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Utilization of a multi-parameter sensor network for online monitoring of the water quality in the lignite mining area of Kozani, Greece

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ABSTRACT

The present study is focused on the examination and evaluation of environmental pressures on the aquatic resources of western Macedonia region (Greece) and particularly in Kozani lignite mines area, and on the development of a water quality monitoring system in the region, in order to identify potential impacts to the adjacent water resources. A multi-parametric sensor system was installed in three representative sites of the target area and the corresponding measured parameters included pH, temperature, conductivity, nitrate ions (NO_3^-), sulfate ions (SO_4^{2-}), and chloride ions (Cl^-) for a period of about 10 months. Additionally, certain other complementary physicochemical parameters (turbidity, hardness, COD, BOD_5. DO, TSS, NO_2^-, NH_4^+, Fe, and Al) were measured in selected grab samples, collected from certain points in the same area, in order to have an integrated view of water quality. The pH values ranged between 7.6 and 8.3 and remained quite stable in all three monitoring stations. Conductivity values ranged from 188 to 1,082 μS/cm; in addition, the wide NO_3^- content—observed only in Ag. Dimitrios Public Power Corporation Station—was attributed to the discharge of partially treated wastewater effluents. A detailed analysis of recorded measurements on a day-to-day level, especially for SO_4^{2-} and Cl^- values, revealed potential pollution incidents. Comparison with meteorological data of the area for the corresponding period did not show any significant correlation between measured concentrations and rainfall quantity, indicating a negligible effect of surface drainage on water quality.

Keywords: Environmental pressures; Water quality monitoring; Multi-parameter sensor network; Kozani lignite mines region; Aquatic resources pollution

1. Introduction

A primary goal of the Water Frame Directive (2000/60/EC) is the uniform and continuous monitoring and evaluation of all water bodies (surface, groundwater, etc.) for a whole territory. Between the physical, chemical, biological, and ecological parameters that should be monitored in appropriate frequency, there are several parameters that should be monitored in real time,

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and they are indicative of a general status of water quality (pH, conductivity, temperature, etc.). Real-time monitoring provides a useful capability, which cannot be obtained by a sampling program consisting in the collection of grab samples. Today, technology permits the transmission and retrieval of data from almost every location. At the same time, there are sensitive areas where deterioration of surface water quality has been observed due to point sources, or due to a number of single incidents of pollution. In such cases, real-time monitoring can support the implementation of preventive or suppressive measures, expanding from a simple data collection system to a warning system, by setting the acceptable value limits for each measured parameter, using the appropriate customized software [1–3].

Operation of a water quality monitoring station provides an almost continuous record of water quality that can be processed and published or distributed directly by telemetry to the Internet. The water-quality record through the variations recording in water quality can also serve as the basis for computation of constituent loads at a specific site. Data from the sensors can be used to estimate potential loading of other constituents, if a significant correlation can be established, often by the application of regression analysis.

Major considerations in the design of a continuous water quality monitoring station include selection of the monitor configuration, types of monitors and sensors, site selection, locations of the sensors in the aquatic environment, use and calibration of field meters, and the actual operation of continuous water-quality monitors. Sensor and site selection are guided by the targets of water quality monitoring and the data objectives. The primary issue in the placement of the sensors is the selection of an appropriate, stable, secure location representative of the aquatic environment [1].

Coal excavation activities may cause significant environmental impacts, affecting adversely the aquatic ecosystems. Waste runoffs with a high pollution loading (i.e. acid mine drainage (AMD)) from regions with active or even abandoned coal mines and from landfills where excavation and thermoelectric power stations by-products (i.e. ash) are disposed, contribute to surface and underground aquatic resources pollution.

Acid rock drainage (ARD) is produced by the oxidation of sulfide minerals, chiefly iron pyrite or iron disulfide (FeS_2). This is a natural chemical reaction which can proceed when minerals are exposed to air and water. The ARD occurring when sulfide ores are exposed to the atmosphere may be enhanced through mining and milling processes where oxidation reactions are initiated. Mining increases the exposed surface area of sulfur-bearing rocks allowing for excess acid generation beyond natural buffering capabilities found in host rock and water resources. Collectively, the generation of acidity from sulfide weathering is termed as AMD. Mine tailings and waste rock, having much greater surface area than in-place geologic material due to their smaller grain size, are more prone to generating AMD. Since large masses of sulfide minerals are exposed quickly during the mining and milling processes, the surrounding environment can often not attenuate the resulting low pH conditions. Metals that were once part of the host rock are solubilized and exacerbate the deleterious effect of low pH on terrestrial and aquatic receptors. Concentrations of common elements such as Cu, Zn, Al, Fe, and Mn dramatically increase in water under low pH. Logarithmic increases in metal levels in water from sulfide-rich mining environments are common, where surface or groundwater pH is depressed by acid generation from sulfide minerals. These environmental, human health, and fiscal consequences, if not mitigated, can have long-lasting effects [4].

The AMD, characterized by acidic metalliferous conditions in water, is responsible for physical, chemical, and biological degradation of stream habitat. Water contaminated by AMD, often containing elevated concentrations of metals, can be toxic to aquatic organisms, leaving receiving streams devoid of most living creatures [4].

On the other hand, combustion of coal in thermal power stations for electricity generation produces large volumes of coal combustion residues and particularly fly ash, which is accumulated in on-site piles and ash ponds within the mines; such a disposal is leading to serious environmental problems, particularly contamination of ground and surface waters due to leaching of trace elements.

From the application of physicochemical and ecotoxicological analyses for the characterization of fly ash samples collected from various coal power plants, rather high concentrations of chromium and sulfate anions were found. The higher toxicity values were observed for the leachates with relatively high chromium concentration and mainly in the case of low alkaline fly ash [5].

In western Macedonia region and particularly in Kozani area, there are significant underground and surface water resources (i.e. lakes Zazari, Cheimaditida, Petron, Vegoritida, Polyfitou, etc.). The main activities, which are deemed to affect the quality characteristics of the above aquifers directly or indirectly [6], are:

- the operation of Public Power Corporation's (PPC) lignite mines;
- the operation of PPC thermal stations;
- agricultural activities;

- livestock activities;
- municipal activities; and
- other industrial activities.

However, the potential pollution sources related to excavation and electrical energy generation activities of PPC are the most critical for the quality of the water resources of the area. The other activities previously described might affect the water quality of the region to a rather limited extent compared to the strong environmental impact due to PPC activities. For example, the extended use of fertilizers in farms contributes to nitrogen pollution, as well as to waste disposal from livestock activities. Municipal wastewater from local residential areas is discharged to the aquatic resources of the area, along with wastewater from other industrial activities (i.e. slaughterhouses, dairy industry, etc.).

In the present study, a water quality continuous monitoring stations network was installed within the environmentally "sensitive" lignite mines area of Ptolemaida in order to monitor the surface and underground water quality of the aquatic resources of the area and to investigate potential pollution incidents.

2. Methodology

2.1. Multi-parameter sensors for water quality monitoring: technical description

The Watertool II system (developed by Terramentor E.E.I.G) was used for the water quality monitoring of the target area bodies. This system comprises in a probe containing the measuring elements (electrodes and other sensors) protected by a robust cylindrical metal casing (Fig. 1). The other basic components are the digitizing and control/storage unit and a data transfer unit [7].

The Watertool II system can measure simultaneously up to 15 physicochemical parameters (channels); for the current study, temperature, conductivity, pH, nitrate ions (NO_3^-), chloride ions (Cl^-), and sulfate ions (SO_4^{2-}) were measured, and the values were recorded every 10 min. Concentrations are measured with ion-selective electrodes which along with the various sensors are fitted at the lower end of the probe [7–9].

The Watertool II was deployed as a network of stations augmented with wireless telemetry (3G ADSM) in order to transfer data through the Internet. Moreover, the system is supported with software for automatic measurement of certain parameters, electrodes calibration, performance of diagnostic tests and verification, and processing and visualization of the data. The software may be used as a warning system, when pollutant concentrations exceed certain predefined thresholds.

In order to ensure the efficient operation of the water quality monitoring systems, special insulated air-conditioned boxes with metal frame were constructed (dimensions $1 \times 1 \times 1\,m^3$) as presented in Fig. 2. These boxes provide the necessary protection of the measuring equipment from exposition to:

- adverse weather conditions (rain, snow, etc.),
- extreme temperature changes (>40°C during summer or <−5°C during winter) which might possibly affect the systems functionality, and
- vandalism, stealing, etc.

Calibration and operational control of the electrodes/sensors were performed periodically (monthly) in the laboratory for each electrode/sensor separately, using standard solutions in order to ensure the proper

Fig. 1. The multi-parameter sensors system (Watertool II).

Fig. 2. Special boxes for the protection of the measuring equipment.

Table 1
Technical and calibration data of electrodes/sensors

Parameter	Range	Accuracy	Resolution	Calibration
Temperature	−2 to +40°C	±0.01°C	0.001°C	From supplier
Conductivity	1–10, 0.1–1 and 0.01–0.1 S/m	±0.03% of range	0.01% of range	Standard KCl solution 0.002–0.005 M (check) and calibration from supplier
pH	0–14 pH units	±0.05 pH units	0.01 pH units	Buffer solutions 4 and 7 pH units
NO_3^-	6.1–50,000 mg/l	0.1	0.01	Standard $NaNO_3$ solutions 0.001–0.01–0.1 M
Cl^-	3.5–30,000 mg/l	0.1	0.01	Standard NaCl solutions 0.001–0.01–0.1 M

operation of the probes and the measurements reliability (see Table 1).

Sulfate ions electrode was periodically calibrated from the supplier depending on performance.

2.2. Installation of the multi-parameter sensors network

The monitoring stations network consisted of three stations. After a thorough study of the wider lignite mines area, three locations were selected for the installation of the water quality monitoring stations (Fig. 3):

- Station 0033 was installed in "Soulou" water stream near a bridge within the lignite mines area;
- Station 0034 was installed in a water drilling within the lignite mine area (near Station 0033); and
- Station 0035 was installed in the effluent stream of Ag. Dimitrios PPC Thermal Station.

Fig. 3. Location of the water quality monitoring stations in Ptolemaida lignite mines area.

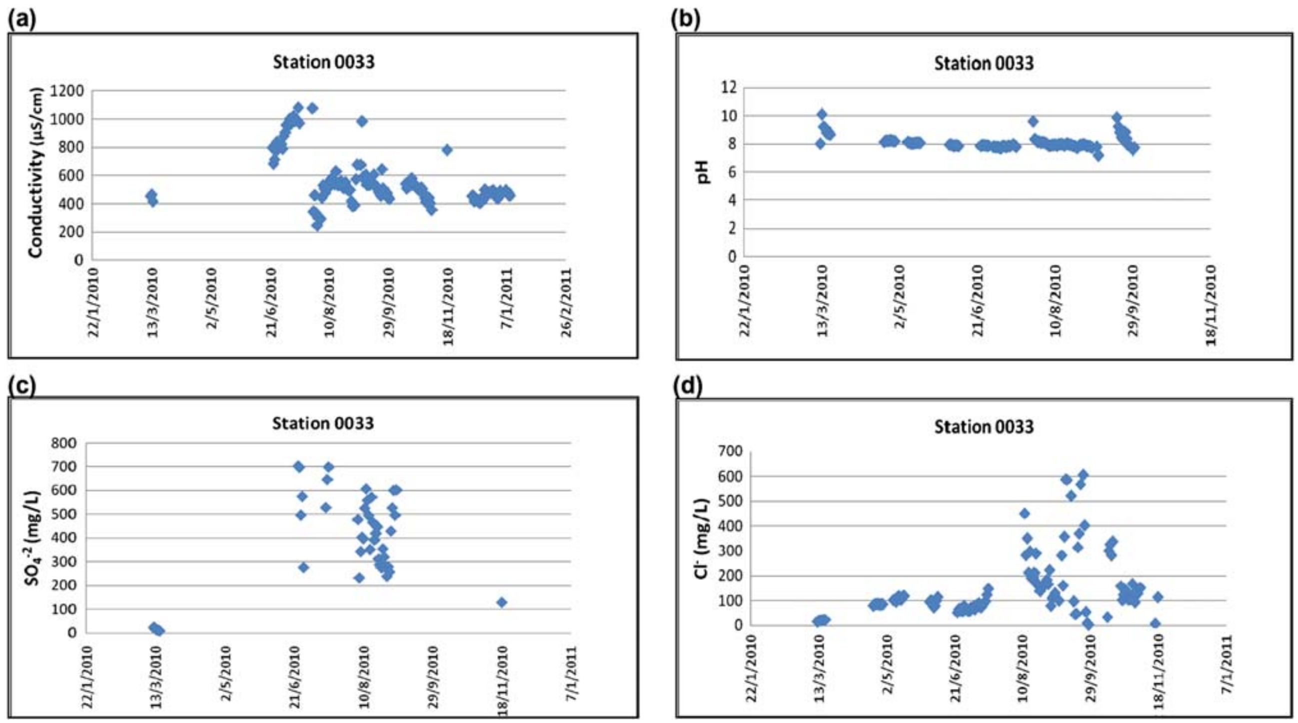

Fig. 4. (a) Conductivity; (b) pH; (c) SO_4^{2-}; and (d) Cl^- daily average values vs time from “Soulou” stream monitoring station (0033).

The main criteria taken under consideration for the location of the monitoring stations were the distance from the lignite mines, the proximity to surface and ground water, previous measurement records, accessibility, safety, etc. All three monitoring stations were installed to the corresponding positions within March 2010.

It should be noted that surface water runoffs from lignite mines area, after treatment in sedimentation basins, are discharged to “Soulou” water stream [10]. During summer period, the water from “Soulou” stream is used for irrigation. “Soulou” water stream ends in Lake Vegoritis, both of which are considered as “sensitive” aquifers according to current national legislation [11].

2.3. Limitations concerning the installation and operation of monitoring systems

Since the beginning of the study and throughout the measurement period certain obstacles and limitations arose which, depending on their nature and importance, were confronted to a certain level, in order not to affect the outcomes of the current study. These issues included [12]:

- delay of the monitoring stations installation within the lignite mines area, due to licensing procedures and bureaucracy;
- complementary infrastructure work during installation (fixation of boxes with cement bases, wiring for electrification, etc.);
- certain adjustments and tests during start-up/trial period in order to ensure the measurements reliability after installation of the water quality monitoring stations;
- problems to the measurements data transfer as well as to the remote desktop control due to periodical failures of the wireless 3G connection (ADSM) as a result of bad signal in the specific area. Several tests and adjustments were made in order to reinforce the wireless connection (rooter replacement, use of external antenna, etc.); however, the problem still existed. Finally, a certain software tool was developed and installed, which periodically checked the existence of wireless connection and in case of failure, it restored the connection;
- technical and operational issues related to software functionality, probes insulation, etc.;
- unpredictable incidents during operation, which resulted to the failure of monitoring stations for a certain time period (i.e. damage in the protective

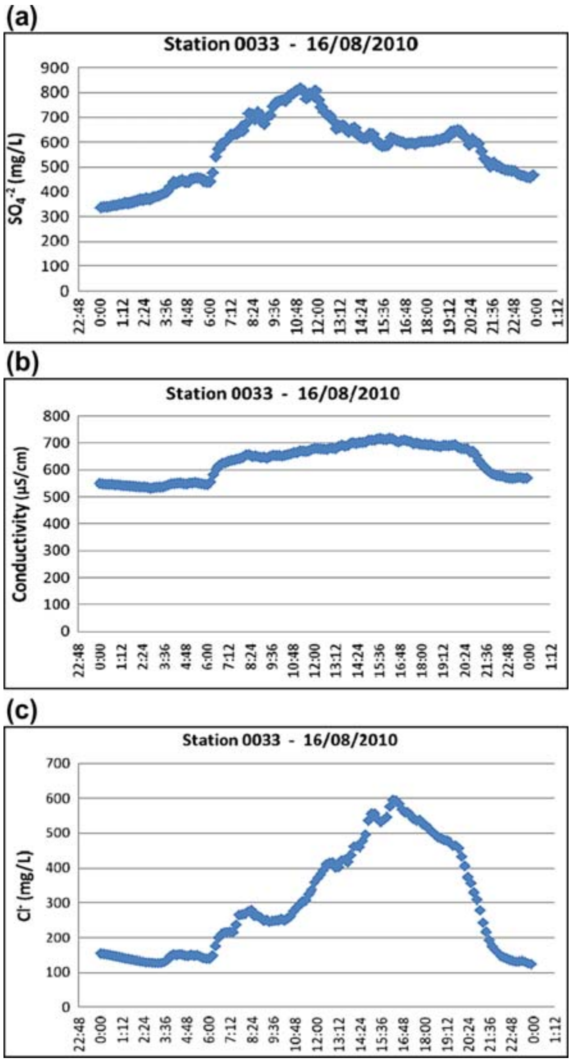

Fig. 5. (a) SO_4^{2-}; (b) conductivity; and (c) Cl^- measurements on 16 August 2010 from "Soulou" stream monitoring station (0033).

shell of Watertool probe 0035 due to turbulent water flow, accidental shut-off of the power supply wiring in Watertool probe 0033);

- limited lifetime of the electrodes. According to the supplier, the electrodes have a lifetime period from 6 to 12 months and after that period, depending on their previous use, the performance is gradually reduced and their replacement is recommended in order to achieve reliable results. Periodical calibration and quality control with standard solutions (monthly) was performed in the laboratory for the electrodes validation.

3. Results and discussion

The recorded data from the three monitoring stations are presented in the following diagrams as daily averages for a measuring period of about 10 months (from March 2010 to January 2011). It should be mentioned that measurements raw data were processed in terms of quality and consistency using descriptive statistics (box plot analysis) as well as expert judgment and, therefore, outliers and extreme values (i.e. due to electrodes operational problems) were excluded.

Regarding "Soulou" water stream (Station 0033—Fig. 4), the measurements showed a rather wide conductivity fluctuation from 248 to 1,082 µS/cm. The measured temperature values were found to be from 4 to 25˚C, depending on the season. The NO_3^- concentration measurements were limited due to electrode's operational problems; however, they varied from 12 to 19 mg/L. The pH values were quite stable with low fluctuations around 8. However, SO_4^{2-} and Cl^- average concentrations appeared higher than expected compared to PPC's available spot measurements in Soulou stream expressed as average concentrations (92.18 mg/L SO_4^{2-} and 17.40 mg/L Cl^-), especially during summer period [10].

Detailed analysis of day-to-day values (measurement every 10 min) was performed; on 16 August 2010, as shown in Fig. 5, a peak in SO_4^{2-} concentration took place with a maximum value of 809 mg/L. Furthermore, this peak appeared to correlate with a corresponding increase in Cl^- content and in conductivity, indicating a pollution incident of the water stream.

Data recorded from the water drilling station within the lignite mines area (Station 0034) are presented in the following diagrams (Fig. 6).

The recorded values from the water drilling monitoring station (Station 0034) showed a conductivity variation from 308 to 912 µS/cm. The measured temperature values were measured from 9 to 26˚C, depending on the season. The NO_3^- average concentration values were varied from 3 to 22 mg/L. The pH values appeared rather stable with an average value of 7.6. SO_4^{2-} and Cl^- average concentrations appeared to have some fluctuations, especially during August and September. It should be noted that the specific drilling operated periodically and Monitoring Station 0034 received water from other drillings of the lignite mines area when the particular one did not operate. This could explain the rather wide variation in the measured values. Detailed analysis of the values showed that (Fig. 7) the observed peaks in SO_4^{2-} concentration were directly related to the corresponding pH values decrease. This could be an indication of AMD; however, further analytical investigation is required for the complete identification of the pollution origin.

Monitoring station of Ag. Dimitrios power plant (Station 0035—Fig. 8) showed a rather wide conduc-

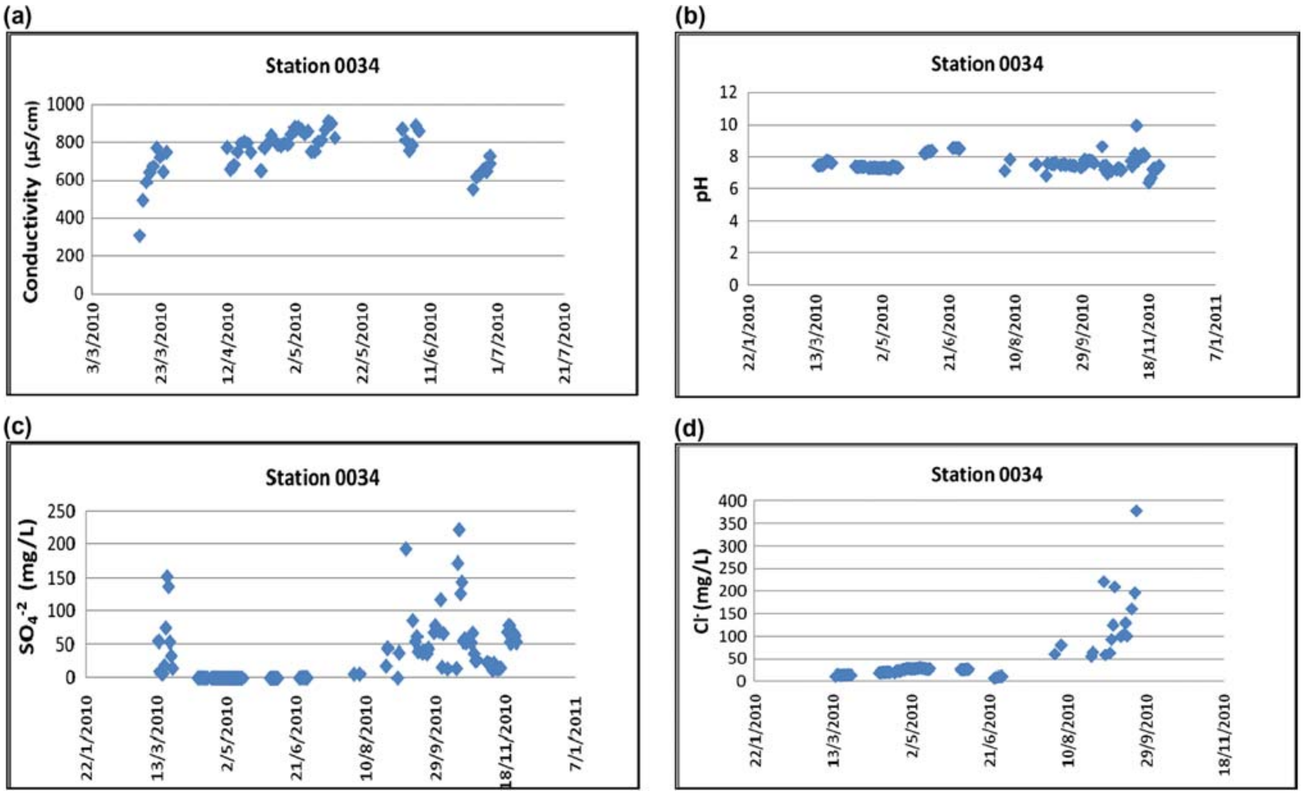

Fig. 6. (a) Conductivity; (b) pH; (c) SO_4^{2-}; and (d) Cl^- daily average measured values vs time from "drilling" monitoring station (0034).

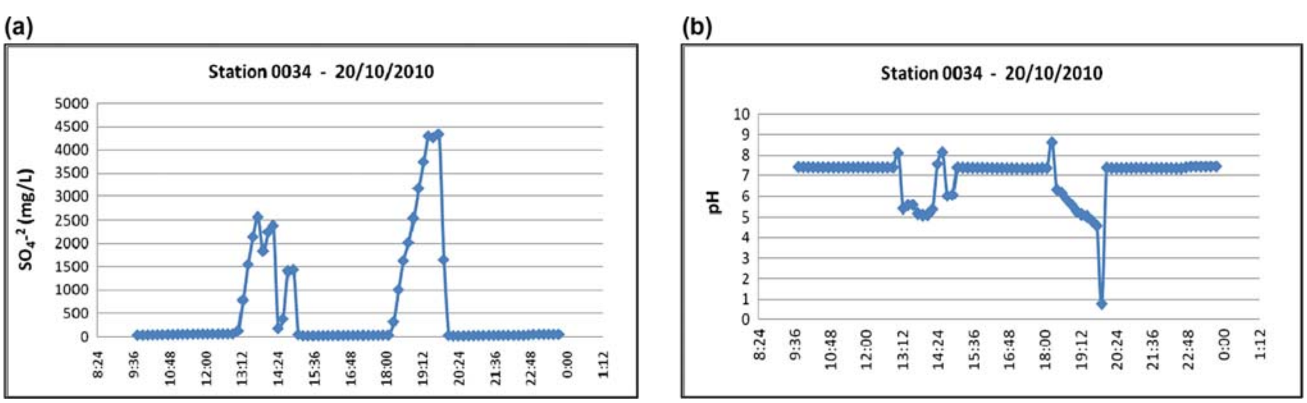

Fig. 7. (a) SO_4^{2-} and (b) pH measured values on 20 October 2010 from "drilling" monitoring station (0034).

tivity distribution from 188 to 839 μS/cm, related to the discharge of the plant wastewater effluent. The temperature values ranged from 20 to 36℃. The pH values were about 8.3; NO_3^- average concentration values were between 8 to 186 mg/L, and were attributed to the wastewater effluent characteristics. The Cl^- average values varied from 13 to 316 mg/L.

In addition to the above online measurements, certain other complementary physicochemical parameters have been measured, based on standard methods, on 20 triplicate samples collected from the same points as the monitoring stations during the same period and the corresponding results are presented in the following Table 2. These parameters did not appear to be correlated with the online measurements.

Furthermore, in order to investigate potential correlation between measured concentrations and rain precipitation level in the area, that could reveal poten-

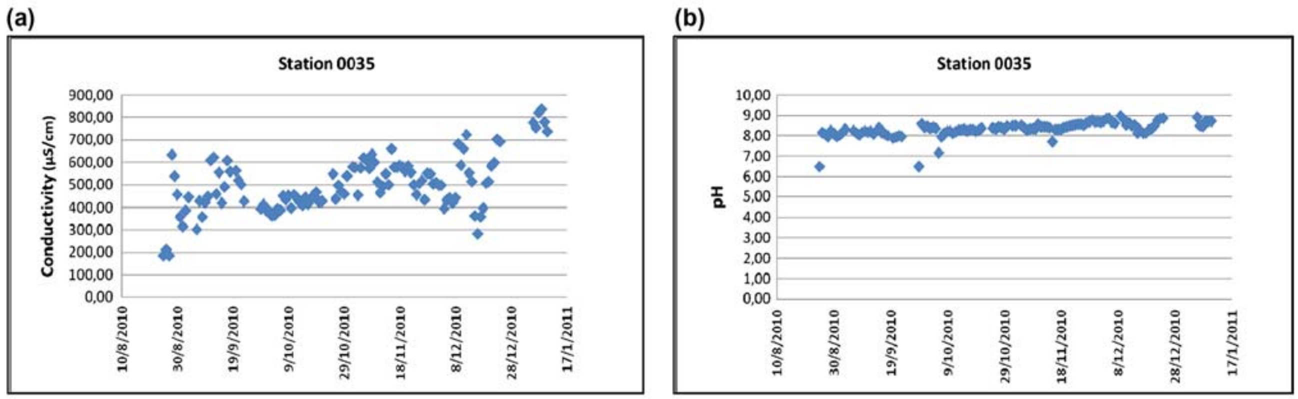

Fig. 8. (a) Conductivity and (b) pH daily average measured values vs time from "Ag. Dimitrios" PPC monitoring station (0035).

Table 2
Physicochemical parameters (average values) measured analytically in 20 triplicate water samples within 2010

Parameter	Method of analysis	"Soulou" water stream	Water drilling—lignite mines area
Turbidity (NTU)	APHA 2130 B SMEWW 21st ed. 2005	72.1	1.22
Hardness (mg/L $CaCO_3$)	APHA 2340 C – Hardness SMEWW 21st ed. 2005	489	291
COD (mg/L)	Merck Method 023 analogous to EPA 410.4, APHA 5220 D SMEWW 21st ed. 2005, and ISO 15705	64	35
BOD_5 (mg/L)	APHA 5210 B-D SMEWW 21st ed. 2005	50	15
DO (mg/L)	APHA 4,500-O G SMEWW 21st ed. 2005	5.5	1.7
TSS (mg/L)	APHA 2540-Solids D SMEWW 21st ed. 2005	862	328
NO_2^- (mg/L)	APHA 4,500-NO_2^- B SMEWW 21st ed. 2005	0.43	0.007
NH_4^+ (mg/L)	APHA 4500-NH3 F SMEWW 21st ed. 2005	0.878	1.76
Fe (µg/L)	APHA 3500-Fe B SMEWW 21st ed. 2005 (& EN ISO 15586:2003)	105.6	< 10
Al (µg/L)	APHA 3500-Al B SMEWW 21st ed. 2005	< 6	< 6

tial pollution dispersion or dilution, meteorological data from the Meteorological Station of Ptolemaida were used on a monthly and daily basis [13]. The rainfall for the period of study varied from 0 to 38 mm (max) on daily basis. However, as presented in the following Figs. 9 and 10, the comparison between the surface water characteristics (Station 0033) and the rainfall level for the corresponding time period did not show any significant correlation.

4. Conclusions

Online monitoring systems provide a very modern and useful tool for monitoring natural dynamic changes, as well as pollution incidents in water ecosystems. During the current study, a network of three multi-parameter sensor systems was installed in the wider lignite mines region of Kozani, since potential pollution problems associated to excavation and power generation activities were expected to mostly affect the quality of the water resources of the area, more than the other environmental pressures (i.e. agricultural activities, municipal wastewater discharges, etc.). The aim of the three multi-parameter sensor systems network was to monitor the surface and groundwater quality of the aquatic resources of the area and to investigate potential impacts due to pollution incidents. The design, installation, and operation for about 10 months of this monitoring network resulted to the following conclusions:

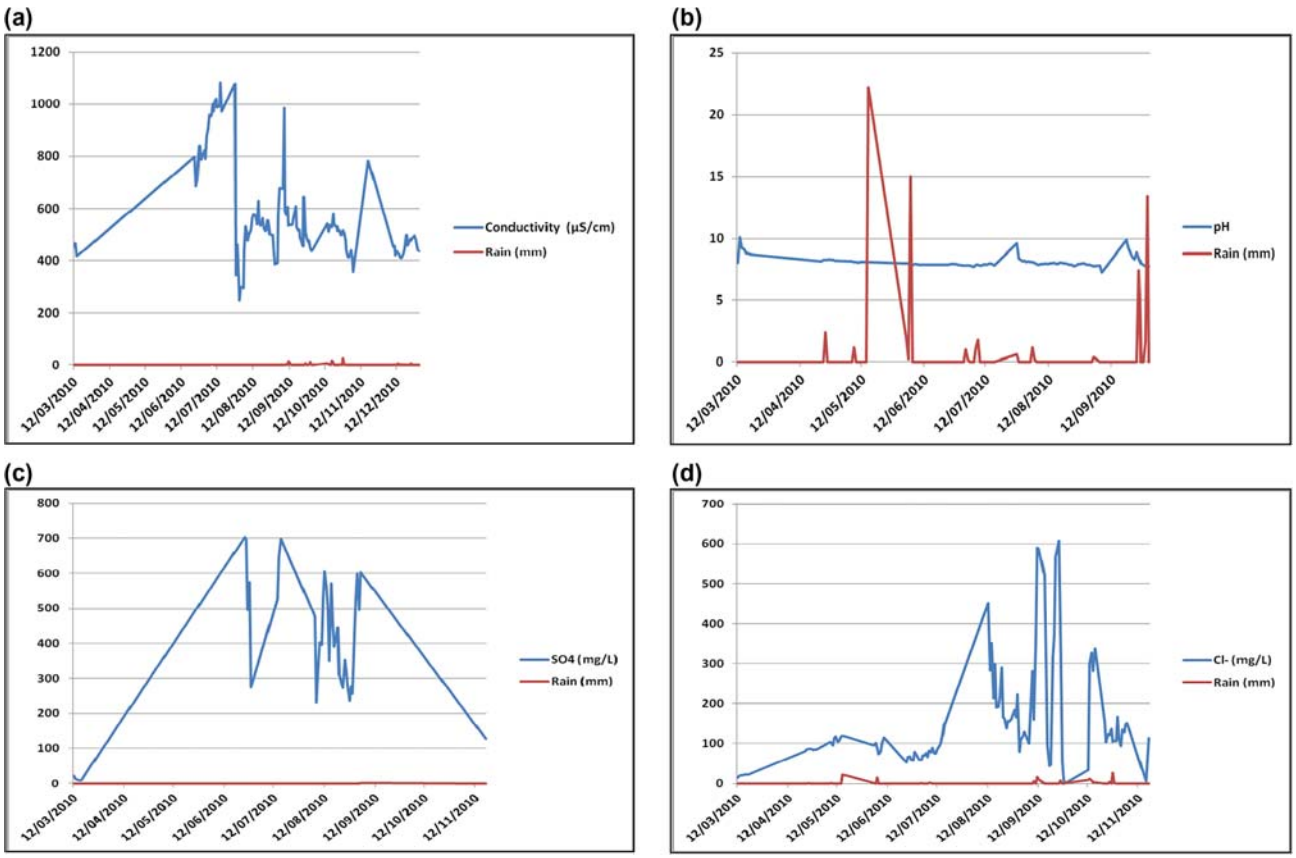

Fig. 9. (a) Conductivity; (b) pH; (c) SO_4^{2-}; and (d) Cl^- daily average values vs rainfall from "Soulou" stream monitoring station (0033).

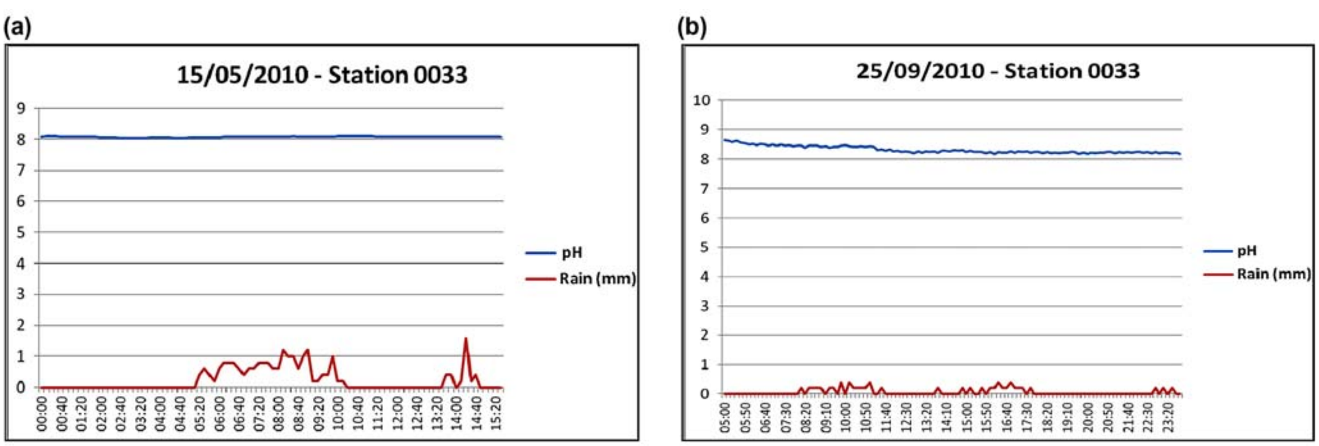

Fig. 10. pH values vs rainfall on 15 May 2010 and 25 September 2010 from "Soulou" stream monitoring station (0033).

- The sampling point selection, the measuring equipment durability/reliability, the protection of equipment, the systematical equipment calibration, and the effective data transfer method are critical factors to the success of the online monitoring network operation; therefore, special attention should be paid in the monitoring process.

- The pH values presented the highest stability with the lowest fluctuation in all three monitoring stations.
- Observed fluctuation in conductivity values appeared to relate directly to the changes in the water quality characteristics especially in the surface water monitoring sites.
- The NO_3^- values showed a wide dispersion only in Ag. Dimitrios PPC Station and were attributed to the discharge of the wastewater treatment plant effluents.
- Detailed analysis of recorded measurements on a day-to-day level, especially for SO_4^{2-} and Cl^- values, might reveal potential pollution incidents. Furthermore, correlation of certain parameters (i.e. SO_4^{2-}, Cl^-, and conductivity or SO_4^{2-} and pH) could possibly be an indication of water pollution (i.e. due to AMD).
- The quantity of rainfall does not seem to have a significant impact (i.e. dispersion or dilution) to the surface water loads for the corresponding time period, as it was derived from relevant data, indicating a negligible effect of surface drainage on water quality.

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