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Water Quality Monitoring and Associated Distributed Measurement Systems: An Overview

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1. Introduction

Water is essential to life, as we know it. However, statistics reveal that, in 2000, one billion people lacked access to safe drinking water and 2.4 billion to adequate sanitation. To achieve United Nations target of reducing by half the proportion of people without sustainable access to safe drinking water by 2015, an additional 1.5 billion people would require access to some form of improved water supply by 2015, that is an additional 100 million people each year (or 274,000/day) until 2015.

Because water sources are limited, it is of paramount importance to keep its quality at the highest level possible. Threats to water are manifold, from industry to natural phenomena, and water quality assurance is a basic environmental issue involving from political to technical aspects and options, but it is obvious that no assessment of water quality is possible without a quantitative identification of some characteristics, a process commonly called water quality monitoring.

This chapter is an overview on water quality and on its monitoring. The text reflects he experience of the authors on the subject, presents some research and development results they obtained in the last decade and includes data gathered from different sources, namely from USEPA reports and North Caroline State University Water Quality Group documents. The text includes remarks about measuring techniques for different water quality parameters that result from the experience acquired by the authors in the implementation of several water quality measuring units. The last part of the chapter proposes architectures and intelligent signal processing techniques for distributed water quality monitoring networks.

2. Water quality

Water quality is commonly defined by its physical, chemical, biological and aesthetic (appearance and smell) characteristics. Water may be used for drinking, irrigating crops and watering stock, industrial processes, production of fish, shellfish and crustaceans, wildlife

habitats, protection of aquatic ecosystems, navigation and shipping, recreation (swimming, boating), and scientific study and education.

2.1 Factors influencing water quality

Water quality is closely linked to the surrounding environment and land use. Liquid water is never pure and is affected by agriculture, urban, industrial and recreation uses. The modification of natural stream flows and the weather can also have a major impact on water quality.

Groundwater is a major source of water and, when close to urban or industrial development, is vulnerable to contamination.

Generally, water quality of rivers is best in the headwaters, where rainfall is often abundant, declining as rivers flow through regions where land use and water use are intense and pollution from intensive agriculture, large towns, industry and recreation areas increases. There are of course exceptions to the rule and water quality may improve downstream, behind dams and weirs, at points where tributaries or better quality groundwater enter the mainstream, and in wetlands.

Rivers frequently act as conduits for pollutants by collecting and carrying wastewater from catchments and, ultimately, discharging it into the ocean. Storm water, which can also be rich in nutrients, organic matter and pollutants, finds its way into rivers and oceans mostly via the storm water drain network.

2.2 Water quality and ecosystems

An ecosystem is a community of organisms - plants, animals, fungi and bacteria - interacting with one another and with the environment in which they live. Protecting aquatic ecosystems is in many ways as important as maintaining water quality, for the following reasons:

- Aquatic ecosystems are an integral part of our environment. They need to be maintained if the environment is to continue to support people. World conservation strategies stress the importance of maintaining healthy ecosystems and genetic diversity.
- Aquatic ecosystems play an important role in maintaining water quality and are a valuable indicator of water quality and the suitability of the water for other uses.
- Aquatic ecosystems are valuable resources. Aquatic life is a major source of protein for humans. In most countries, like Portugal, commercial and sport fishing is economically important.

2.3 Water quality assessment

The presence of contaminants and the characteristics of water are used to indicate the quality of water. These water quality indicators can be categorized as:

Biological: algae, bacteria

Physical: temperature, turbidity and clarity, color, salinity, suspended solids, dissolved solids, sediment

Chemical: pH, dissolved oxygen, biological oxygen demand, nutrients (including nitrogen and phosphorus), organic and inorganic compounds (including toxicants)

Aesthetic: odors, taints, color, floating matter

Radioactive: alpha, beta and gamma radiation emitters.

Measurements of these indicators can be used to determine and monitor changes in water quality and to determine whether the quality of the water is suitable for the health of the natural environment and the uses for which the water is required.

The design of water quality monitoring systems is a complex and specialized field. The range of indicators that can be measured is wide and other indicators may be adopted in the future. The cost of a monitoring system to assess them all would be prohibitive, so resources are usually directed towards assessing contaminants that are important for the local environment or for a specific use of the water.

The paragraphs that follow detail several aspects of these quantities, algae, bacteria and radiations excluded. The paper includes a short reference to systems for on-line, in-situ water quality monitoring and ends with a list of references.

3. Water quality parameters and measuring techniques

3.1 Temperature

Temperature is an important water parameter because it is an influence quantity for the generality of other water parameters and also because it determines many physical characteristics of a water body. In the winter, water's temperature-dependent density allows aquatic life to survive. Ice is formed at 0 ^{o}C and thus remains at the top of the water body. Sun shining through the ice will serve to warm the water below slightly, keeping the temperature just above freezing. Water at 4 ^{o}C is the densest, and will sink to the bottom and be replaced by lighter 1 - 3.9 ^{o}C water. The continual process of heating and sinking keeps the water body from freezing entirely [1].

In addition, temperate lakes stratify during the summer because of water's temperature-dependent density. Stratification prevents the mixing of oxygen and nutrients in the water body, and often encourages dissolved oxygen depletion. During the spring, stratification will break down allowing mixing of oxygen and nutrients. During the fall, the water body loses heat until its temperature is uniform at 4 ^{o}C. Wind creates circulation, which distributes oxygen and nutrients throughout the water body (fall overturn). Eventually, the surface water layer falls below 4 ^{o}C, becomes less dense, and remains at the surface. Ice will form if temperatures are low enough; otherwise, this upper layer will remain just above 0 ^{o}C. Deeper water will remain roughly at 4 ^{o}C until spring [1].

Higher temperatures often exacerbate low dissolved oxygen level problems in lakes and reservoirs. High temperatures encourage the microbial breakdown of organic matter, a process that requires dissolved oxygen. Unfortunately, warm water naturally holds less

dissolved oxygen. Thus, persistent warm conditions may lead to a depletion of dissolved oxygen in the water body.

3.1.1 Measuring techniques

3.1.1.1 Temperature probes

Temperature range is usually from 0 to 30 ºC. Thus thermistor, platinum or even electronic based probes are adequate. Some manufacturers, like Quanta, commercializes probes that can measure several water parameters, including temperature (multi-parameter probes).

3.2 Turbidity

Turbidity is a quantity quantifying the degree to which light traveling through a water column is scattered by the suspended organic (including algae) and inorganic particles. Light scattering increases with the quantity of solids suspended in water. According to the research work developed by Campbell Scientific, usually the values of turbidity are correlated with the suspended solids concentration –SCC (Fig. 1); however, cases are also reported where no correlation between these two quantities is registered. Turbidity is commonly measured in Nephelometric Turbidity Units (NTU).

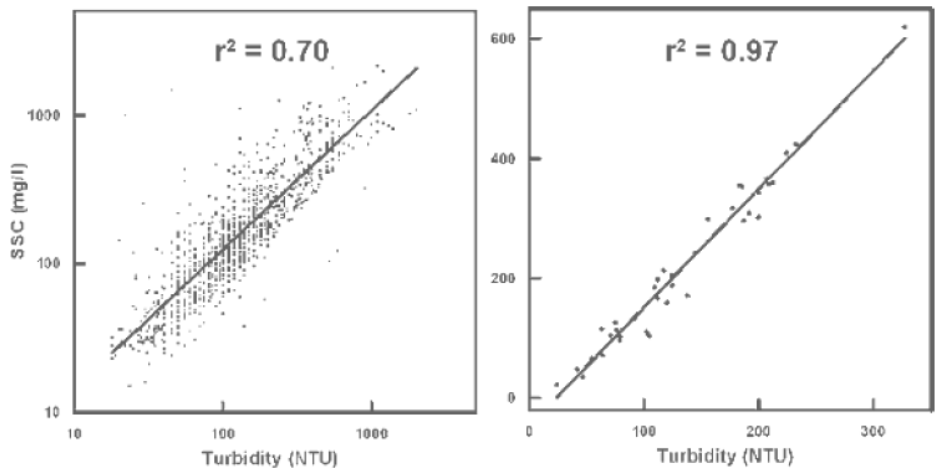

Fig. 1. The graph on the left provides measurements of runoff from a freeway, which indicates a bad correlation between SSC and turbidity. The graph on the right provides measurements from San Francisco Bay that indicates a good correlation between SSC and turbidity (Campbell Scientific document)

The velocity of the water resource largely determines the composition of the suspended load. Suspended loads are carried in both the gentle currents of lentic (lake) waters and the fast currents of lotic (flowing) waters. Even in flowing waters, the suspended load usually consists of grains less than 0.5 mm in diameter (Table 1). Suspended loads in lentic waters usually consist of the smallest sediment fractions, such as silt and clay [2].

Sediment class	Size (mm)
Sand	
V. Coarse	1.5
Medium	0.375
V. Fine	0.094
Silt	
V. Coarse	0.047
Medium	0.0117 (not visible to the human eye)
V. Fine	0.0049
Clay	< 0.00195

Table 1. Size classification of sediments (adapted from [3]).

3.2.1 Numerical categories

Designated Use	Acceptable Ranges
Recreation	5 NTU [4]
Aquatic Life	< 50 NTU instantaneously or
	< 25 NTU for a 10 day average [5]
	< 10 NTU for trout waters or
	< 25 NTU for streams (non-trout waters) or
	< 50 NTU for lakes and reservoirs (non-trout waters) [6]

Human Consumption 1 to 5 NTU (up to 5 NTU is allowed if the water supplier can demonstrate that this level does not interfere with:

1. disinfection
2. maintenance of a disinfecting agent
3. microbiological determination [7]

Turbidity may be due to organic and/or inorganic constituents. Organic particulates may harbor micro organisms. Thus, turbid conditions may increase the possibility for waterborne disease. Inorganic constituents have no notable health effects.

If turbidity is largely due to organic particles, dissolved oxygen depletion may occur in the water body. The excess nutrients available will encourage microbial breakdown, a process that requires dissolved oxygen. In addition, excess nutrients may result in algal growth. Although photosynthetic by day, algae respire at night, using valuable dissolved oxygen. Fish kills often result from extensive oxygen depletion.

3.2.2 Measuring techniques [8]

Nephelometric Method: Comparison of the light scattered by the sample and the light scattered by a reference solution [9].

- *Detection limits:* Should be able to detect turbidity differences of 0.02 NTU with a range of 0 to 100 NTU.

- *Interferences:* Rapidly settling coarse debris, dirty glassware, presence of air bubbles, and surface vibrations.

It is important to underline that turbidity is a measurement of the light scattering intensity relatively to the one that is obtained with the turbidity calibration standards. Visual clarity, measured as Secchi [10][11] or black disc visibility, is a direct measurement of the amount of suspended solids in water but its measurement requires more expensive equipments. Nevertheless, clarity measurements are more precise than turbidity measurements.

3.3 Salinity

The total dissolved solids (TDS) in water consist of inorganic salts and dissolved materials. In natural waters, salts are chemical compounds comprised of anions such as carbonates, chlorides, sulphates, and nitrates (primarily in ground water), and cations such as potassium (K), magnesium (Mg), calcium (Ca), and sodium (Na) [12]. In ambient conditions, these compounds are present in proportions that create a balanced solution. If there are additional inputs of dissolved solids to the system, the balance is altered and detrimental effects may be seen. Inputs include both natural and anthropogenic sources.

3.3.1 Numerical categories

Designated Use	(mg/l)
Human Consumption	500 TDS
	250 chloride
	250 sulphate
Irrigation	500-1 000 TDS (dependent upon crop sensitivity)
	250 mg/l chloride
Industry *	
Brewing	
Light beer	500 TDS
Dark beer	1000 TDS
Pulp and paper	
Fine paper	200 TDS
Ground wood paper	500 TDS
Boiler feed water	50 to 3000 TDS depending on pressure
Canning/Freezing	850 TDS
Aquatic Life	Varies, depending on natural conditions

*Industry can de-ionize water to meet requirements; economics is the limiting factor [12].

Table 2. Salinity: designated use limits [13].

3.3.2 Total dissolved solids and conductivity

The presence in water of different anions and cations in different proportions leads to different values of water electric conductivity. However, even if it exists almost a linear relation between salinity and conductivity, that relation depends on the type of the dissolved salt. Moreover, conductivity is a non-selective measurement because instead of salinity, it gives the contribution of all charge carriers and not of a specific one. Notwithstanding, commonly, salinity is indirectly measured using conductivity meters.

As an example, Fig. 2 represents the experiment results of the relation that is obtained between TDS and conductivity for a variable amount of NaCl dissolved in water. In this case, the correlation coefficient between both variables is almost equal to 1, meaning that the relation between both variables is practically linear.

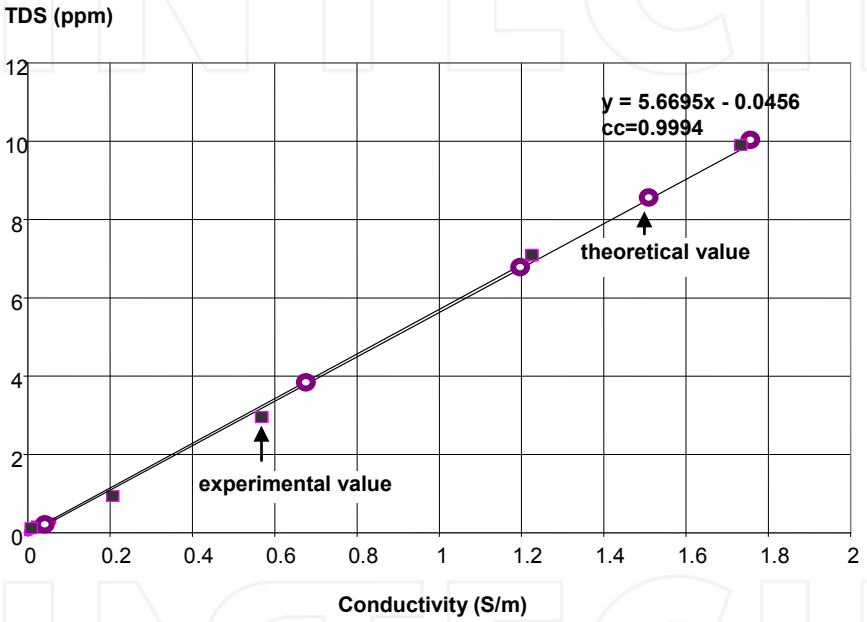

Fig. 2. Experiment results of the relation that is obtained between TDS and conductivity for different values of NaCl dissolved in water (square symbol: experimental data; circle symbol: theoretical data).

It is important to underline that the equation of the straight line that is represented in the graph, namely its slope, depends mainly on the type of salt and on the ionic activity of the elements that are dissolved in the water and on the temperature of the solution.

3.3.3 Measuring techniques [14][15]

1. **Electric Conductivity (EC):** Uses a conductivity bridge calibrated with standard seawater solution. The solution's ability to transmit electricity is facilitated by increasing

salt content. The EC is normally measured in mhos/cm, mmho/cm, or umho/cm (non-SI units) or siemens per meter (S/m) (SI units), depending on dissolved salt concentration.

The conversion of EC values into the total quantity of dissolved salts depends on the dissolved salts and manufacturers of this type of meter use conversion factors such that:

TDS (mg/l) = 50 to 70*EC (S/m) = 500 to 700*EC (mmho/cm).

Note that, in this context, 1 mg/l is approximately equal to 1 ppm and that these conversion factors are some ten times higher than the value obtained from Fig. 2.

A simple sensor for water (or any liquid) electrical conductivity measurement is the two electrode cell [16][17]. The current that flows between two electrodes immersed in the water, when a voltage is applied between them, is a function of all dissolved ionized solids in the solution. Theoretical results of conductivity, σ, are determined from the sensor measured conductance (1/R), using a geometric coefficient or "cell constant" (K_C) that reflects the ratio between the length (d) and the cross-section area (A) of the sampled water volume in which the electrical current actually flows:

$$\sigma = \frac{d}{A}\frac{1}{R} = K_C \frac{1}{R} \tag{1}$$

The cell and associated conditioning circuits are projected to reduce electrode-water interface contributions to the measurement. For instance, almost invariably, alternating current is used in order to minimize the polarization effects [18]. Notwithstanding, these effects cause a nonlinear variation of the cell constant K_C, that can only be compensated by calibration. Thus, it is not convenient to consider K_C as the geometric value of the ratio d/A for the cell, but the value obtained experimentally using solutions of accurate known conductivity.

For high conductance measurements, when coating and electrodes fouling are a concern, the four-electrode based conductivity measuring circuit, as the one presented in Fig. 3, is a more suitable solution [19]. Current is imposed across two drive electrodes and the other two sense electrodes are used for a null-current voltage measurement. Polarization at the drive electrodes has no effect on the measurement, provided the drive voltage is able to maintain the control current through the cell.

Another way to eliminate polarization effects and to obtain contact less measurements is to use an inductive sensing structure [20]. The basic principle consists in the presence of eddy currents induced in the interior of the body under test. These currents are due to the time variation of the magnetic flux originated by the primary coil current. The intensity of the induced currents is related to the electric conductivity of the salty water and there is a correlation between the electrical parameters that can be assessed and the medium conductivity to be determined. In Fig. 4 the simplest form of inductive conductivity sensor is depicted. The sensor is shunted with a capacitance C. It is a transformer whose secondary coil is the surrounding liquid. The primary current phasor, $\bar{I}$, is the sensor signal output.

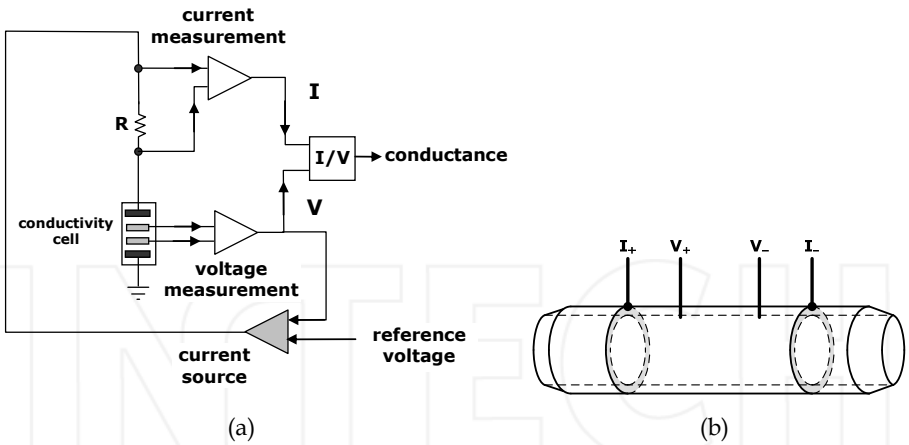

Fig. 3. Four-electrode conductivity cell: (a) measuring circuit and (b) cell structure.

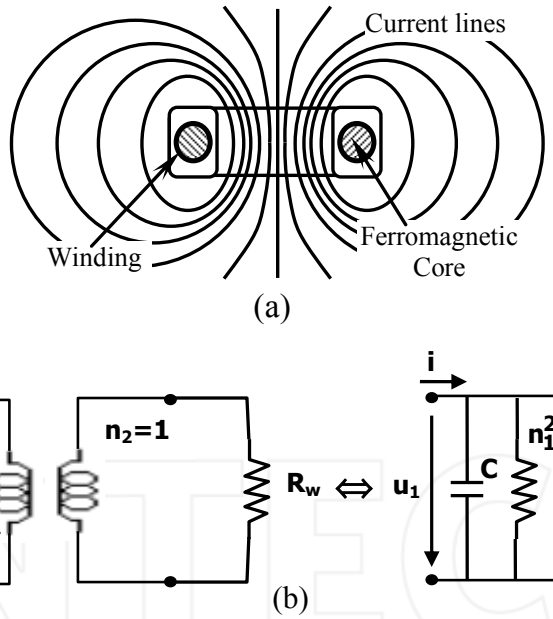

Fig. 4. (a) Inductive sensor with a single ferromagnetic core; (b) Equivalent electrical circuit (Rw- water resistance).

Based on the equivalent circuit of the sensor, presented in Fig.4 (b), the relationship between the applied voltage, u_1, and the sensor output current, i, is:

$$\bar{I} = \left(\frac{1}{n_1^2 R_w} + \frac{1}{j\omega L_{11}} + j\omega C \right) \bar{U}_1 \tag{2}$$

where n_1 is the number of windings, L_{11} the inductance of the coil, C is the capacitance of the shunt capacitor, $\omega=2\pi f$ and f the frequency. By choosing C so that $\omega C=1/\omega L$, the quadrature component of the current is null and the primary current phasor becomes an exact measure of R_W $\bar{I}=\left(\bar{U}_1 / n_1^2 R_W\right)$.

Finally, it is important to underline that conductivity depends on temperature, exhibiting a dependence coefficient approximately equal to 2 %/ºC for salt waters. Hence, it is necessary to normalize the conductivity measurements to a reference temperature, usually equal to 25 ºC.

2. **Density Method:** Uses a precise vibrating flow densimeter.
3. **Gravimetric Method** [8]: As an example, magnesium is measured using the gravimetric method. Diammonium hydrogen phosphate precipitates magnesium in ammonical solution as magnesium ammonium phosphate. The test can be performed two ways. First, the ammonium salts and oxalate can be destroyed, followed by precipitation of magnesium ammonium phosphate. Second, the diammonium hydrogen phosphate can undergo double precipitation without pre-treatment (preferable option). Sample is then dried and weighed.

   Interferences: Presence of aluminium, calcium, iron, manganese, silica, strontium, and suspended matter might interfere with test. Solution should not contain more than 3.5 g NH_4Cl.

3.4 Sediment

Sediment is composed of organic and inorganic particles of various sizes. The major classes of sediment, from largest to smallest, are boulders, cobbles, pebbles, sand, silt, and clay [3],

Class	Size (mm)	Approx size
Boulders	> 256	> Volleyball
Cobbles	> 64	> Tennis ball
Pebbles	> 2	> Match head
Sand		
V. Coarse	1.5	
Medium	0.375	
V.Fine	0.094	
Silt		
V. Coarse	0.047	
Medium	0.0117 (no longer visible to the human eye)	
V.Fine	0.0049	
Clay	< 0.00195	

(Adapted from [3]).

Table 3. Sediment classes.

Sediments are classified into four broad categories, according to their origin in relation to the basin of water in which they are deposited: extrabasinal, carbonaceous, pyroclastic, and intrabasinal.

1. **Extrabasinal (terrigenous) particles:** Terrigenous particles have been eroded from the land outside the body of water experiencing the deposition. The particles either retain their chemical make-up, or become chemically altered to clays and iron oxides.
2. **Carbonaceous particles:** These particles are organic in nature and are derived from either solid carbonaceous material (coal, amber, wax, and kerogen), reworked from other geologic formations, or from modern plant detritus.
3. **Pyroclastic particles:** These particles are derived during the explosive action of a volcano. Particles include rock fragment, single crystals, or bits of volcanic glass.
4. **Intrabasinal particles:** These particles grow biochemically or chemically in the waters experiencing deposition. These particles include carbonate biocrystals, silica biocrystals, particles composed of evaporated minerals, and minerals that grow at the water/sediment interface.

Sediment introduced into surface water is either deposited on the bed of the stream or lake or suspended in the water column (suspended load). Bed load is large sediment particles that move by bouncing along the bottom. Generally, the suspended loads in lotic (flowing) water consist of grains less than 0.5 mm in diameter [2]. Lentic (lake) suspended loads usually consist of the smallest sediment fractions, such as silt and clays [2]. A water body's suspended load is a component of the total turbidity. Any sediment transported by water is subject to deposition as flow velocity decreases [21].

The amount of sediment deposited on a rocky substrate can be quantitatively defined by an estimation of the percent embeddedness. The percent embeddedness is the degree to which fine sediments such as sand, silt, and clay fill the interstitial spaces between rocks on a substrate.

3.4.1 Numerical categories

Acceptable Ranges to Maintain Designated Use

Optimal Ranges	Designated Use
	Aquatic life [22]
< 25% embeddedness	Excellent Conditions
25 - 50% embeddedness	Good Conditions
50 - 75% embeddedness	Fair Conditions
> 75% embeddedness	Poor Conditions
	Industry (total solids) [4]
	Boiler Feedwater
500 – 3000 mg/l	0 - 150 psi
500 – 2500 mg/l	150 - 250 psi
100 – 1500 mg/l	250 - 400 psi
50 mg/l	> 400 psi
200 mg/l	Photographic Processing
200 mg/l	Clear Plastic Production
100 mg/l	Pulp Production

Table 4. Sediment: designated use and optimal ranges.

3.4.2 Measuring techniques

3.4.2.1 Total Suspended Solids (TSS) sampling technique

A number of different methods are available for sampling suspended sediment in streams. Two types of suspended sediment samplers are available for perennial streams: depth-integrating and point-integrating. Both samplers are usually made from cast aluminium or bronze and have a tail fin to orient the sampler's intake nozzle upstream. The depth-integrating sampler is designed to sample continuously as it is lowered at a constant speed from the water surface to the stream bed and back. The point-integrating sampler is equipped with a mechanism at the end of the sampler that can open and collect a sample at a specified depth in the stream [23].

Ephemeral streams are sampled using rising-stage samplers. These samplers have a number of bottles arranged on top of one another in a frame. Each bottle is equipped with kinked tubing pointed into the flow and will collect a sample as the water rises. This sampler is better suited for sampling silts and clays because the intake flow velocity is slower than the stream velocity and larger particles might settle before entering the sampler [23].

Many automated samplers are also available. They differ in cost, ease of maintenance, run time, and ability to extract a representative sample. The samplers extract samples by pumping water from the stream and retaining some in a sample bottle. The samplers can be set to extract samples at set intervals or can be attached to a float that will automatically trigger the sampling process when a pre-selected stream stage is reached [23].

Finally, suspended sediment concentration is often monitored with a turbidity meter. Although turbidity can be influenced by other factors such as size distribution, shape, and absorptivity of the sediment, and the color of the water, turbidity meters give satisfactory estimates [23].

3.4.2.2 Percent embeddedness technique

The amount of sediment deposited on a rocky substrate can be quantitatively defined by an estimation of the percent embeddedness. This method is only applicable on substrates of coarse pebbles, cobbles, or rubble. Percent embeddedness is measured at transect points of an area of known size (e.g. a square 0.5m X 0.5m). The percentages normally assigned to various substrate conditions are [24]:

- *100% embeddedness*= Rocks are completely surrounded by sediment and completely covered by sediment.
- *75% embeddedness*= Rocks are completely surrounded by sediment and half covered by sediment.
- *50% embeddedness*= Rocks are completely surrounded by sediment but are not covered by sediment.
- *25% embeddedness*= Rocks are half surrounded by sediment and are not covered by sediment.
- *0% embeddedness*= No fine sediments on substrate.

3.4.2.3 Assessment of capacity loss due to sedimentation

The rate of sediment-induced storage loss in lakes and reservoirs can be measured with a series of sedimentation or bathymetric surveys. Transects and sampling points are often established perpendicular to the main axis of tributary inflow or the main axis of the lake. Some base strata (original lake or reservoir bottom) should be established to track the rate (cm/yr) of deposition. A long pole may be used in shallow areas to measure sediment depth. For deeper areas, sonar or a SCUBA diver can record sediment depth measurements. Although measurements every year may not be needed, the same transects and stations should be monitored periodically. Major changes in land use, best management practices, or stream bank erosion that could increase sedimentation should also be monitored [25].

Sediment accumulation (deposition rates) can also be determined by measuring radionuclides in the sediment [26]. Cesium-137, a fallout product of nuclear testing, binds tightly to soil particles and can be used to estimate the time of sediment deposition. Measurable levels of Cesium-137 were introduced into the atmosphere during the beginning of the nuclear age and can only be used to estimate deposition after 1957.

Lead-210 may also be used to measure sedimentation rates [26]. Lead-210 is a naturally-occurring uranium isotope that is a decay product of radon. When atmospheric radon decays, the lead-210 is deposited on the earth's surface. Lead-210 will bind to soil particles and can be used to measure sedimentation rates for the past 100 years [26].

3.5 pH

pH is defined as the negative log-base 10 of the hydrogen ion activity:

$$pH = - \log_{10} [a_{H+}] \tag{3}$$

As long as the hydrogen ion concentration is not too high (less than 10^{-3} M), this activity is approximately proportional to the hydrogen ion concentration, more precisely:

$$[a_{H+}]=\gamma \cdot [H^+] \tag{4}$$

where γ represents the activity coefficient.

This coefficient is always lower than one and is almost equal to one for low hydrogen ion concentration.

The pH is a log-base 10 scale that measures acidity of a solution on a scale of 0 to 14. The pH of neutral solutions, such as pure water, is equal to 7. Alkaline solutions will have high pHs (8-14) and acidic solutions will have low pHs (1-6).

Since the pH is a log-base-10 scale, the pH changes 1 unit for every power of ten changes in [H+]. For example, water with a pH of 3 has 100 times the amount of [H+] that is found in a pH 5 water. Because $pH = - \log_{10} [H+]$, the pH will decrease as the [H+] increases [27].

3.5.1 Numerical categories

Although near-neutral pH values are preferred, industry as a whole can tolerate a wide pH range, depending on the intended water use. The Environmental Protection Agency reports

that the widest pH range is between 3.0 and 11.7 for process waters, and between 5.0 and 8.9 for cooling waters. Specific industries will require more limited ranges. An industry can usually prepare water of the proper pH to meet its needs [12].

Optimal pH Ranges	Designated Use
6.0 -8.5	General Agriculture [28]
6.8 - 8.5	Dairy Sanitation
4.5 - 9.0	Irrigation water [12]
5.0 - 9.0	Human Consumption [28]
6.5 - 9.0	Freshwater aquatic life
6.5 - 8.5	Marine aquatic life [12]
	Industry [28]
> 8.0	Boiler Feedwater
6.5 - 7.0	Brewery
6.5 - 7.5	Cooling Water
> 7.5	Cannery
6.0 - 6.8	Laundering
> 7.0	Oil Well Flooding
7.8 - 8.3	Rayon Manufacturing
6.8 - 7.0	Steel Manufacturing
6.8 - 8.0	Tanning

Table 5. pH ranges for different designated use.

A reduction in pH (more acidic) may allow the release of toxic metals that would otherwise be absorbed to sediment and essentially removed from the water system. Once mobilized, these metals are available for uptake by organisms. For many metals, the rate of uptake is directly proportional to the levels of metal availability in the environment. Thus, a decrease in pH increases metal availability, lending itself to greater metal uptake by organisms. Metal uptake can cause extreme physiological damage to aquatic life [29].

An increase in pH may cause heightened ammonia concentrations [12]. At low pH, ammonia combines with water (H2O) to produce an ammonium ion (NH4+) and a hydroxide ion (OH-). The ammonium ion is non-toxic and not of concern to organisms. Above a pH of 9, ammonia (un-ionized) is the predominant species [30]. The un-ionized ammonia (NH3) is very toxic to organisms. Thus, organisms experience ammonia toxicity more readily at higher pH [31].

Experiments have shown that a pH decrease of 1.4 units of pH can disturb the aquatic community.

3.5.2 Measuring techniques [27]

1. **Electronic pH Meter:** A probe containing an acidic aqueous solution encased in a special glass membrane allows migration of hydrogen ions (H+). If the water has a pH different from that of the solution within the probe, an electric potential results.

   Usually, electrochemical sensors are used to measure pH. According to the Nernst equation, the voltage difference (E) that is obtained from these sensors is given by:

$$E = -\frac{2{,}3R(T + 273{,}15)}{nF}(7 - pH) \tag{5}$$

   where E represents the voltage difference between measuring and reference electrodes, T represents temperature in ^{o}C, F represents the Faraday constant and n represents the number of electrodes that participate in the REDOX reaction. This value is equal to one for the auto-ionization reaction of water:

$$2H_2O \leftrightarrow OH^- + H_3O^+ \tag{6}$$

   Fig. 5 represents a pH measuring diagram based on a glass membrane pH sensor and its equivalent electrical circuit. The electrical circuit contains multiple resistors and voltage sources that are associated with all resistive and polarization effects existing inside the measuring cell.

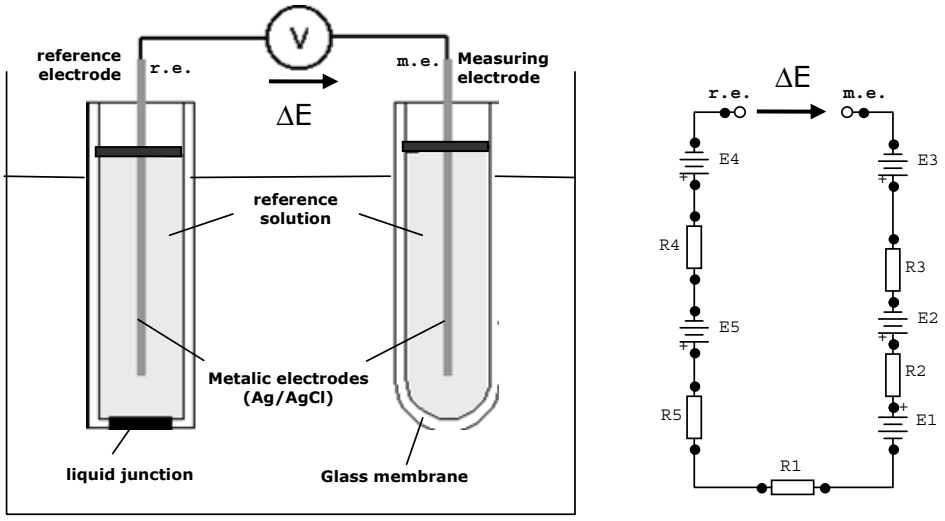

Fig. 5. Structure of a glass membrane pH sensor and its equivalent electrical circuit.

   Regarding temperature effects, pH measurements must be compensated for the explicit effect of temperature defined in Nernst equation and also for the variation of the ionic product of the water [32][33] with temperature that is approximately given by:

$$K_W = 10^{-14.00 - 0.0331(25 - T) + 0.00017\cdot(25 - T)^2} \, mol^2.l^{-2} \tag{7}$$

where T represents the temperature in ^{o} C.

Finally, it is important to underline that because the internal resistance (R_S) is very high, sometimes higher than 500 MΩ, an accurate measurement of the low voltage delivered by the pH transducer requires an amplifier with a very high input resistance. Usually the maximum bias currents of the amplifier must be lower than a few pA. As an example, Fig. 6 represents an equivalent electrical circuit of a signal conditioner that can be used for such a pH sensor.

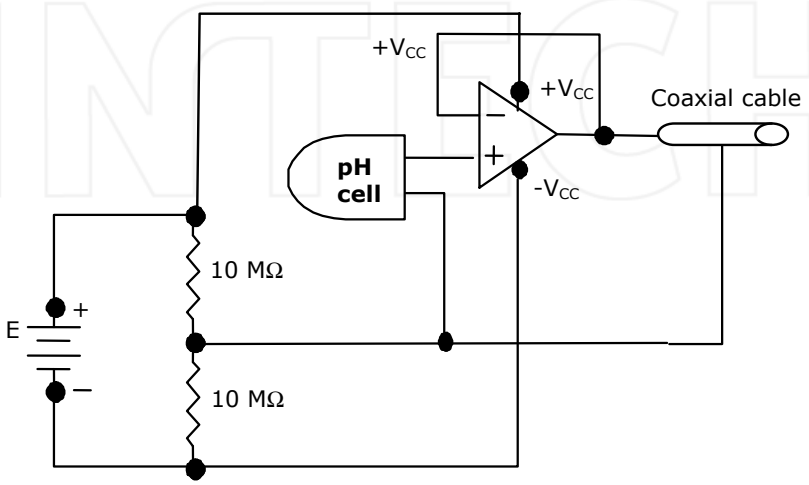

Fig. 6. Signal conditioning for a glass membrane pH sensor.

2. **Electronic devices:** a semiconductor device, usually a JFET or MOSFET, whose electrical characteristics change with the hydrogen ion concentration.

3.6 Dissolved oxygen

Dissolved oxygen (DO) refers to the volume of oxygen that is contained in water. Oxygen enters the water by photosynthesis of aquatic biota and by the transfer of oxygen across the air-water interface. The amount of oxygen that can be held by the water depends on the water temperature, salinity, and pressure. Gas solubility increases with decreasing temperature (colder water holds more oxygen). Gas solubility increases with decreasing salinity (freshwater holds more oxygen than does saltwater). Both the partial pressure and the degree of saturation of oxygen will change with altitude. Finally, gas solubility decreases as pressure decreases. Thus, the amount of oxygen absorbed in water decreases as altitude increases because the atmospheric pressure decreases [1].

Microbes play a key role in the loss of oxygen from surface waters because they use oxygen as energy to break down long-chained organic molecules into simpler, more stable end-products such as carbon dioxide, water, phosphate and nitrate [2]. If high levels of organic matter are present in water, microbes may use all available oxygen.

3.6.1 Numerical categories

Criteria to maintain designated use	
Designated Use	**Lowest acceptable DO levels (mg/l)***
Aquatic life	
Warm water fish	5.0
Cold water fish	6.0
Spawning season	7.0
Estuarine biota	5.0
Recreation	
Primary Contact	3.0
Secondary Contact	3.0
* Summary of state standards.	
Preferred ranges for designated use	
Designated Use	**Ranges (mg/l DO)**
Industry	
Boiler Feed Water	
High Pressure	0
Low Pressure	0.1 - 1.4

Table 6. Dissolved oxygen designated use and lowest acceptable levels.

3.6.2 Measuring techniques

1. **Iodometric Method:** Most reliable method. Requires the addition of divalent manganese solution, followed by a strong alkali, in a stoppered glass bottle. The dissolved oxygen oxidizes to manganous hydroxide precipitate. With the addition of iodide, the oxidized manganese reverts back to divalent state, releasing iodide equivalent to original dissolved oxygen content. Iodide is titrated with thiosulphate.
   - *Interferences:* Oxidizing agents may release iodines from iodides (false positive). Reducing agents may reduce iodine to iodide (false negative). Air entrapped in the sample bottle will also interfere.
2. **Azide Method:** This method is suitable for samples containing more than 50 ug/l nitrite and not more than 1 mg/l of ferrous iron.
   - *Interferences:* Oxidizing and reducing agents may provide false positives or negatives.
3. **Permanganate Modification:** This method is suitable for samples containing ferrous iron.
   - *Interferences:* High concentrations of ferric iron will interfere. Can be overcome by the addition of 1 ml KF.

4. **Alum Flocculation Modification:**
   - *Interferences:* High suspended solids may consume iodide in acid solution. This interference is removable by alum flocculation.
5. **Membrane Electrode Method:** This method is ideal for field testing. Not applicable for industrial and domestic wastewater. Polarographic or galvanic oxygen-sensitive membrane electrodes are composed of two metal electrodes in contact with a supporting electrolyte that is separated from the test solution by a selective membrane.
   - *Interferences:* The presence of hydrogen sulphide gas will desensitize the electrode cells.

3.7 Nitrogen

Nitrogen makes up 78% of the atmosphere as gaseous molecular nitrogen, but most plants can use it only in the fixed forms of nitrate and ammonium. Nitrate and nitrite are inorganic ions occurring naturally as part of the nitrogen cycle [1].

The nitrogen cycle is composed of four processes. Three of the processes - fixation, ammonification, and nitrification - convert gaseous nitrogen into usable chemical forms. The fourth process, denitrification, converts fixed nitrogen back to the unusable gaseous nitrogen state [1].

- **Nitrogen fixation** is the conversion of nitrogen in its gaseous state to ammonia or nitrate. Nitrate is the product of high-energy fixation of atmospheric nitrogen and oxygen. High-energy fixation accounts for little (10%) of the nitrate entering the nitrogen cycle. In contrast, biological fixation accounts for 90% of the fixed nitrogen in the cycle. In biological fixation, molecular nitrogen (N2) is split into two free N molecules. The N molecules combine with hydrogen (H) molecules to yield ammonia (NH3).
- **Ammonification** is a one-way reaction in which organisms break down amino acids and produce ammonia (NH3).
- **Nitrification** is the process in which ammonia is oxidized to nitrite and nitrate, yielding energy for decomposer organisms.
- **Denitrification** is the process in which nitrates are reduced to gaseous nitrogen. This process is used by facultative anaerobes.

In temperate zones, soil nitrate concentrations will vary seasonally with temperature and moisture levels. Fall and winter rains thoroughly remove all nitrates from the soil. During the spring and summer, the increased nitrogen-fixing activity of organisms and the addition of fertilizer cause the concentration of nitrates in the soil to steadily increase. Most of this nitrate is absorbed by plants. Thus, the removal of crops in the fall increases the chances for large flushes of nitrate from the soil to water bodies. Some leaching may occur in the spring if crops are not well- established enough to absorb the nitrogen [34].

3.7.1 Numerical categories

Water contaminated with nitrate is very difficult and costly to treat. Thus, if contamination affects a large water supply, the best alternative may be a new water source [35].

Generally, phosphorus is the limiting nutrient in freshwater aquatic systems. If all phosphorous is used, plant growth will cease, no matter the amount of nitrogen available. In contrast to freshwater, nitrogen is the primary limiting nutrient in the seaward portions of most estuarine systems [36]. Thus, nitrogen levels control the rate of primary production. If a nitrogen limited system is supplied with high levels of nitrogen, significant increases in phytoplankton (algae) and macrophyte (larger aquatic plants) production may occur. The recommended level of nitrogen in estuaries to avoid algal blooms is 0.1 to 1 mg/l, while the phosphorus concentration is 0.01 to 0.1 mg/l.

Limits suggested to maintain designated use:

Designated Use	Limit (mg/l)(AWWA 1990 [4])
Nitrate (NO3-N):	
Human Consumption	10.0
Aquatic Life	
Warm water fish	90.0
Industry	
Brewing	30.0
Nitrite (NO2-):	
Human Consumption	1.0
Aquatic Life	
Warm water fish	5.0
Nitrate+Nitrite:	
Human Consumption	10.0
Agriculture (Livestock etc.)	100.0
Aquatic life	
Estuaries (recommended)	
maximum diversity	0.1 (and phosphorus 0.01)
moderate diversity	1.0 (and phosphorus 0.1)

Table 7. Nitrogen designated use and corresponding limits.

3.7.2 Measuring techniques

A. Nitrate-Nitrogen [8]

1. **Ultraviolet Spectrophotometer Screening Method:**
   - *Detection limits:* Used to screen non-contaminated samples (low inorganic matter) to determine most suitable method.
   - *Interferences:* Dissolved organic matter, surfactants, NO2(-) and Cr(+).
2. **Ion Chromatography Method:**
   - *Detection limits:* 0.1 mg/l nitrate
   - *Interferences:* N/A
3. **Nitrate Electrode Method:**
   - *Detection limits:* NO3(-) ion activity between 0.00001 and 0.1 M (0.14 to 1400 mg/l)
   - *Interferences:* Chloride and bicarbonate, when their weight ratios to nitrate are >10, or >5, respectively.

4. **Cadmium Reduction Method:** Nitrate is reduced to nitrite in the presence of cadmium. The nitrite concentration is determined by diazotizing with sulphanilamide and coupling with NED dihydrochloride to form a colored azo dye that is measured colorimetrically.
   - *Detection limits:* 0.01 mg/l to 1.0 mg/l nitrate. Recommended especially for nitrate concentrations below 0.1 mg/l, when other methods lack sufficient sensitivity.
   - *Interferences:* Suspended matter in the column will restrict sample flow.
5. **Automated Cadmium Reduction Method:**
   - *Detection limits:* 0.5 mg/l to 10 mg/l nitrate.
   - *Interferences:* Turbidity, color
6. **Titanous Chloride Method:** Nitrate is determined potentiometrically using an NH3 gas-sensing electrode after nitrate is reduced to NH3 by a titanous chloride reagent.
   - *Detection limits:* 0.01 mg/l to 10 mg/l nitrate.
   - *Interferences:* NH3 and NO2(-), if present, are measured with NO3(-). Measure separately and subtract.
7. **Automated Hydrazine Reduction Method:** Nitrate is reduced to nitrite by hydrazine sulphate. The nitrite concentration is determined by diazotizing with sulphanilamide and coupling with NED dihydrochloride to form a colored azo dye that is measured calorimetrically.
   - *Detection limits:* 0.01 mg/l to 10 mg/l nitrate.
   - *Interferences:* Color, sulphide ion concentrations of less than 10 mg/l.

B. Total Kjeldahl Nitrogen [8][37]

1. D**igestion followed by distillation.**
2. **Automated Phenate Colorimetric Method:** Reaction produces indophenol, an intensely blue compound.
   - *Detection limits:* 0.05 mg/l to 2.0 mg/l.
   - *Interferences:* Iron and chromium ions tend to catalyze, while copper ions will inhibit the color reaction.

3.8 Phosphorus

Phosphorus (P) is an essential nutrient for all life forms. It plays a role in deoxyribonucleic acid (DNA), ribonucleic acid (RNA), adenosine diphosphate (ADP), and adenosine triphosphate (ATP). Phosphorus is required for these necessary components of life to occur.

Phosphorus does not exist in a gaseous state. Natural inorganic phosphorus deposits occur primarily as phosphate in the mineral apatite. Apatite is found in igneous and metamorphic rocks, and sedimentary rocks. When released into the environment, phosphates will speciate as orthophosphate according to the pH of the surrounding soil.

Phosphate is usually not readily available for uptake in soils. Phosphate is only freely soluble in acid solutions and under reducing conditions. In the soil it is rapidly immobilized as calcium or iron phosphates. Most of the phosphorus in soils is adsorbed to soil particles or incorporated into organic matter [1][38][39].

Phosphorus in freshwater and marine systems exists in either a particulate phase or a dissolved phase. Particulate matter includes living and dead plankton, precipitates of

phosphorus, phosphorus adsorbed to particulates, and amorphous phosphorus. The dissolved phase includes inorganic phosphorus (generally in the soluble orthophosphate form), organic phosphorus excreted by organisms, and macromolecular colloidal phosphorus.

The organic and inorganic particulate and soluble forms of phosphorus undergo continuous transformations. The dissolved phosphorus (usually as orthophosphate) is assimilated by phytoplankton and altered to organic phosphorus. The phytoplankton is then ingested by detritivores or zooplankton. Over half of the organic phosphorus taken up by zooplankton is excreted as inorganic phosphorus. Continuing the cycle, the inorganic P is rapidly assimilated by phytoplankton [1][39].

The EPA water quality criteria state that phosphates should not exceed 0.05 mg/l if streams discharge into lakes or reservoirs, 0.025 mg/l within a lake or reservoir, and 0.1 mg/l in streams or flowing waters not discharging into lakes or reservoirs to control algal growth [12]. Surface waters that are maintained at 0.01 to 0.03 mg/l of total phosphorus tend to remain uncontaminated by algal blooms.

3.8.1 Numerical categories

Designated Use	Limit	
Freshwater		
Aesthetics		
Federal criteria		
	streams/rivers:	0.1 mg/l
	streams entering lakes:	0.05 mg/l
	lakes/reservoirs:	0.025 mg/l
Example. State criteria used:		
Reservoirs (CO)	chlorophyll a	15 ug/l
	Total P	0.035 mg/l
(Minn.)	Total P	0.015 mg/l
Impoundments (EPA Region 4)		
water supply Total P .015 mg/l		
aquatic life	Total P	0.025 mg/l
Lakes (NC)	chlorophyll a	40 ug/l
	Total P	0.05 mg/l
mountain lakes		0.02 mg/l
(VT)	Total P	0.014 mg/l
Estuaries (recommended)		
Aquatic life support	0.1 ug/l elemental phosphorus	
maximum diversity	0.01* total phosphorus (and nitrogen < 0.1) mg/l	
moderate diversity	0.1* (and nitrogen < 1.0) mg/l	

*These figures are recommended; eutrophication is also dependent on freshwater influx, nutrient cycling, dilution, and flushing of a pollutant load in a particular estuary [40].

Table 8. Phosphorus designated use limits.

Generally, phosphorus (as orthophosphate) is the limiting nutrient in freshwater aquatic systems; if all phosphorus is used, plant growth will cease, no matter how much nitrogen is available. The natural background levels of total phosphorus are generally less than 0.03 mg/l. The natural levels of orthophosphate usually range from 0.005 to 0.05 mg/l [2]. As mentioned before, in contrast to freshwater, nitrogen is generally the primary limiting nutrient in the seaward portions of estuarine systems. Systems may be phosphorus limited, however, or become so when nitrogen concentrations are high and N:P>16:1 [41].

3.8.2 Measuring techniques

Total Phosphorus and Orthophosphate: Analysis involves two procedural steps:

1. conversion of the phosphorus form into dissolved orthophosphate by a digestion method, and
2. colorimetric evaluation of the dissolved orthophosphate concentration [8].

Step 1. Digestion methods

1. **Perchloric Acid Digestion:** Recommended only for extremely difficult-to-analyze samples, such as sediments.
2. **Nitric Acid-Sulphuric Acid Method:** Recommended for most samples.
3. **Persulphate Oxidation Method:** This simple method should be cross-checked with one or more thorough techniques and adopted if results are identical.

Step 2. Colorimetric methods

1. **Ascorbic Acid Method:** Ammonium molybdate and potassium antimonyl tartrate react with orthophosphate to form a heteropoly acid that is reduced to molybdenum blue by ascorbic acid.
   - *Detection limits:* Ranges change with light path used.
   - *Interferences:* Arsenates react with the molybdate to form a similar blue color. Nitrite and hexavalent chromium interfere to yield results 3% less than actual at 1 mg/l and 10% to 15% less than actual at 10 mg/l.

Range (mg/l as P)	Path (cm)
0.3 - 2.0	0.5
0.15 - 1.3	1.0
0.01 - 0.25	5.0

Table 9. Ascorbic acid method detection limits as a function of light path length.

2. **Automated Ascorbic Acid Reduction Method:** Ammonium molybdate and potassium antimonyl tartrate react with orthophosphate in an acid medium to form an antimony-phosphomolybdate complex that forms a blue color suitable for photometric measurements when reduced by ascorbic acid.

- *Detection limits:* 0.001 to 10.0 mg/l as P when photometric measurements are performed at 600 to 650 nm in a 15mm tubular flow cell, or 880 nm in a 50mm tubular flow cell.
- *Interferences:* >50 mg/l Fe(3+), 10 mg/l Cu, and 10 mg/l SiO2. Turbidity, color may interfere. Arsenate provides a positive interference.

3. **Vanadomolybdophosphoric Acid Colorimetric Method:** Ammonium molybdate reacts under acid conditions to form a heteropolyacid. In the presence of vanadium, yellow vanadomolybdophosphoric acid is formed, the intensity of which indicates the amount of orthophosphate present.
   - *Detection limits:* 1 to 20 mg/l as P. This method is not good for water samples - best for soils.
   - *Interferences:* Silica and arsenate interfere in heated samples. Blue color is formed by ferrous iron, but does not interfere if iron concentration is < 100 mg/l.
4. **Stannous Chloride Method:** Molybdophosphoric acid is formed and reduced by stannous chloride, forming intensely colored molybdenum blue.
   - *Detection limits:* 0.001 to 6 mg/l as P.
   - *Interferences:* Silica and arsenate interfere in heated samples. Blue color is formed by ferrous iron, but does not interfere if iron concentration is < 100 mg/l.

3.9 Heavy metals

Heavy metals are elements having atomic weights between 63.546 and 200.590, and a specific gravity greater than 4.0. Living organisms require trace amounts of some heavy metals, including cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc. Excessive levels of essential metals, however, can be detrimental to the organism. Non-essential heavy metals of particular concern to surface water systems are cadmium, chromium, mercury, lead, arsenic, and antimony.

All heavy metals exist in surface waters in colloidal, particulate, and dissolved phases, although dissolved concentrations are generally low. The solubility of trace metals in surface waters is predominately controlled by the water pH, the type and concentration of ligands on which the metal could adsorb, and the oxidation state of the mineral components and the REDOX environment of the system [29].

The behaviour of metals in natural waters is a function of the substrate sediment composition, the suspended sediment composition, and the water chemistry. Sediment composed of fine sand and silt will generally have higher levels of adsorbed metal than will quartz, feldspar, and detrital carbonate-rich sediment. Metals also have a high affinity for humic acids, organo-clays, and oxides coated with organic matter [29].

Heavy metals in surface water systems can be from natural or anthropogenic sources. Currently, anthropogenic inputs of metals exceed natural inputs.

3.9.1 Numerical categories

Numeric aquatic life guideline criteria extracted from several US codes are:

Designated Use	Metal	Water Hardness (mg/l)	Limit (ug/l)
Fresh Water Aquatic Life			
	As		50.0 #
	As(III)		190.0 *
	As(III)		360.0
	Be		130.0
			5.3 *
	Cd	50	0.66 *
			1.80
		150	1.10 *
			3.90
		200	2.00 *
			8.60
	Cu	50	6.50 *
			9.20
		150	12.00 *
			18.00
		200	21.00 *
			34.00
	Hg		0.012 *
	Ni	50	56.00 +
		150	96.00 +
		200	160.00 +
	Pb	50	1.30 *
			34.00
		150	3.20 *
			82.00
		200	7.7
		200	7.70 *
			200.00
	Se		5.0 #
	Zn	50	180.00 ++
		150	320.00 ++
		200	570.00 ++
			47.00 +

* Four-day average concentration
One-hour average concentration
+ Twenty-four hour average concentration
++ Level not to be exceeded at any time
(Adapted from [42][43][44]).
[45]

Table 10. Limits of heavy metals concentration in fresh water.

Designated Use	Metal	Water Hardness (mg/l)	Limit (ug/l)
Estuarine/ Coastal Aquatic Life		N/A	
	As		50.0 #
	Ag		0.10 #
	Cd		8.00 *
	Cu		2.90
	Hg		0.025 *
	Ni		7.10 +
	Pb		5.80 *
	Se		71.0 #
	Zn		76.6 *

* Four-day average concentration
One-hour average concentration
+ Twenty-four hour average concentration
(Adapted from [42][43][44][46][47][48]).
[45]

Table 11. Limits of heavy metals concentration in estuarine and coastal water.

Designated Use	Metal	Water Hardness (mg/l)	Limit (ug/l)
Human Consumption	As		0.05 (mg/l)
	Ba		1.0 (mg/l)
	Cd		10.0 *
	Cr		0.05 (mg/l)
	Cu		1.0 ++
	Hg		144.0 ng/l *
	Ni		632.0 *
	Pb		50.0 * (adults)
	Zn		5.0 *

* Ambient water criteria
Maximum contaminant level [42]
++ Level not to be exceeded at any time
(Adapted from [4][42][49]).

Table 12. Limits of heavy metals concentration in water for human consumption.

Designated Use	Metal	Water Hardness (mg/l)	Limit (ug/l)
Irrigation	Cd	N/A	10
	Cu		200
	Pb		5000
	Zn		2000

(Adapted from [49]).

Table 13. Limits of heavy metals concentration in irrigation water.

3.9.2 Criteria for the nine national toxics rule states - Dissolved metals criteria

Freshwater dissolved metals criteria that are not hardness dependent

Metal	Total Recoverable Metals Criteria		Dissolved Metals Criteria	
in ug/l	CMC	CCC	CMC	CCC
Arsenic	359.1	188.9	360	190
Chromium (VI)	15.74	10.80	15	10
Mercury	2.428	0.0122	2.1	N/A

CMC= Criteria Maximum Concentration
CCC= Criteria Continuous Concentration

Table 14. Freshwater dissolved metals criteria (not hardness dependent).

For Hardness-Dependent Freshwater Criteria see the Federal Register notice of May 4, 1995 (60 FR 22230). The hardness-dependent criteria require site specific calculations.

Saltwater dissolved metals criteria

Arsenic	68.55	36.05	69	36
Cadmium	42.54	9.345	42	9.3
Chromium (VI)	1079	49.86	1100	50
Copper	2.916	2.916	2.4	2.4
Lead	217.16	8.468	210	8.1
Mercury	2.062	0.0250	1.8	N/A
Nickel	74.6	8.293	74	8.2
Selenium	293.8	70.69	290	71
Silver	2.3	N/A	1.9	N/A
Zinc	95.1	86.14	90	81

Table 15. Saltwater dissolved metals criteria.

- Total recoverable metals criteria is from EPA National Ambient Water Quality Criteria Documents - Criteria Maximum Concentration (CMC) is the highest concentration of a pollutant to which aquatic life can be exposed for a short period of time (1 hour average) (acute); - Criteria Continuous Concentration (CCC) is the highest concentration of a pollutant to which aquatic life can be exposed for an extended period of time (4 days) without deleterious effects. - A more conservative approach to aquatic life protection may be preferred; in such cases the total recoverable metals criteria may be used.

Human Consumption

	Water and Organisms	Organisms Only
	ug/l	
Arsenic	0.018	0.14
Mercury	0.14	0.15
Nickel	610	4600

Table 16. Arsenic, mercury and nickel concentration in water for human consumption.

Ingestion of metals such as lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), barium (Ba), and chromium (Cr), may pose great risks to human health. Trace metals such as lead and cadmium will interfere with essential nutrients of similar appearance, such as calcium (Ca2+) and zinc (Zn2+).

Lead can substitute for calcium and included in bone. Lead that is stored in bone is not harmful, but if high levels of calcium are ingested later, the lead in the bone may be replaced by calcium and mobilized. Once free in the system, lead may cause nephrotoxicity, neurotoxicity, and hypertension. Cadmium may interfere with the metallothionein's ability to regulate zinc and copper concentrations in the body. Mercury poses a great risk to humans, especially in the form of methyl mercury. When mercury enters water it is often transformed by micro-organisms into the toxic methyl mercury form. Chronic poisoning is usually a result of industrial exposure or a diet consisting of contaminated fish (mercury is the only metal that will bio accumulate). Arsenic ingestion can cause severe toxicity through ingestion of contaminated food and water. Ingestion causes vomiting, diarrhea, and cardiac abnormalities. The presence of abundant chromium anions in the water is generally a result of industrial waste. The chronic adverse health effects are respiratory and dermatologic.

3.9.3 Measuring techniques

Total Metals: Includes all metals, organically and inorganically bound, both dissolved and particulate [8]. Most samples will require digestion before analysis to reduce organic matter interference and to convert metal to a form that can be analyzed by Atomic Absorption Spectroscopy or Inductively Coupled Plasma Spectroscopy.

General methods:

1. **Direct Atomic Absorption Spectroscopy or Inductively Coupled Plasma Spectroscopy:** Sample must be colorless, transparent, odorless, single phase, and have turbidity <1 Nephelometric Turbidity Unit. Otherwise, sample must first be digested.
2. **Voltammetry:** It is an electrochemical measuring technique where metal ion concentration is evaluated through its REDOX properties. The electrons transfer present in every metal oxidation or reduction reaction originate currents at given potential values that can be used to identify individual metals present in a solution and the correspondent concentrations. Voltammetry is a very sensitive and accurate analysis technique that is particularly suited for the detection of low level concentration of heavy metals (HM) in the lower parts per billion (ppb) region [50][51].
3. **Dedicated solutions:**
   Fig. 7 represents the data acquisition system and the schematic diagram of an electrical circuit that can be used for HM measurements [52][53]. The circuit includes the following main elements: a three electrodes measuring cell (MC), a data acquisition unit (DAQu), and an inverter sum amplifier (OA1) whose input voltage signals come from the DAQu (VDAC) and from a voltage follower circuit (V02). It is important to underline that the linear working condition of OA1 is assured by the negative feedback loop that is closed through the electrolyte solution contained in the MC.

Basically, after a pre-concentration phase, a positive potential, with linear variation, is applied to the counter electrode of the MC and current peaks associated with the REDOX potential of each metal dissolved in the solution are generated and detected by the current to voltage converter that is connected to the working electrode of the MC. Before the measurement the oxygen must be removed from the solution in order to avoid large measurement errors [54].

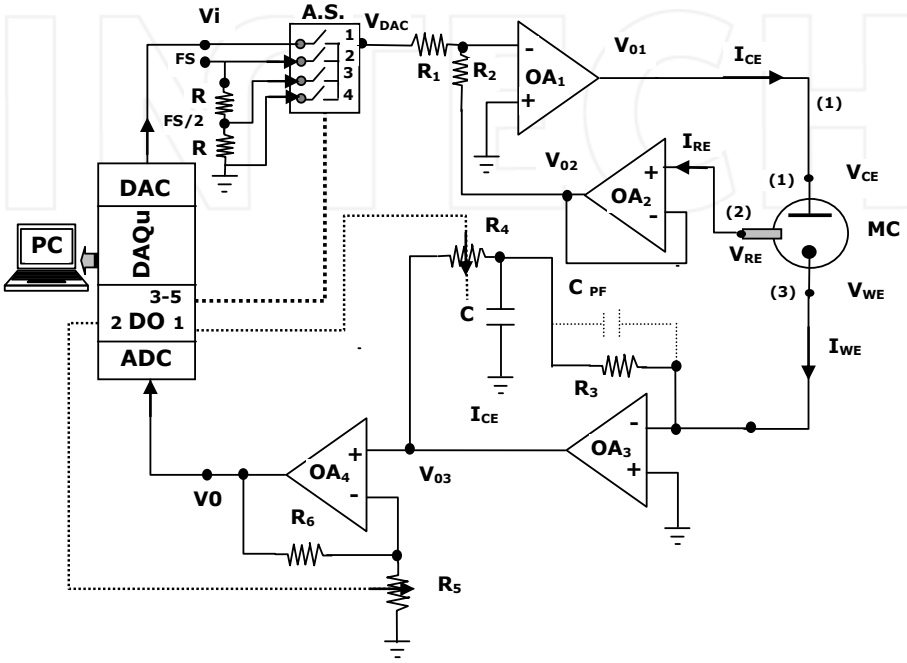

Fig. 7. Data acquisition system and the schematic diagram of an electrical circuit that can be used for HM measurements (MC-measuring cell, DAQu- data acquisition unit, ADC- analog to digital converter, DAC- digital to analog converter, OA- operational amplifier, AS- analog switch).

Digestion methods:

- **Nitric Acid Digestion:** Digestion is complete when solution is clear or light-colored.
- **Nitric Acid - Hydrochloric Acid Digestion:** Digestion is complete when digestate is light in color.
- **Nitric Acid - Sulphuric Acid Digestion:** Digestion is complete when solution is clear.
- **Nitric Acid - Perchloric Acid Digestion:** Digestion is complete when solution is clear and white HClO4 fumes appear.
- **Nitric Acid - Perchloric Acid - Hydrofluoric Acid Digestion:** Digestion is complete when solution is clear and white HClO4 fumes appear.

4. Distributed measuring systems architectures

In paragraph 3 the principal quantities commonly used to evaluate water quality were reviewed and for each quantity, the measuring techniques for its measurement briefly mentioned. To continuous measure the water quality parameters for extended areas, distributed measurement system architectures are usually used [55][56] rather than individual instruments. Generally, a distributed measurement system for water quality monitoring includes a main unit - typically a base unit that can store a server application and also additional software for data processing, and data presentation - and field nodes each with the capability of measuring quantities of water quality. The sensor for each quantity should be able to translate the quantity to the electric domain because the nodes must have several capabilities only possible if data is supported on digital format electric signals. Contrary to the main unit that is land based, most nodes should be placed on the water body to be monitored, which leads to the following considerations:

1. Node's equipment must be placed in a raft or buoy;
2. Even if anchored, the raft or buoy should have geographical position tracking capabilities (e.g. GPS) both for an accurate identification of its localization and to detect when anchorage is lost and the buoy or raft drifts away;
3. The equipment must be rugged and contained in a waterproof enclosure;
4. Node's equipment must include the hardware required to immerge the sensors in the water or to take samples of the water into a container accessible to the sensors;
5. Long term, unattended operation requires provision for periodic calibration of at least some of the sensors. The hardware and the procedure must be implemented within the node's hardware. The authors overcome 4 and 5 by choosing the type of solution depicted in Fig. 8, taken from [57] and also described in [58].
6. Electric power consumption of the whole equipment must be carefully planned. Components design should aim at minimum power consumption and high power capacity of the powering batteries should also be an objective;
7. Long term, unattended operation requires provision for re-chargeable batteries and for means for its recharge (e.g. solar panels or power harvesting solutions);
8. Power considerations also impacts on the management of the network, namely on nodes' measuring rates, on periods when the nodes are in sleeping mode, and on how data goes from each node to the main unit; Issues 6, 7 and 8 were addressed in several publications of the authors included in the references.
9. A decision concerning node's data processing capabilities must be taken beforehand. Each node must have a processing unit embedded but the characteristics and performance of that unit and of its interfaces depend on the algorithms and data they act upon, that is to say, on how distributed the system is in terms of data processing. Network nodes are thus designed as smart sensing nodes. Solutions based on FPGA [59], SDI-12 [60], and FieldPoint [61] technologies have been reported by the authors.
10. The characteristics of the network, namely the area covered by the network and its hosting medium, advise the use of wireless communications. This option means not only that nodes must have the hardware able to implement it, but also that all problems related to wireless data transmission, including data flow, data integrity, data security, access control, and protocol must be addressed before implementation of each node and of the whole network.

The references include several publications of the authors describing topologies and discussing technologies both for node implementation and for wireless data transmission. Regarding distributed systems practical implementations, different architectures were also developed by the authors and already reported in [9] and [57][58][62-96]. The main types of architectures designed and implemented are based on real time sensing nodes and are presented in Fig. 8 and Fig. 9.

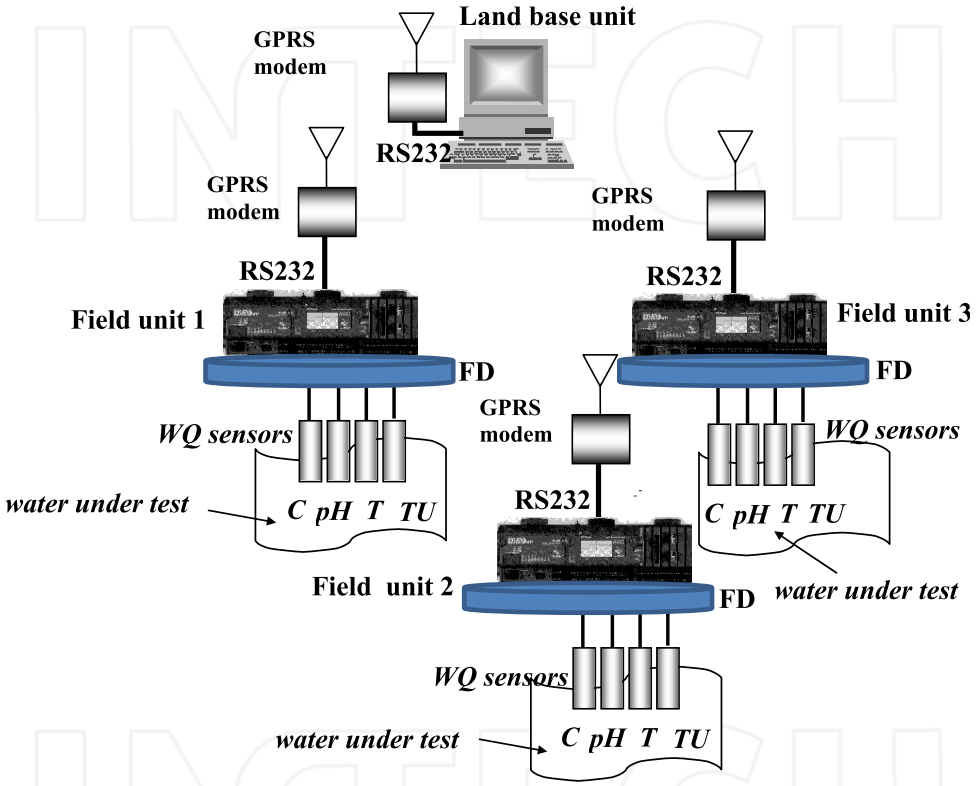

Fig. 8. Water quality (WQ) monitoring architecture based on FieldPoint embedded systems and GPRS modems.

FieldPoint based nodes are presented in Fig. 8 that depicts a wireless local area network (WLAN) with nodes with 3G communication capability and a land based unit expressed by a PC provided with interned connection. Fig. 9 presents an architecture that includes real time water quality monitoring nodes Wi-Fi compatible that are part of a WLAN including a base unit mounted in a ship. The values from the water quality monitoring nodes are uploaded through a 3G/UMTS connection in a web based information system that provides information about the water quality of the monitored area.

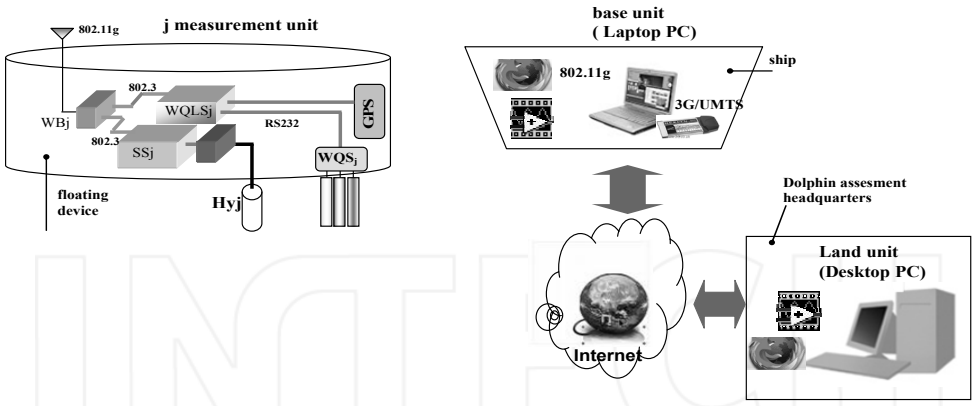

Fig. 9. The WLAN with web based WQ information system architecture (SSj – underwater acoustic signal server, WQLSj - water quality parameter and localization server, WQSj – water quality sensing unit, Hyj- hydrophone, GPS – global positioning system unit, 3G/UMTS – mobile Internet modem, WBj – Ethernet bridge).

As can be observed for the presented architectures, the land-based unit, which must be also compatible with the wireless data transmission solution, is mainly in charge of processing data received from the measuring nodes and of organizing and presenting the information according to the purposes it aims, including web server functionality. The basic processing at node's level should yield the values of the measured quantities (water parameters) but it is common that the node's processing unit implements algorithms for purposes such as sensor's inverse modeling, sensor's characteristics linearization, correction of influence quantities, sensors auto-calibration, node's self-testing, etc. The main unit, usually with better processing resources and data presentation means, is also the interface of the network with the outside world. The type of information output by the whole wireless distributed measuring system assumes many possible forms, depending mainly on the use given to that information. Because the system covers a more or less wide area, it is normal to want to know the water parameters values in the points where the nodes are installed and eventually pollution events. The knowledge of parameter values and the tendency of the evolution of those values can be used not only to foresee pollution events, but also to detect pollution sources. Sensors' data fusion, data mining, artificial neural networks, and Kohonen maps are some of the techniques that can be and have been used and referenced here by the authors for those purposes.

The availability and access to the information is nowadays made easier through the internet. The implementation of data bases allows users with the appropriate privileges to explore stored data and to search for data satisfying specific criteria. A geographic information system (GIS) not only allows data presentation in a user's more friendly way, but also to use an adequate browser to view the data. The integration of a low cost GPS device in each node allows the implementation of a web based geographical information system. Work regarding GIS implementation associated with WQ monitoring is reported by the authors in [97][98].

The authors also lead a team that implemented a geographic information system (GIS - SonicQualSado) designed to monitor not only the evolution of the water quality in Sado Estuary, but also to acquire and process Sado's dolphins population emitted sounds and anthropogenic produced sounds in order to establish possible correlations between dolphins behavior and water quality parameters. Thus, the GIS was designed to receive the data from the base unit that is a part of the architecture presented on Fig. 9. More elements associated with hardware and software architecture of the system are represented in the UML deployment diagram presented in Fig. 10.

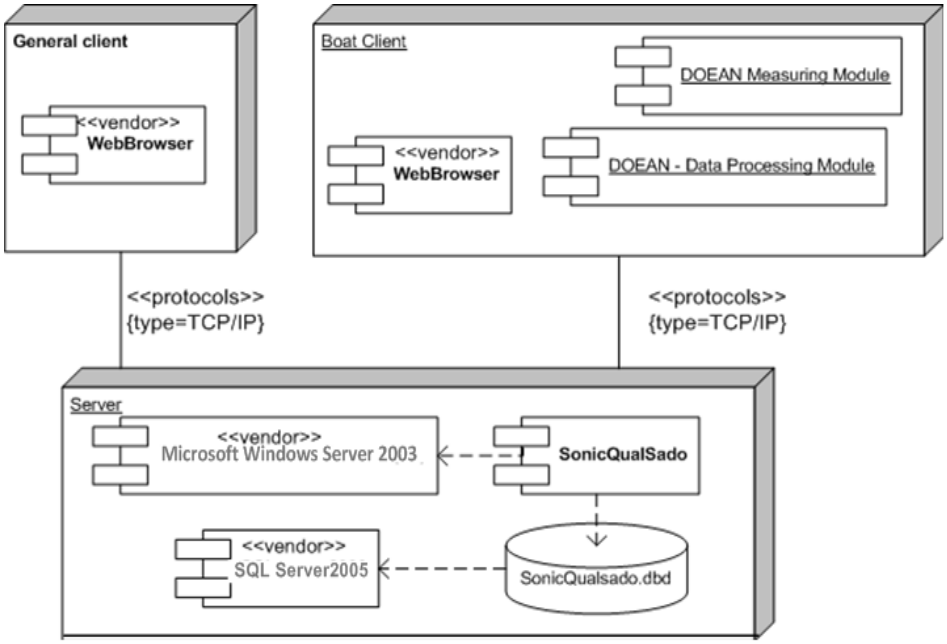

Fig. 10. GIS SonicQualSado software block diagram.

The number of the measured water parameters depends on the used measuring probe. Thus, using a low cost measuring probe, temperature, conductivity and turbidity are measured while with the utilization of a commercial multi-parameter measuring probe (Quanta Hidrolab) additional parameters, such as pH and dissolved oxygen, are also measured.

Concerning the GIS software implementation, the ASP.net was mainly used. Additionally, the Microsoft SQL Server software technology was used to develop the database and to perform the data management tasks. The GIS server implemented in the land computer uses the Microsoft Windows Server 2003 operating system. The GIS interface with the user is made through a browser (e.g. Internet Explorer). The user can verify through the developed SonicQualSado site [98] information about the latest field measurement on a digital map of the Sado Estuary. This data mapping functionalities were implemented using the Google Map APIs and .net software. The implemented GIS assures automatic data storage, map description of the measurement points, data searching, and data extraction for post-

processing tasks. Some graphical elements of the implemented GIS are presented in Fig. 11. The figure presents an example of how data of one measurement point is shown to the user. In this example, the water quality measurements have also associated dolphins' pictures and sounds. The access to the pictures and to the sound reproduction is made through the picture tab and the sound tab, respectively.

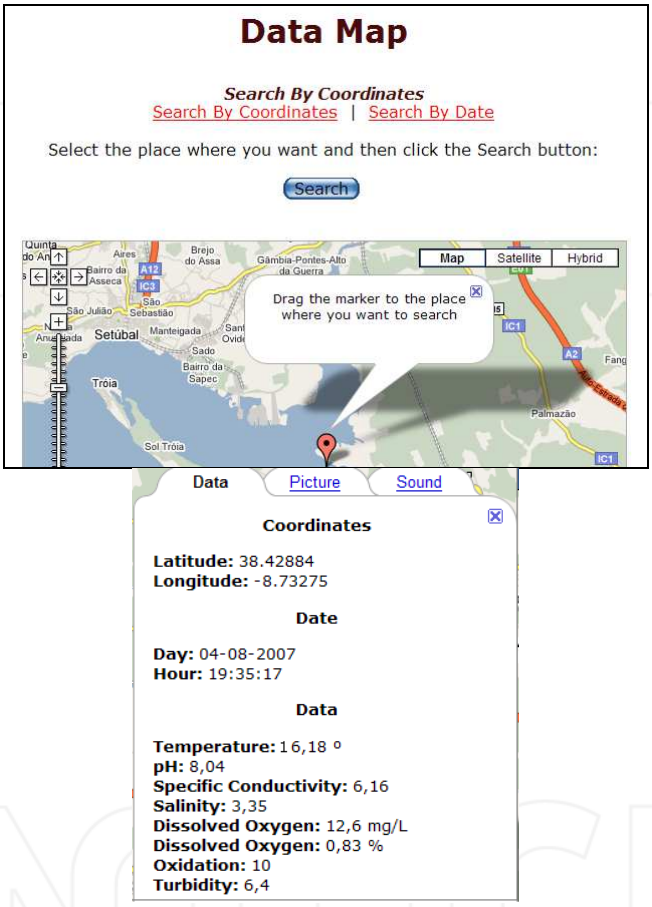

Fig. 11. The GIS SonicQualSado GUI and the data frame example associated with water quality and underwater acoustic sound monitoring.

The GIS uses a digital map as the main element of the user interface (GUI). The map is used both for visualization purposes and to entry data for searching tasks.

5. Conclusion

Water quality monitoring is a complex issue because there are a large number of parameters that can be used to access its quality. Understanding the meaning of each parameter requires a good knowledge of different areas, namely electrical, electrochemical and

biological engineering, among others. Measuring techniques is still an open field for some variables, particularly in which concerns in-situ and on-line measurement systems. As referred in the introduction, this chapter contains an initial overview related with water quality parameters based on the information available from different entities accredited in the field. However, some remarks about measuring techniques for different water quality parameters were introduced by the authors according to their experience in the field. The last part of the paper focus different water quality monitoring architectures that were used by the authors for distributed sensing and intelligent signal processing network for water quality monitoring.

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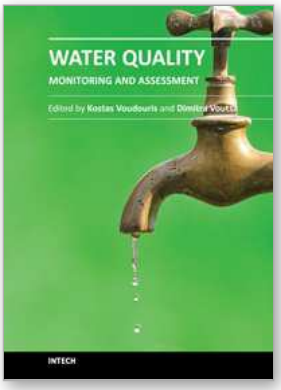

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