Interest and Difficulty in Continuous Analysis of Water Quality

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Abstract. The attempt of this study is both important and complex. Whether sanitation in general, or more closely purification technology, measures and analyzes practice that we aim to characterize the state of water, which is a speculative because the water is usually a heterogeneous, spatial and temporal medium. It is impossible to deal thoroughly in a short time also to meet a demand made to us, so we will try to present the theoretical framework of the issue, but evading demonstrations, that we can verify head rested in the literature. We split about 3 parts: why is necessary the continuous measurement, problems associated with collecting and data associated with water neutralization.

Key-Words: Biomedical liquid waste, Continuous measurement, Permanent monitoring, Water quality

1 Introduction
An important issue of environmental protection process is the water resources sustainable development [1], [2] that includes wastewater management as a key point of the strategy for responsible planning of collecting, continuous monitoring data and wastewater processing. The physico-chemical and biological nature of these wastewaters, their toxicity and potential hazard are different, necessitating different methods and options for their treatment [3]. The treatment methods of wastewater must take into account the possibility of biomedical liquid waste generated from any of the infected areas of the hospitals to flow into the sewages. Consequently, an effective management needs to encompass a continuous monitoring of wastewater and treated water after an appropriate neutralization. Whether sanitation in general, or more closely purification technology, measures and analyzes practice that we aim to characterize the state of water, which is a speculative because the water is usually a heterogeneous, spatial and temporal medium. From the outset, it should be noted that the question we pose [4], [5]. For example, it may seek to determine:

• the average state: may agree to consider a charge or a power self-purification plant, and can obtain the average state by analysis of a sample, or by calculating the average multiple measurements;

• a percentile (or quintile) determines: may be necessary for the calculation of a book restraint, it requires to study the distribution of values (and therefore also the type of distribution) and not the values themselves.

Increasingly, discharge authorizations are written in probabilistic terms: for example, require that the pH remains within a range determined for 95% of the time over 24 hours, and for 99% of the time on one month, the Guidelines Communities European for waters provide that certain parameters must be in accordance with the standard in 95% of the samples (or 1 in 20 in transgression), which
incidentally fits poorly with a routine monthly analysis: just in this case a measure transgression (1 of 12) for a bathing is closed, the flow of low flow of a river is defined as an average sliding on a minimum ten years, and so on.

• the extreme states, either absolute or corresponding percentiles of high concern toxicity studies, or the average is irrelevant, because a toxic mass does not have the same effect if it appears in one long period. It may be maximum (toxic) or minimum (oxygen).

• the time series: complete, for many samples or, ideally, by registration, they are required to study trends and the evolution of a system.

The state of the water is very variable, for climatic and techniques reasons, its characterization may require digital impressive number of measures to achieve reasonable accuracy (e.g. + / -5%). The experiments show that systematic thus is not legion, but here are the findings of eloquent three of them.

Table 1. Number of necessary measurements

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Precision obtained on threshold</th>
<th>Number of needed measures</th>
<th>Site</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-NH$_4^+$</td>
<td>+/- 0.2 mg/l</td>
<td>180</td>
<td>Trent (UK)</td>
</tr>
<tr>
<td>DCO</td>
<td>+/- 5 %</td>
<td>81</td>
<td>Craiova (RO)</td>
</tr>
<tr>
<td>Mat. susp.</td>
<td>+/- 5 %</td>
<td>102</td>
<td>Meuse (Liege)</td>
</tr>
</tbody>
</table>

The continuous measurement is a priori as the supreme quality of metrology. It allows theoretically answer any questions that may arise to interpreter: determine an average, any percentile, an extreme condition, cycles, trends, random fluctuations, triggering an alarm [7]. The application of the principle of common sense "who can do more can do less" encourages a resort as often as possible a continuous measurement. It is not free of difficulties, both in the collection, as one of the holding, as it will be shown.

2 Problems Associated with Continuous Collection

The first and most important of these problems is that of sampling, because the continuous measurement, even perfect, does not contain sampling error. It is in effect before the next classic situation (Fig.1). Sampling and analysis introduce both an error and most often the first is much higher than the second [6]. The aim of the sampling programs is to minimize overall error, i.e. to obtain with an analytical effort the most accurate possible result. In practice, a sampling plan will always be a compromise between information research and the cost (or work) needed to acquire.

The choice of a sampling program is extremely important. It is always cheaper to think the measures and take into account any prior knowledge about them, as the amplitude variations or the existence of cycles. All unidentified sources of variation are supposed random, and applied to the resulting usual statistical formulas. For any number $n_a$ of samples and $n_s$ sample analysis, the general formula is:

$$\sigma_i^2 = \frac{\sigma_c^2}{n_e} + \frac{\sigma_a^2}{n_a n_s}$$  \hspace{1cm} (1)

This relationship shows that increasing $n_a$, there is a limit in reducing $\sigma$ feasible as only the second term tends towards zero. It can be seen immediately that it is often unnecessary to use a very precise analytical methods if samples for its part, introduced an error unchanged and ten times
higher, which is often the case. In general, we can retain both precepts following technical health:

- It is more useful to make only a determination on three samples than a double dose on two samples;
- It is more useful to make only a determination on four samples, than a double dose on three samples.

As an example of decomposition of error, we reproduce below the results of a study of transversal and temporal uniformity of Meuse. The cross examination was 4.5 m x 120 m, and 240 samples were collected at a rate of one every 1 ½ hours to 3 over 5 depths and vertical. The statistical analysis covers:

1. a dissolved gas (O₂) by penetrating the surface and consumed in water and bottom;
2. a dissolved salt (CL⁻) for which there is no problem likely to create a concentration gradient;
3. a particulate matter (MS) that the sedimentation can lead to accumulate at the bottom.

The average speed of the river during measurement, was +/ - 13 cm / sec.

Under this factorial analysis, we see that the residual error on O₂ is the same both the analytical error, but considerably exceeds it for the other two dosages. The effect is most marked for the three types of pollutant, while none of them there are vertical gradient.

<table>
<thead>
<tr>
<th></th>
<th>O₂(mg/l)</th>
<th>CL⁻ (mg/l)</th>
<th>MS(mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>6.67</td>
<td>29.74</td>
<td>15.07</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>+/-1.34***</td>
<td>+/-2.57*</td>
<td>+/-13.48***</td>
</tr>
<tr>
<td>At the time of</td>
<td>+/-1.01</td>
<td>+/-1.78</td>
<td>+/-3.89</td>
</tr>
<tr>
<td>On the width of</td>
<td>0.43***</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>On the depth of</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Residual error</td>
<td>+/-0.11</td>
<td>+/-0.10</td>
<td>+/-1.32</td>
</tr>
<tr>
<td>Analytical error</td>
<td>+/-0.10</td>
<td>+/-0.10</td>
<td>+/-1.32</td>
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A transverse gradient is detected for oxygen, precisely because the residual error on the dosage is low, which makes the F test more sensitive.

The conclusion on this point is that any sophistication on the continuous measurement must be accompanied by an equivalent sophistication of sampling. The term "continuous measurement" is often used improperly for a designer to repeated short intervals. For example, an automatic sampler called "continuing" can not take at intervals of less than 2 min., A spectrophotometer recorder type Perkin-Elmer makes 17 to 25 steps per segment curve, etc.

The mere possibility of a visual or reading obligation to freeze the signal for as short a time as you like, and even dampen its variations electrically or mechanically. It is therefore obvious that the choice of this interval deserves our attention.

Two cases are considered: the measures analogy (continuous varies) and that measures digital (still fundamentally broken). But in advance it is useful to consider the various possible types of variability of a signal, and wonder what we important to preserve.

The recommendations that we can on this subject based on assumptions but more or less fragile:
- Assumed that the cycles obey really periodic functions and implement the Nyquist criterion;
- We assume that the distribution of residual differences is normal.

In this case the maximum interval between two measures may be set by the Nyquist criterion: it must be equal to half the period of the shortest cycle that we wish to identify with certainty. In practice we will choose instead a third or a quarter, but higher than 3d-1 (i.e. a peak every 8 hours), this restriction will not affect the technology of the measure.

When against by the "noise" that affects a digital signal is high, it can hide the information and make inaccurate or imperceptible. It should stabilize in these cases the signal by an adequate damping or an appropriate smoothing. Two smoothing techniques among many others seem to be recommended

1. smoothing method by the Whittaker-Robinson:

\[ Q = \Sigma R^2 + \lambda^2 \Sigma (A^i y_i)^2 \text{ minimize } (2) \]

2. smoothing convolution: (example smoothing quadratic and cubic for n = 9)
These formulas are far superior to the conventional moving average or slippery because they introduce a weighting in values. Therefore it does not force the experimental curve to be broken into small segments of straight, but on contrary it adjusts quadratic curve segments and / or cubic ones with an inflection point [8]. Many of continuous measurements are obtained from analog probes: oximetry, phmetre, thermometers. These probes do not provide an instant response. They have a time constant T defined as the time required to obtain 63% of the total answer, assuming (which is usually the case) a phenomenon of order one. The signal provided by these sensors is still lagging behind the stimulation and el is theoretically 3T to 95% of the total answer, it is conceivable that the records were screwed by a T probes high. It usually plays on these characters advocating such a T oxymeters high (25 or 30 s) to stabilize charts long-term probes and to T low (5 s) to store kinetic. Here is an example of response rising and descending an OXYMETER laboratory [9]. It is possible to correct responses based on equations Hovanssian, Linkek occasions.

3 Correction of Fixed Sensor
Dynamic Order 1

Answer fractional M = f (t):

\[ M = 1 - 2e^{-kt} + 2e^{-2kt} - 2e^{-3kt} \ldots \] (4)

Hence we draw (equation De Linek):

\[ y_i' = y_i + T \left( \frac{dy}{dt} \right) \] (5)

where:

\[ y_i' \approx y_i + T \frac{y_i - y_{i-At}}{At} \] (6)

with T, time constant (63% of the total response), select (examples: oxymeters - thermometers - pH-meters)

We see that the correction is possible in almost real time, provided they know both the value and its derivative measured as a function of time.

4. Conclusion
A continuous data collection provides an infinite number of values. Only the controller of water quality and compliance standards can be content with graphic gross values over time. He draws a horizontal corresponding to the norm, and identifies immediate transgressions, scope and duration. Any further exploitation of the results requires a contraction of data to synthesize and to bring some significant numbers easily interpretable and usable. There is therefore a double movement: a source tends to increase values, but on arrival we must reduce the number. So that finally we practice two samples: the first physically on the population (the "middle") and the second mathematically in the recordings. This is not without many problems, that we can only scratch here [5]:

- rejection of outliers,
- restoration of missing data (stations of the network continues SACQUE sometimes up to 50% of gaps, and it takes 1 h/j interruption for autosizing)
- operating distributions truncated (even when they are due to steps "out of range")
- sought cycles by spectral analysis or self-correlation (which introduces two periods dummy impossible to eliminate);
- stationarity tests,
- detection of trends

We will deliberately provoke a few comments. The simple calculation of an average may be full of pitfalls, as there is arithmetiques averages weighted (quadratic or cubic), harmonic, geometric. The cases of pH are clear: we can not practice on him as geometric means, and their interpretation remains in any event subject to the knowledge systems - buffer present. The ion-metrical measures are corrected electronically, at the source, for the same reason. The overall average simple arithmetic can be validly calculated only on a normal variable. But many environmental variables are log-normally distributed, which imposes a geometric mean.

At the end of the interpretative approach infinite mass of data is often surprisingly small. The monitoring network SACQUE established in Romania included some stations, analyzing 6 parameters at a parameter every 15 to 60 s. They bring their share of difficulties in maintaining them in good works, but what interests me here is the method of calculating final: recordings from continuing primary, secondary graphics were prepared using a value all 5h. The application of Nyquist shows that the shorter the cycle found interesting was the diurnal cycle (5/24 =1/4,8).

The impertinent question that we can ask is: why
not make a direct analysis every 5 hours? In a publication [4] of French authors establish a very detailed flow influx for plants by retaining only the daily flows.

It seems to us that these findings bring us back to our departure: the justification that continuous measurement depend exactly all environmental issue that we want to provide an answer. It is therefore wise to think carefully before any decision.

References