Δελτίο της Ελληνικής Γεωλογικής Εταιρίας τομ. ΧΧΧΧ, 2007 Πρακτικά 11^{ου} Διεθνούς Συνεδρίου, Αθήνα, Μάιος 2007 Bulletin of the Geological Society of Greece vol. XXXX, 2007 Proceedings of the 11th International Congress, Athens, May, 2007

WATERTOOL™: AN AUTOMATED SYSTEM FOR HYDROLOGICAL INVESTIGATIONS WITH APPLICATION AT THE AREA OF KATO SOULI (NE ATTICA, GREECE)

Sotiropoulos P.¹, Tzanis A.², and Sideris G.¹

¹ TerraMentor E.E.I.G., Sarantaporou 26 and General Tobra, Agia Paraskevi 15342, Greece; terramen@otenet.gr

² Department of Geophysics – Geothermy, University of Athens; atzanis@geol.uoa.gr

Abstract

Surface and groundwater resources are important assets for the economic and social welfare of the population of a given area; they are renewable and with proper management, they contribute substantially to sustained development. Unfortunately, the expansion of industrial and agricultural activities lead to increasing withdrawal of water from the aquifers, excessive use of pesticides and fertilizers and (frequently illicit) disposal of industrial waste. This results in rapid reduction in the quantity and quality of water reserves. There's a compelling call for the development of advanced and inexpensive means to monitor the quantitative and qualitative characteristics of water resources. In response to such requirements, as specified by Directive 2000/60 of the European Commission, TerraMentor E.E.I.G. has spearheaded the development of a multi-channel sensor and system to measure up to 15 physical and chemical parameters (pollutant concentration) facilitating the evaluation of water quality in real time (WatertoolTM). The system uses the Ion-Selective Electrode technology, which is thoroughly described. Its effectiveness is demonstrated with an application in the area of Kato Souli (NE Attica), which suffers from intense salination (seawater intrusion) and pollution of the aquifer. It is shown that the Watertool is an inexpensive, accurate and fast method to map the quality of groundwater reserves and assist aquifer managers in making effective decisions.

Key words: Water quality, water pollution, aquifer management, Ion-selective electrodes.

Περίληψη

Οι επιφανειακοί και υπόγειοι υδάτινοι πόροι αποτελούν σημαντικότατο παράγοντα οικονομικής και κοινωνικής ευημερίας για τον πληθυσμό μίας περιοχής· είναι ανανεώσιμοι και με την κατάλληλη διαχείριση μπορούν να συμβάλλουν στην αειφόρο ανάπτυζη. Δυστυχώς, η αυξανόμενη άντληση των υπογείων υδάτων, η άμετρη χρήση φυτοφαρμάκων και η παράνομη διάθεση των βιομηχανικών αποβλήτων που συνεπάγεται η ανάπτυξη γεωργικών και βιομηχανικών δραστηριοτήτων, σε συνδυασμό με την αύξηση του πληθυσμού, έχουν σαν αποτέλεσμα τη δραματική μείωση και υποβάθμιση της ποιότητά των. Κατά συνέπεια, υπάρχει αυξανόμενη ανάγκη ανάπτυξης προηγμένων τεχνικών ολιγοδάπανης παρακολούθησης και αποτίμησης των ποσοτικών και ποιοτικών στοιχείων των υδάτινων πόρων. Αποκρινόμενη στην ανάγκη αυτή, όπως προδιαγράφεται και από την Κοινοτική Οδηγία 2000/60, η TerraMentor Ε.Ο.Ο.Σ. πρωτοστάτησε στον σχεδιασμό και κατασκευή ενός πολυ-παραμετρικού συστήματος μέτρησης και ψηφιακής καταγραφής έως και 15 φυσικών και χημικών παραμέτρων (συγκέντρωση ρυπαντών) που αποτιμούν την ποιότητα των υδατίνων πόρων σε πραγματικό χρόνο (WatertooITM). Ο αισθητήρας χρησιμοποιεί τεχνολογία ιοντοεπιλεκτικών ηλεκτροδίων, η οποία περιγράφεται διεξοδικά.. Τέλος, παρατίθεται παράδειγμα εφαρμογής στην περιοχή Κάτω Σουλίου (BA Αττική), η οποία εμφανίζει σημαντικά προβλήματα υφαλμύρινσης και μόλυνσης του υπογείου υδροφορέα· με αυτήν καταδεικνύεται η αποτελεσματικότητα της μεθόδου για ταχεία, ολιγοδάπανη και ακριβή αποτύπωση της ποιότητας του υδροφορέα και τα πολλαπλά οφέλη που προσφέρονται στους διαχειριστές υδάτινων πόρων.

Λέξεις κλειδιά: Ποιότητα νερού, μόλυνση υδάτων, διαχείριση υδροφορέων, ιοντοεπιλεκτικά ηλεκτρόδια.

1. Introduction

The dramatic decrease in subterranean water reserves, together with the increasing deterioration of water quality due to various forms of pollution, are two serious environmental problems confronting water reserve managers, both in Greece and abroad. These problems have obvious adverse effects on the agriculture, the economy, the natural environment and, most importantly, on the health of water consumers; if left unchecked they may jeopardize the welfare of entire populations. The prevention (or mitigation) of such problems requires careful planning and bold administrative measures. In order to be effective, especially in the event of a fast developing crisis, such measures must be taken on the basis of reliable information, deliverable to the planners and decision makers securely and rapidly.

One such indispensable piece of information pertains to the quality of the water in the aquifers, namely its (im)purity and concentration of unwanted (polluting) chemicals. Conventional methods to assess water quality require direct sampling of the aquifer (through boreholes and wells) and precise chemical analysis in the laboratory, although some parameters may be measured in the field using specialized chemical kits. At any rate, chemical analysis is accurate and reliable, but at the same time slow and rather costly (e.g. Wilson and Hunt 1986, Clesceri *et al.* 1989). The *fast and inexpensive* acquisition of dependable data requires application of novel technologies, minimally dependent on chemical analysis. This paper discusses such a technology, which exploits the physico-chemical properties of ions in solution to measure the concentration of certain elements and radicals, hence provide information to assess water quality – in essence it performs chemical analysis using the physical properties of ions.

In attempting to realize this technology as a dependable and affordable application, TerraMentor E.E.I.G., acting as co-ordinator of an international consortium, has spearheaded the design and development of an innovative system to enable the fast assessment of water quality by measuring up to 15 physicochemical parameters (channels) simultaneously. Introduced under the trade mark *Watertool*TM, the system is briefly described henceforth, together with an example of its application and performance in real field conditions, at the area of Kato Souli (Marathon, NE Attica, Greece).

2. The WatertoolTM system

2.1. General Description

The *Watertool* comprises an immersible probe containing the measuring elements (electrodes and other sensors) and protected in robust cylindrical titanium casing (Fig. 1). With dimensions 600×48 mm, the probe can easily be inserted in boreholes with a minimum diameter of 60 mm. The other major components are the digitizing and control/ storage unit and a data transfer unit.

The measured quantities include temperature, hydrostatic pressure, density, total hardness, electric conductivity, pH (accurate to within 0.05 units), Eh, oxygen concentration (accurate to within 0.05mg/lt) and pollutant concentration (NH_4^+ , NO_3^- , Na^+ , Cl^- , Ca^{2+} , F^- and H_2S , all accurate to within 0.1 mg/lt). Concentrations are measured with *ion-selective electrodes* (ISE) which will be described in Section 2.3 – for quick but thorough information see Wikipedia (2006). The various sensors and the ISE's are fitted at the lower end of the probe; they have dimensions 175×8 mm, may withstand pressures up to 25 Kg/cm², be immersed to depths of 250 m and operate at temperatures up to 60 °C. The wide-range conductivity sensor (10-10⁻² S/m and accurate to within 0.03 %) may be used in all kinds of environments, from sweet spring waters to brines. Moreover, the design of the probe is such, that the user may switch between different ISE's and measured parameters in a matter of minutes and according to the requirements or developing circumstances.

The *Watertool* can be deployed in two ways: either as a portable station for single-site measurements (Fig. 1) or, as a network of stations augmented with two-way wireless telemetry (TCP/IP over GSM telephony). In either mode, the system is supported with software to automate measurements, calibrate the electrodes, perform diagnostic tests and, verify, process and visualize the data (TerraMentor 2004). The software can also set off an alarm when pollutant concentrations exceed some predefined thresholds; this is particularly useful when the *Watertool* is deployed in the network operating mode and at high risk areas, or during developing crises.



Figure 1 – Left: The Watertool[™] probe complete with ISE's during calibration with standard solutions. Right: The probe while inserted in a well. In this case, the Watertool is configured for single-site measurements and in addition to the probe it comprises a data logger and a laptop or palmtop computer to control data acquisition and storage

2.2. Physical basis

An Ion-selective electrode is a transducer which converts the activity of a specific ion dissolved in a solution into an electrical potential which can be measured by a voltmeter or pH meter. The basis for all potentiometric measurements with the use of the Ion Selective Electrodes is the Nernst equation, which has the empirical form:

$$E = E' \pm \theta \cdot \log \alpha_x$$

(1)

where: *E* is the emf of the electrode (electrochemical element) measuring circuit; *E'* is the same in a (standard) solution where the activity of the measured anion or cation is $a_x = 1$ (log $a_x = 0$); θ is the temperature factor (Nernst curve), which has the sign (+) for cations and the sign (-) for anions. Moreover, $\theta = RT/Fz$ where *R* is the molar gas constant, 8.31 J K⁻¹ mol⁻¹, *T* is the temperature in °K, *z* is the charge of the ion and *F* is the Faraday constant, 96496 C mol⁻¹; θ is represented in the electrochemical units (V/gram-equivalent).

2.3. Ion-Selective Electrodes and other sensors

The principles of ISE's can be studied in several standard sources (e.g. Covington 1979, Morf 1981, Koryta and Stulik 1983, Koryta 1994, Christian 1994). Herein, only essential information will be given, concerning their implementation in the *Watertool*. The sensing unit of the *Watertool* probe is a multi-electrode electrochemical element consisting of a flow-through potentiometric cell. The measurement electrodes are connected to the high-impedance input of the potentiometer, and the reference electrode (RE) is connected to the low-impedance input. The potentiometer affords measurement of the emf with accuracy ± 1 mV and sensitivity 0.1 mV.

All measurement electrodes, as well as the reference electrode, are pressure-compensated. The connecting end of the electrode is a piston-type hermetic current input (Fig. 2). This enables the user to change electrodes easily and also extends significantly the list of electrodes that may be used. Such a design alsO enables the use of electrodes suitable for specific or targeted hydrogeo-chemical survey. For the RE, a special hub has been designed, although it is also changeable.



Figure 2 – Anatomy of the ISE: Electrodes used for potentiometric measurements *in situ*. Hermetic current input: 1 – case, 2 – hub, 3 – isolator, 4 – current supply, 5 – *LEMO* connector, 6 – plug-in outlet made of electro-isolated material, 7 – sealing rubber rings

The sensing part of the electrode is usually made as an ion-specific membrane, along with a reference electrode. Depending on the application, the following types of ISEs are used with the *Watertool*.

Glass membrane ISE: These are used for measurements of H^+ and Na^+ ion activities. There are two variants of the glass pH electrodes, one for measurements in acidic media and one for neutralalkaline solutions. The main electrochemical characteristics of pH electrodes are shown in Table 2. In practice, this electrode is absolutely selective with respect to hydrogen ions, and any macro- and micro-components that may be present in natural waters do not influence its potential. Its selectivity coefficient in relation to the majority of hindered ions is 10^{-15} . The electrodes made of sodiumselective glass are so highly selective that their use in natural hydrochemical environments is usually problem-free (see Table 1). In anthropogenic hydrochemical conditions (e.g. in waste dumps), and especially in acidic media, one may need to consider a possible drift of the electrode's potential in the presence of increased H^+ , K^+ and NH_4^+ concentrations. It is possible to ignore the influence of other single-charged cations, because their content in such waters is lower than the concentration of sodium by 4 - 5 orders of magnitude.

Main function	pH	pNa	
Active phase of membrane	Lithium glass	Sodium-lanthanum-silicate glass	
Ions determining potential	$\mathrm{H}^{+} >> \mathrm{Na}^{+}$	$Ag^{+} > H^{+} > Na^{+} > K^{+}$	
Measurement diapason, pX	0-12.5	-24	
Selectivity coefficient	Influence of Na under pH>12.5. For any ground waters compo- nent/element < 10 ⁻¹⁵	H ⁺ ~1000; Ag ⁺ ~500; K ⁺ , Li ⁺ , Cs ⁺ ~10 ⁻³ ; Tl ⁺ ~2·10 ⁻³ ; Rb ⁺ , NH ₄ ⁺ ~3·10 ⁻⁵	
Recommended pH range	0 - 12.5	pH-pNa > 3.5	
Temperature range °C	-5 - 100	5 - 100	
Resistance at 25°C, MΩm	10 - 80	30-150	

Table 1- Main electrochemical characteristics of glass membrane electrodes

Liquid-membrane ISE: The concentrations (activities) of nitrate, potassium and ammonium ions, are determined with solid-contact electrodes having liquid membranes (Table 2). Notably, nitrate and ammonium concentrations are *not* stable if a water sample is kept for some time before chemical analysis and it is *recommended* to measure them *in situ*. In potentiometric ionometry, the activities of measured ions are conventionally expressed in the pX, where $pX = \log a_x$, and a_x is the activity of the measured ion. The lower threshold for the determination nitrate, ammonium and potassium ions is $pX \approx 4$ and in weight-to-volume form 6.1 mg/lt for the nitrate and 1.8 mg/lt for ammonium. The niTrate ions enjoy high selectivity with respect to similar ions; for instance, the presence of sulphates, even in concentrations as high as 20 gr/lt (anthropogenic solutions), does not affect the measurement of nitrates with normal concentrations (of the order of 10 - 700 mg/lt).

Main function	pNO ₃	pNH ₄	pCa
Membrane material	Nickel-phenantronil complex in onitrocimol	Nonactinmonactin in 3-(2-ethilhexyl) phosphate	Ca ²⁺ -salt of dodecyl- phosphor acid in polyvinyl-chloride matrix
Ions determining potential	ClO_4 , I, ClO ₃ , NO ₃	NH4 ⁺	Ca ²⁺
Measurement diapason, pX	-14	-14	-14
Selectivity coefficient	$\begin{array}{c} ClO_{4}^{-} \times 10^{3};\\ ClO_{3}^{-} \times 10^{2};\\ Br^{-} 0.9; S^{2-} 0.6;\\ NO^{2-} 6 \times 10^{-2};\\ CN^{-} 2 \times 10^{-2};\\ SO_{4}^{2-} 6 \times 10^{-4};\\ H_{2}PO_{4}^{-};\\ PO_{4}^{3-} \sim 3 \times 10^{-4};\\ HPO_{4}^{-} \sim 8 \times 10^{-5} \end{array}$	$ \begin{array}{l} K^{+} \sim 0.12; \\ Rb^{+} \sim 4.3 \times 10^{-3}; \\ H^{+} \ 1.6 \times 10^{-2}; \\ Li^{+}, \ Cs^{+} \sim 4 \times 10^{-3}; \\ Na^{+} \sim 2 \times 10^{-3}; \\ Ca^{+} \sim 2 \times 10^{-4} \end{array} $	$Zn^{2+} \sim 1-5;$ $Al^{3+} \sim 0.9;$ $Mn^{2+} \sim 0.38;$ $Cu^{2+} \sim 0.07;$ $Fe^{2+} \sim 0.045;$ $Co^{2+} \sim 0.042;$ $Mg^{2+} \sim 0.032;$ $Ba^{2+} \sim 0.02;$ $Li^{+} \sim 10^{-4};$ $Na^{+} \sim 10^{-5};$ $K^{+} \sim 10^{-6}$
Recommended pH range	2 - 12	2-12	3.5 - 9
Temperature range °C	0 - 50	0-50	5-45
Resistance at 25°C. MOm	25	<1	<20

Table 2 - Main electrochemical characteristics of liquid-membrane electrodes

Solid-state ISE: The activity of sulphide ion (S^{2-}) is determined with a polycrystalline fully hardcontact sulphide-silver electrode. The electrode has a very high selectivity for sulphide ions, which is determined by the extremely low solubility of Ag₂S, the low electrical resistance and stability with respect to chemical oxidants and reducers. Ag⁺ and Hg²⁺ affect the selectivity. For Ag⁺, this electrode is also specific, as for the sulphide; in consequence, silver ions do not disturb the measurements. The influence of Hg²⁺ is controlled by the presence of mercury sulphides. These substances have low solubility and they may form a hard film on the surface of the pS-electrode, turning the electrode into a Hg-specific one. However, natural waters always contain chlorine and both silver and mercury combine with chlorine into practically insoluble substances. Moreover, silver and mercury may only be present in ground waters in trace amounts (even in anthropogenic solutions), so they can hardly influence the sulphide-specific function of the pS-electrodes.

Chlorine ISE: The activity of the chlorine ion (Cl⁻) is determined with a polycrystalline fully hard-contact silver chloride electrode. The electrode has a high selectivity for chlorine ions that is determined by the extremely low solubility of AgCl, low electric resistance and stability in relation to chemical oxidants and reducers. CN⁻, Br⁻ and I⁻ affect selectivity, their respective coefficients being 10^{-4} , 10^2 and 10^{-6} . At the same time, H₂S, S²⁻, S₂O₃²⁻ must *not* be present in the solution because sulphide ions react with the membrane material and the electrode is converted to sulphide-specific. It is therefore necessary to avoid working with this electrode in water containing hydrogen sulphide.

Fluorine ISE: Monocrystals of lanthanum fluoride are used as membrane material. The measurement diapason for fluorine ions is 0-6 pF, the working pH diapason is 4-8 and the operational temperature range is 5-45 °C. The electrode has a high selectivity under normal operating conditions and only very high concentrations of bromine, chlorine, iodine, and nitrate ions may influence the measurements; for these ions the selectivity coefficient is $\sim 10^{-3}$.

3. Application at the area of Kato Souli, NE Attica

The geology and geomorphology of the broader Kato Souli area is detailed in a number of publications (e.g. Boetechtel and Papadeas 1968, Lozios 1991, 1993, Margonis *et al.* 2002, Seni *et al.* 2004, Pavlopoulos *et al.* 2006). For the limited scope of the present study, a short description will be provided forthwith.

The main part of the study area extends over the plane of Kato Souli and is bounded by the Schinias wetlands to the south and the highlands of Drakonera to the east, Terokoryfi to the north and Strati to the west (Fig. 3). The plain is covered by Holocene alluvial deposits of thickness up to 30 m, but the northernmost stations are located on Pleistocene terrestrial deposits (Pt.tr in Fig. 3, with a thickness of at least 30 m). The Pleistocene sediments are laid unconformably on the local bedrock which comprises upper Triassic to upper Cretaceous marbles, intercalated with a narrow zone of middle Cretaceous schists (the Ramnounta schists, Km.sch in Fig. 3). The flanks of the highland areas to the north and east of the study area are covered by undivided scree and talus cones (Pt.sc.cs in Fig. 3); only the two easternmost stations (27 and 28) are located on such a formation.

With respect to hydrogeological conditions, the sedimentary and karstic aquifer system developing beneath and about the Kato Souli Plain suffers from intense salination (sea water intrusion), as evident in the springs of Agia Marina, Ramnounta and Kato Souli. An unconfined aquifer develops within the alluvial and terrestrial sediments throughout the Kato Souli Plain, which also experiences salination effects, as it appears to be recharged from the deeper water beds; this is expected to be further degraded by pollution from the intense agricultural activity and other anthropogenic factors. The area undergoes intense development, while there's also considerable environmental sensitization because of the nearby Schinias wetland and pine forest.

The quality of the water in the unconfined aquifer is being monitored with a network of 41 wells and boreholes, established in two phases (26 in the Spring and 15 in the Autumn of 2006). The distribution of the monitoring stations is illustrated in Figure 4. Measurements are taken intermittently, with the *Watertool* configured for single-site operations. The surveys were conducted by a crew of two observers at a time and were completed within several hours, but certainly in time less than one working dAy (a single observer may also perform the same work but at a somewhat slower pace).



Figure 3 – Distribution of the water quality monitoring stations (down triangles) and geological setting of the study area. al: Alluvial deposits; Pt.sc.cs: Pleistocene scree and talus cones, undivided; Pt.tr: Pleistocene terrestrial deposits; M.ms: middle-upper Miocene lacustrine deposits; Ks.mr: U. Cretaceous marbles; Km.sch: Ramnounta schists; Kj.mr: Lower Cretaceous marbles. The figure is based on the 1:50000 standard issue geological map published by the Institute of Geological and Mining Exploration (IGME)

Herein we present data from three surveys conducted in March, June and November of year 2006, focusing on parameters that indicate the evolution of salination (Na⁺ and Cl⁻ concentrations), as well as and pollutants pertaining to agricultural activity (NO₃⁻).

Figure 4 shows the variation of pollutant concentration with time at two example sites. In both cases, Na^+ and Cl^- show elevated values in June, which can be attributed to the increased salination expected at summertime, as a consequence of increasing extraction of freshwater from the aquifer and decreasing precipitation levels. Note, however, that sodium and chlorine concentration is remarkably higher at site 14, which indicates significant local variability of the salination process. At site 2, the nitrate content is well below the alarm level of 50 mg/lt and shows a decreasing trend. Conversely, at site 14 the nitrate concentration is exceedingly high during (11 times the alarm level) in March, when fertilizers, pesticides and herbicides are used in large quantities and exhibits a decreasing trend throughout the rest of the year (June and November) when such chemicals are used more sparingly. Note also that site 2 is situated at the margin of the cultivated zone and within fields that were left to fallow during the entire year 2006, a fact that might explain the low nitrate content. Site 14 is located in a heavily cultivated zone and right next to large greenhouses, therefore it shows clear signs of anthropogenic pollution in addition to the natural salination process.



Figure 4 – Variation of NO₃⁻ (continuous line), Cl⁻ (broken line) and Na⁺ (dotted line) with time at Stations 2 (left) and 14 (right)



Figure 5 – The variation of nitrate concentration (left) and chlorine concentration (right) at all stations, as a function of time

Figure 5 shows the measured nitrate and chlorine concentration at all stations, as a function of time. Although not deducible from Figure 5 alone, it is easy to verify that at sites neighbouring with intensely cultivated land – greenhouses in particular – nitrate concentrations are exceedingly high during March (several times above the threshold) and decrease towards the end of the year to the threshold level, but still remain above acceptable limits. The observed significant variability of nitrate concentration between sites is a function of the intensity of nearby agricultural activity and is also consistent as a function of time. The variation in chlorine concentration is even more interesting. As mentioned above, natural salination processes call for an increase in Cl^{-} and Na^{+} concentration in summer and a decrease in winter. This is indeed observed at several locations, particularly those associated with little nearby agricultural activity (also see Fig. 4). However, there are sites where the chlorine content observed in March 2006 is considerably higher than that observed in June. It should also be noted that high chlorine content at those sites correlates fairly well with high nitrate content. This might suggest that at those locations, there are processes additional to salination at work, quite possibly related to agricultural and other anthropogenic activity. The detailed analysis and discussion of the processes giving rise to the observations of Figure 5 are beyond the scope of this presentation and will be given elsewhere.

Figures 6 and 7 respectively illustrate the spatial distribution of nitrate and chlorine concentrations on 6 November 2006. Figure 6 shows that nitrate content is low at the south and east of the investigated area, which are generally housing districts at the margin of the wetland with little or



Figure 6 – Spatial distribution of NO3⁻ concentration on 6 November 2006



Figure 7 – Spatial distribution of Cl⁻ concentration on 6 November 2006

low intensity cultivation. The exception at site 17 confirms the canon (locally intense cultivation). Conversely, the more heavily exploited stretch of land around the centre of the investigated area shows high nitrate concentrations, well above the acceptable upper limit. As easily seen in Figure 7, the chlorine content exhibits significant variability, with high concentrations observed at the NE and SE corners of the investigated area and a general NE-SW trend. The chlorine data show significant localization, which in part may be attributed to corresponding localization of salination processes, hence to the structure and permeability of the bedrock formations. Nevertheless, it is rather difficult to provide detailed explanations on the basis of this data set alone. At any rate, both Figures 6 and 7 illustrate how intricate may be, the distributions of pollutants in unconfined aquifers, hence the complex of regional and local processes leading to their creation.

In a final comment, note that Figures 6 and 7 are only *snapshots* of pollutant distributions, obtained in a matter of hours by a small crew of only two observers. Thus, they exemplify the wealth and quality of information afforded by modern measurement technologies such as those implemented in the *Watertool* and its potential significance in optimizing aquifer and environmental management decisions.

4. Discussion and conclusions

The quality of surface and ground waters is routinely being monitored in many advanced countries, albeit in a conventional way that does not keep pace with modern technological developments: water samples from the aquifers are still being taken to the laboratory and analyzed for the desired parameters. Only a few parameters are measured *in-situ*. However, with the introduction of the European Water Framework Directive in year 2000, the monitoring of water quality has been made mandatory and before long, all EU countries will have to meet rather strict monitoring specifications.

The development of advanced physical and chemical sensors (ISEs), together with modern data acquisition and analysis technology and communications facilities, make possible to monitor water quality *in-situ* and on-line. By linking the sensors to a wireless network (for instance GSM) it is possible to make measurements from any distance and manipulate the data through the Internet. In addition, the analysis made with ISEs has the advantage of being cheaper and much faster than conventional methods. Furthermore, the affordable volume of information is very many times greater.

The *Watertool*TM system was developed to satisfy requirements such as outlined above. Based on the literature and concurrent Internet searches, there are no other multi-parameter probes available in the market, which can register as many as 15 water quality parameters simultaneously, fit easily into a 64mm wide water well and transmit the data to any desired location using the TCP protocol. Thus, the *Watertool* may be used to:

- Monitor water quality for certified applications (e.g. drinking water standards).
- Monitor water quality for non-certified applications (e.g. mapping groundwater pollution).
- Monitor water quality for academic research and insight into soil processes.

Multi-parameter studies are useful for certified applications, only if water quality standards fall within the measuring range of the multi-parameter probe, which *is* the case for the *Watertool*. In all three research fields mentioned above, measurements with ISEs offer a large added value in comparison to laboratory measurements. For frequent use, (see below), such measurements are cheaper and permit a much larger body of data to be collected over a much shorter period of time, thus providing a much more comprehensive body of knowledge with respect to the distribution, behaviour and evolution of polluting agents.

The case study conducted in the area of Kato Souli demonstrates and confirms these assertions. It has provided a large amount of *in-situ* data on groundwater quality and quantity, which enabled the

correlation of the temporal (seasonal) and spatial variation of the measured parameters with regional and/or localized natural processes (salination) and anthropogenic pollution (agricultural activity). It has thus shown the usefulness and effectiveness of the *"Watertool concept"* in researching and confronting environmental hazards that are very common in the coastal areas of South Europe and the world at large.

In conclusion, the specifications and performance of the *WaterTool* concept and system are in complete accordance with the Water Framework Directive of the European Union. Moreover, it was demonstrated to comprise an effective and valuable tool for the management of the groundwater reserves.

5. Acknowledgments

The *Watertool* was developed through funding by programme CRAFT, contract No COOP-CT - 2003-507259, "An innovative tool for multi-element analysis of ground and surface water (WATERTOOL)". The acquisition and analysis of data in the area of Kato Souli is co-funded by the European Social Fund and Greek National Resources – (EPEAEK II), PYTHAGORAS II.

6. References

Boetechtel, J., and Papadeas, G., 1968. Tectonic aereal interpresration in the Mediterranean region exemplified by the metamorphic series at eastern Greece, near Marathon, *Photogrammetria*, 26, 201-210.

Christian, G.D., 1994. Analytical chemistry, Wiley.

- Clesceri, L.S., Greenberg, A.E., and Trussel, R., Rhodes (eds), 1989. Standard methods for the examination of water and wastewater, Published by the *Am. Publ. Health Assoc., Am. Water Works Assoc. and Water Pollution Control Fed.*
- Covington, A. K., (ed.) 1979. Ion Selective Electrode Methodology, Volumes 1 & 2, CRC Press. Boca Raton.
- Koryta, J., and Stulik, K., 1983. ISEs, 2. edition, Cambridge University Press.
- Koryta, J., 1994. Principles of Electrochemistry, Wiley.
- Lozios, S., 1991. Microtectonic observations in the metamorphic system of the Varnavas Ramnounta area, NE Attica, Bull. Geol. Soc. Greece, 25(1), 439-453. (in Greek)
- Lozios, S., 1993. Tectonic analysis of the metamorphic formations of NE Attica, OHD Thesis, University of Athens, 299pp. (in Greek)
- Margonis, S., Syridis, G., Psilovikos, A.R., Trontsios, G. Steinhauer, G., Vouvalidis, K., and Mouzouris, G, 2002. The evolution of the natural environment in the area of Schinias wetlands, Matathon, from the ancient era to date, *Proceedings, 6th Panhellenic Geographical Congress*, Thessaloniki, October 2002, 159-165. (in Greek)
- Morf, W.E., 1981. The Principles of ISEs and of Membrane Transport, Elsevier.
- Pavlopoulos, K., Karkanas, P., Triantaphyllou, M., Karymbalis, E., Tsourou, Th., and Palyvos, N., 2006. Paleoenvironmental Evolution of the Coastal Plain of Marathon, Greece, during the Late Holocene: Depositional Environment, Climate, and Sea Level Changes, *Journal of Coastal Research*, 22 (2), 424-438.
- Seni, A., Kapsimalis, V., and Pavlopoulos, K., 2004. Determination of recent geomorphological changes in the Marathonas coastal plain (Attica, Greece), using geographical information systems, 6th Panhellenic Geographical Congress, Mytilini, Greece, October 2004. (in Greek, available at http://www.ath.aegean.gr/srcosmos)

- TerraMentor E.E.I.G, 2004. "WATERTOOL": Information and measuring system for hydrological/ hydrogeological investigations, *Technical Description and Users Guide*, Athens.
- Wikipedia, 2006. Ion selective electrode. Retrieved 05:57, November 30, 2006, from http://en.wikipedia.org/w/index.php?title=Ion_selective_electrode&oldid=90339686
- Wilson, A.L., and Hunt, D.T.E., 1986. *The chemical analysis of water: general principles and techniques*, 2nd ed., The Royal Society of Chemistry, London.