AUTOMATED MONITORING OF GROUNDWATER QUALITY WITH ION-SELECTIVE ELECTRODES AND AN APPLICATION AT THE KATO SOULI AREA (NE ATTICA, GREECE).

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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. This paper introduces a multi-channel system, developed in response to the requirements specified by Directive 2000/60 of the European Commission, to measure up to 15 physical and chemical parameters (pollutant concentration) facilitating the evaluation of water quality in real time. The system uses the Ion-Selective Electrode technology and its effectiveness is demonstrated with an application in the area of Kato Souli (NE Attica), which suffers from intense salination (sea-water intrusion) and pollution of the aquifer. It is shown that it comprises 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.*

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. 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 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 chemical analysis in the laboratory, although some parameters may be measured in the field with 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 introduces the development and implementation of such a technology, which exploits the physico-chemical properties of ions in solution to measure their activity and concentration. In essence it performs chemical analysis using the physical properties of ions. It comprises an innovative system to enable the fast assessment of water quality by measuring up to 15 physicochemical parameters simultaneously. The system is briefly described herein, together with an example of its application and performance in real field conditions, at the area of Kato Souli (Marathon, NE Attica, Greece).

MEASUREMENT DEVICE AND SENSORS

The system comprises an immersible probe containing the sensors and protected in a robust cylindrical titanium casing (Figure 1). With dimensions 600×48mm, the probe can easily be inserted in boreholes with a minimum diameter of 60mm. The other major components are the digitizing unit, the control/ storage unit and the 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). The wide-range conductivity sensor ($10\text{-}10^{-2}$ S/m and accurate to within 0.03%) may be used in all kinds of environments, from sweet spring waters to brines.

Figure 1. **Left:** The probe complete with ISE's during calibration with standard solutions. **Right:** The probe while inserted in a well. In this case, the system 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.

Ion activities and concentrations are measured with *ion-selective electrodes* (ISE). An ISE 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 physical basis for all potentiometric measurements with Ion Selective Electrodes is the Nernst equation and their principles can be studied in several standard sources (e.g. Covington, 1979; Morf, 1981; Koryta and Stulik, 1983; Koryta, 1994; Christian, 1994; for quick but thorough information see Wikipedia, 2006).

The sensing unit of the probe is a multi-electrode electrochemical element consisting of a flow-through potentiometric cell fitted at the lower end of the probe. The measurement electrodes are connected to the high-impedance input of the potentiometer, and the reference electrode is connected to the low-impedance input. The potentiometer affords measurement of the emf with accuracy ±1mV and sensitivity 0.1 mV. The electrodes used with the system are glass membrane to measure H^+ and Na^+ activities, liquid-membrane to measure nitrate (and ClO_4^-, ClO_3^-), potassium and ammonium activities, and solid-state to measure sulphide (S^{2-}), chloride (Cl^-) and fluorine (F^-) activities. In general they afford high selectivity, typically of the order of 10^{-2} – 10^{-5} with respect to the hindered ions.

All measurement electrodes, as well as the reference electrode, are pressure-compensated; they may withstand up to 25 Kg/cm^2 and be immersed to depths of 250m while operating at temperatures up to 60°C. They have dimensions 175mm×8mm and their connecting is a piston-type hermetic current input. This design enables the operator to switch between electrodes and measured parameters in a matter of minutes and according to the requirements or developing circumstances, while extending significantly the list of electrodes that may be used. It also enables the use of electrodes suitable for specific or targeted hydrogeochemical surveys. The reference electrode is protected in a specially designed hub, although it is also changeable.

The system can be deployed in two ways: either as a portable station for single-site measurements (Figure 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 system is deployed in the network operating mode and at high risk areas, or during developing crises. Additional details on the system's technical characteristics, performance, caveats and precautions to be taken in case of special field conditions can be found in the Technical Reference Manual (Terramentor, 2004), available from the principal author.

APPLICATION AT THE AREA OF KATO SOULI, NE ATTICA, GREECE.

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, only a short description will be provided (see Figure 2).

The main part of the study area extends over the plain of Kato Souli. The plain is covered by Holocene alluvial deposits of thickness up to 30m, but the northernmost stations are located on Pleistocene terrestrial deposits (Pt.tr in Figure 2, with a thickness of at least 30m). 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 Figure 2). 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 Figure 2); only the two easternmost stations (27 and 28) are directly located on such a formation.

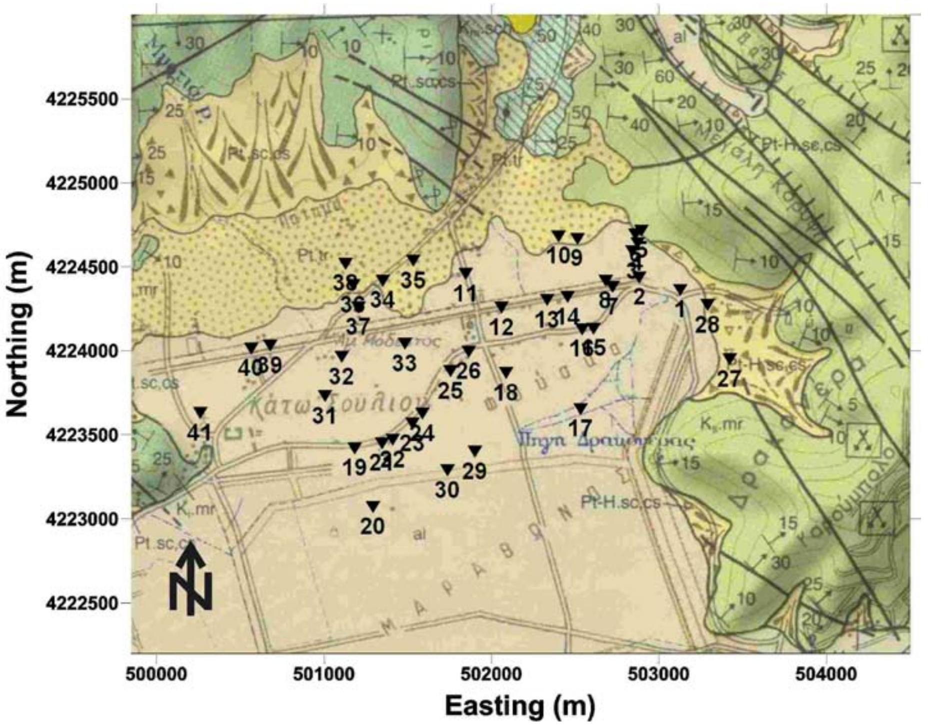

Figure 2. Network for monitoring water quality (down triangles) and geological setting of the study area. al: Alluvial deposits; Pt.sc.cs: Pleistocene scree and talus cones, undivided; Pt.tr: Pleistocene terrestrial deposits; M.ms: middle-upper Miocene lacustrine deposits; Ks.mr: U. Cretaceous marbles; 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).

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). 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 concern for 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 (Figure 2). Measurements are taken intermittently, with the system configured for single-site operations. The surveys were conducted by a crew of two observers and were in time less than one working day (a single observer may also perform the same work but at a somewhat slower pace). 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 (NO_3^-).

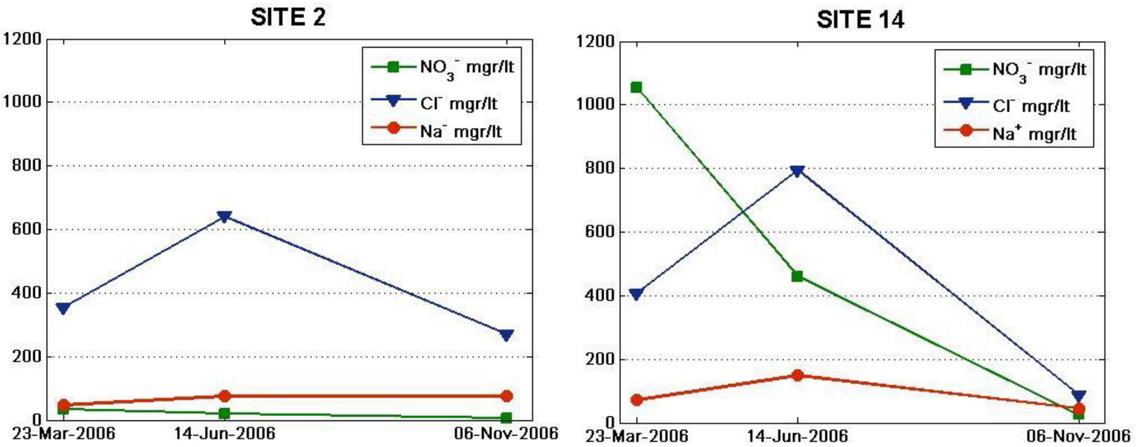

Figure 3. Variation of NO_3^{-}, Cl^{-} and Na^{+} (dotted line) with time at Stations 2 (left) and 14 (right).

Figure 3 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 chloride 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 (11 times the alarm level) in March, when fertilizers, pesticides and herbicides are massively used 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 shows the measured nitrate and chloride concentration at all stations, as a function of time. Although not deducible from Figure 4 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 chloride 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 Figure 4). However, there are sites where the chloride content observed in March 2006 is considerably *higher* than that observed in June. It should also be noted that high chloride 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 4 are beyond the scope of this presentation and will be given elsewhere.

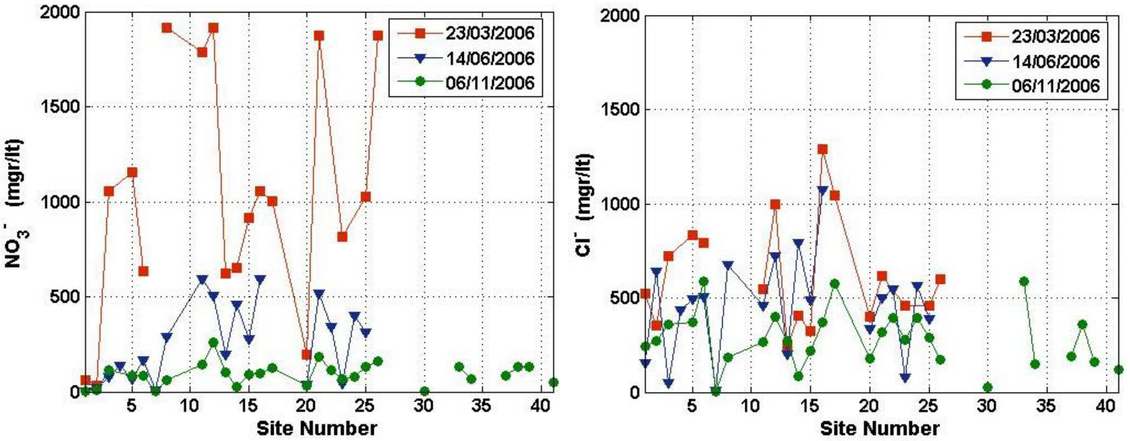

Figure 4. The variation of nitrate concentration (left) and chloride concentration (right) at all stations, as a function of time.

Figures 5 illustrate the spatial distribution of nitrate and chloride concentrations on 6 November 2006. The left panel 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 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 the right panel, the chloride 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 chloride 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 5 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 Figure 5 presents only *snapshots* of pollutant distributions, obtained in a matter of hours. Thus, they exemplify the wealth and quality of information afforded by modern measurement technologies and its potential in optimizing management decisions.

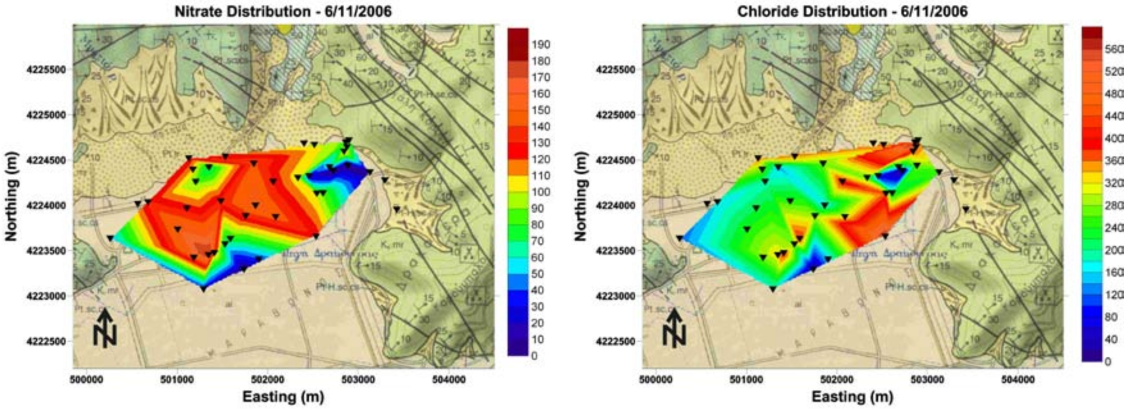

Figure 5. Spatial distribution of NO_3^- (left) and Cl^- concentrations on 6 November 2006.

4. DISCUSSION AND CONCLUSIONS

The quality of surface and ground waters is routinely being monitored in many advanced countries, albeit in a conventional way: water samples from the aquifers are still being taken to the laboratory and analyzed for the desired parameters. The European Water Framework Directive 2000/60 mandates the monitoring of water quality and before long, all EU countries will have to meet rather strict monitoring specifications. The development of advanced physico-chemical sensors (ISEs), together with modern data acquisition analysis and communications/ networking capabilities, facilitate the monitoring of water quality *in-situ* and on-line. In addition, the analysis made with ISEs has the advantage of being cheaper and much faster than conventional methods, while the affordable volume of information is very many times greater. Thus, they may be used to monitor water quality for certified applications (e.g. drinking water standards), for non-certified applications (e.g. mapping groundwater pollution), as well as 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 technology described herein. In all three research fields mentioned above, measurements with ISEs offer a large added value in comparison to laboratory measurements. For frequent use, 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 evidence on the distribution, behaviour and evolution of polluting agents. All this allows for the fast amortization of the capital invested in establishing the network and significant savings thereafter.

The case study conducted in the area of Kato Souli 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 ISE based technology in researching and confronting modern environmental hazards that are very common in the coastal areas of South Europe and the world at large.

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