, 21(4): 737-750.

Post V.E.A., 2004. Groundwater salinization processes in the coastal area of the Netherlands due to transgressions during the Holocene. PhD thesis, Vrije Universiteit Amsterdam, 138 pp.

Stamatis, G., Alexakis, D., Guvroula, D. Migiros G., 2011, Groundwater quality assessment in Oropos–Kalamos basin, Attica, Greece, *Environ Earth Sci*, 64: 973. [https://doi.org/10.1007/s12665-011-0914-2](https://doi.org/10.1007/s12665-011-0914-2)

Stigter T.Y., et al., 1998. A hydrogeological and hydrochemical explanation of the groundwater composition under irrigated land in a Mediterranean environment, Algarve, Portugal. *Journal of Hydrology*, 208, 262–279.
Stringfield V.T., Le Grand H.E., 1969. Salt water intrusion in the coastal aquifer of the southern Po Plain, Italy: Relation of sea water to fresh water in carbonate rocks in coastal areas, with special reference to Florida, U.S.A. and Cephalonia (Kephallinia), Greece. *Journal of Hydrology*, 9(4): 387–404

Stuyfzand P.J., 1993. Hydrochemistry and hydrology of the coastal dune area of the western Netherlands, PhD thesis, Vrije Universiteit Amsterdam, 366 pp.

Todd D.K., 1980. Groundwater hydrology 2nd edition NY: John Wiley and Sons, 535 pp.