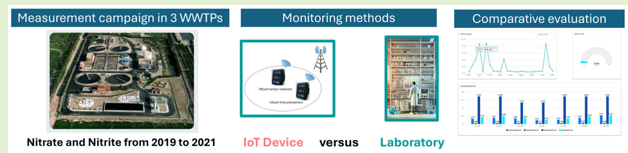
Evaluation of the IoT Device for Nitrate and Nitrite Long-Term Monitoring in Wastewater Treatment Plants

Juan Miguel Navarro, Abderrazak El Aatik, Antonio Pita, Ramón Martinez, and Nuria Vela

***Abstract*—Water pollution is an issue of global concern that requires continuous monitoring to maintain the integrity of surface and groundwater. This growing concern about environmental contamination has prompted the development and use of physical and chemical systems to control water quality in situ in most ecosystems, including wastewater treatment plants (WWTPs). In most water reuse projects, effluents must meet applicable water quality standards, regardless of whether they are discharged to surface or groundwater bodies, for irrigation or industrial reuse. In this article, an evaluation of the performance of the Internet-of-Things (IoT) device for long-term monitoring and detection of nitrate and nitrite in wastewater is presented. This device is integrated in the IoT system with these main components: an ion chromatography (IC) sensor to provide accurate data, together with mechanical elements for water sample acquisition and electronic circuits for the control of the whole monitoring process, a communication module to send real-time information, and a cloud software platform to store, analyze, and visualize the obtained water quality metrics. This evaluation was carried out by comparing traditional laboratory results with data captured by the remote device during a long-term measurement campaign at three WWTPs located in Murcia, Spain. The results show a satisfactory validation against standardized laboratory values, demonstrating the long-term measurement capability of the system. Specifically, the coefficient of determination of the regression between laboratory and device procedures reaches 96.7% on average in the three WWTPs for both nitrate and nitrite and influent and effluent streams.**



***Index Terms*—Internet of Things (IoT), monitoring, nitrate, nitrite, pollution, wastewater.**

I. Introduction

ENVIRONMENTAL water quality has come to the forefront due to concerns about increasing pollution of the resource, which has led to a push for water quality trends [1]. Concurrently, water quality on our planet has been greatly altered by increasing urbanization and industrialization, and scientific evidence shows a remarkable trend toward a positive relationship between human activities and water demand, which has gradually triggered the deterioration of water quality due to decreasing volumes of natural water resources [2].

The release of untreated or inadequately treated urban wastewater—including domestic, industrial, agricultural, and sanitary waste—into water bodies, such as lakes, rivers, aquifers, and oceans, has detrimental effects on both the environment and human health. This practice indirectly leads to the loss of biodiversity in aquatic ecosystems and exacerbates economic and social disparities, hindering sustainable development in modern societies. Effective wastewater sanitation systems, which encompass collection and distribution networks as well as treatment plants, are crucial for the sustainable social and economic progress of communities. In 2015, the United Nations General Assembly acknowledged the importance of sanitation. Strategies were established through the Millennium Development Goals (MDGs) and further outlined in the Sustainable Development Goals (SDGs), particularly Goal 6: ensure availability and sustainable management of water and sanitation for all [3]. Unfortunately, the SDGs are not being achieved.

One of the most common groundwater and surface contaminants in rural areas is nitrates and phosphates, which primarily originates from fertilizers, septic systems, and manure storage or spreading operations. Excessive accumulation of these

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nutrients especially in areas with intensive agriculture causes multiple problems, such as eutrophication, leading to hypoxia (or oxygen depletion) and harmful algal blooms that can destroy aquatic life in affected areas, which can collapse natural ecosystems and pose an additional serious risk to human health [4]. Nitrate compounds are soluble, and the nitrate ion is not retained in soil, making it the nitrogen species most susceptible to leaching. Excess levels of nitrate in drinking water are particularly hazardous for infants, as their immature digestive systems can reduce nitrate to nitrite, leading to methemoglobinemia [5].

Most wastewater treatment plants (WWTPs), designed to effectively manage this water resource and alleviate water scarcity, are unable to completely remove pollutants. In this context, the treatment of these pollutants requires special government-driven monitoring and management programs [6]. Recently, the European Council reached an agreement on a proposal to revise the Urban Wastewater Treatment Directive, establishing several priority measures. These measures include the mandatory installation of collection and secondary treatment systems, the implementation of tertiary treatment, and the introduction of quaternary treatments to remove contaminants [7]. These guidelines and objectives are integral parts of the European Green Deal [8] and the "Zero Pollution" Action Plan [9]. Consequently, water quality monitoring is an area of great importance in the field of clean water required by the strict regulations of the European Union.

In recent decades, the growing concern about environmental nutrient pollution has been the subject of significant research and studies focused mainly on the determination and analysis of nutrients in natural water and wastewater [10]. Accurate and long-term monitoring of water quality parameters has become a necessary practice to determine spatial trends and temporal variations in their distribution, especially of macronutrients, such as phosphate (PO_4^{3-}), nitrate (NO_3^-), and nitrite (NO_2^-) [11]. The determination of these inorganic anions in water is one of the most important tasks of analytical chemistry that can provide important information about their dynamics, as it can significantly reduce the level of hydric deterioration and the cost of remediation of the problem [12].

It is common to use different laboratory techniques for the detection of nutrients in water samples, either optical and/or electrochemical techniques based on automated colorimetric approaches or ion chromatography (IC) [13]. This method was first demonstrated by Li et al. [14] for chemical analysis by direct detection of nitrate and nitrite absorbance and Beaton et al. [15], who implemented a colorimetric laboratory-on-chip (LOC) system with a membrane sample filter to measure nitrate.

However, these methods are slow, laborious, and expensive, involving many sacrifices and a lot of work that is reflected in additional costs. In this context, the need arose for novel technologies in wastewater treatment that can perform in situ measurements for long-term monitoring of nutrients, instead of the traditional measurement of nutrients and other chemical parameters that requires taking samples, either manually or with autosamplers, and then transporting them to a laboratory for analysis [16]. To overcome this challenge, field-deployable sensors have emerged as an extremely interesting approach for nutrient monitoring in water [17], [18]. These automatic sampler and measurement devices require very low volumes of chemical reagents and can measure over a wide range of concentrations [19].

In recent years, these monitoring sensors are incorporating the Internet-of-Things (IoT) technology to add connectivity to communication networks and enable remote management of the equipment, creating the IoT system [20]. Many different sectors are adopting this technology to simplify, improve, automate, and control different processes, and water quality monitoring is one of the principal areas of research [21], [22]. Currently, constant, in situ monitoring of a water body, instead of analyzing samples in the laboratory, is a reality that allows continuous sampling, unlimited sample size and immediate results without delay, which increases the efficiency of environmental management decision-making. This benchmarking highlights the differences between remote and laboratory-based monitoring methods in terms of the duration of management pathways [23], [24], [25].

With the development of affordable and easy-to-use IoT devices for water quality monitoring, it is possible to accelerate and minimize the costs of obtaining water quality data, thus improving water quality and consequently water safety [26], [27]. The combination of the IoT devices coupled to online cloud computing with an integrated analysis technique, such as IC, enables smart water quality monitoring that gathers more information for better water quality management and pollution risk analysis, in particular, for nitrate and nitrite, which are considered indicators of undesirable pollutants in wastewater [28], [29], [30]. These IoT devices are deployed in remote sites in different locations with the aim of taking measurements over a long period of time and requiring as little maintenance as possible. However, the performance and accuracy of these devices in long-term measurement campaigns have not been studied in recent literature.

This research aims to address nutrient pollution in wastewater by evaluating an IoT device for long-term nitrate and nitrite monitoring in three WWTP in Murcia, Spain. By comparing traditional laboratory results with remote system data, the study assesses the effectiveness of low-cost, portable analytical devices for continuous in situ monitoring of nutrients.

After this introduction, the applied procedures to capture and obtain nitrate and nitrite level values, the IoT device-based versus laboratory analytical method, as well as the characterization of the wastewater from each WWTP are described in Section II. Section III presents the results of the comparison together with a discussion and analysis of the results. Finally, Section IV summarizes the main conclusions of this work.

II. Materials and Methods

A. Laboratory Analytical Method

1) Reagents, Chemicals, and Solvents: All analytical solutions were prepared using analytical grade reagents and deionized water. The eluent solution was composed by

Na_2CO_3 and $NaHCO_3$. The suppressor solution was prepared by H_2SO_4 (Sigma-Aldrich, 95.0%). The nitrite and nitrate standard solutions were prepared by $NaNO_3$ (purity > 91.5%) and $NaNO_2$ (purity > 91.0%) and were purchased from Merck (Barcelona). The reagent solutions were prepared with high-purity water from Millipore Milli-Q purification system. Working standard solutions were prepared by diluting the respective stock standard solutions to the desired concentration with water. Nitrite and nitrate standards were prepared from their respective sodium salts (Sigma-Aldrich). Analytical grade chemicals (Merck, Spain) were used to analyze nitrate and nitrite from three WWTPs. All glassware and other sample containers were rinsed with double distilled water and sterilized before use, and all samples were analyzed in triplicate.

2) Laboratory Equipment: A 25-μL sample loop was used for the entire work. Standard solutions of inorganic anions were purchased as anionic concentration standard of different ppm from Aldrich and diluted as required with Milli-Q water treated by Millipore (Bedford, MA, USA) was used to prepare the standard solutions and eluents.

A Thermo ScientificTM Dionex ICS-2100 IC coupled to a Dionex AS, Dionex Ion Pac AS19 column (2 × 250 mm). The optimized hydroxide eluent gradient was 0–10-mM isocratic, 10–25-mM gradient from 10 to 45 mM, flow rate: 1 mL$\cdot$min^{-1}, column temperature 30 °C coupled to a Dionex ASRS300, and 4-mm suppression current 120 mA. A Thermo Scientific ICS-2100 IC with an Ion Pac AS 19 column (250 mm, 4-mm ID) and KOH as eluent (10 mM from 0 to 10 min, 10–45-mM KOH from 10 to 40 min) at a low rate of 1 mL min^{-1} (30 °C) was used for anion analysis (nitrite and nitrate), instrument control.

B. Water Quality IoT Device

This section describes the IoT device that is evaluated in this work. This is an autonomous analyzer inside a portable suitcase for monitoring nitrite and nitrate in wastewater that is based on rapid IC and ultraviolet (UV) detection, integrated into the unit (IoT device) and connected to the IoT cloud platform [31]. The wastewater sample is continuously pumped by a basic peristaltic pump through an in-line filter to an automated injection valve injection loop, which is adjusted for analysis in the same manner as traditional methods based on flow injection analysis (FIA). To create an affordable, easy-to-use analyzer for in situ monitoring of nitrite and nitrate, compared with other options in the market, such as FIA and direct UV systems, this design incorporates a deep-UV LED. This addition offers improved energy efficiency and a longer lifespan than conventional UV lamps, while eliminating the need for hazardous materials, such as mercury. Furthermore, this portable, low-cost system utilizes 3-D-printed pumps and a uniquely engineered microfluidic optical detector cell. The data transmitted by the IoT device are captured, stored, analyzed, and finally represented in the IoT cloud platform, through a web-based user interface by means of different customizations [32].

Prior to the installation of the equipment in the WWTPs, a calibration was performed to ensure optimal performance and high accuracy. For this purpose, 100-mL samples with calibration and quality control standards are used. This process allows a successful full range calibration of the system. Once the analyzer is calibrated, users can select from different calibration ranges, low, medium, and high, according to the expected concentrations within the sample to analyze. For this use case, the low range is applied, which has an upper limit of 50 mg/L for nitrate and 10 mg/L for nitrite.

Fig. 1. Pictures of the IoT device deployed at WWTPs.

Throughout the measurement campaign, a maintenance routine has been carried out to ensure a correct and reliable operation of the measuring device. Monthly, after approximately 600 sample cycles for a sampling frequency of 1 h, the eluent is refilled, and the container is emptied. Moreover, the condition of the four syringes, the desiccant, and possible internal leaks are checked. Every year, the battery, desiccant, column, and inlet filter are replaced.

Two portable IC devices inside a portable suitcase were installed at each WWTP, one in the influent and one in the effluent, and placed as closer as possible from the water body. Fig. 1 shows a picture of the in situ nitrate and nitrite analyzer evaluated in this work deployed in a WWTP. The IoT device was configured to continuously sample and analyze samples in real time, which can be used to extract useful information from each WWTP. Daily real-time monitoring of nitrate and nitrite in wastewater was carried out, see more details in Section II-D2, which can be used to extract useful information from each WWTP.

C. Description of the IoT Devices Deployment Locations

Six IoT devices, as presented in Section II-B, were deployed in situ at three WWTPs to monitor nitrate and nitrite levels in influent and effluent wastewater and collect experimental data from March 2019 to January 2021. Every WWTPs in this field deployment are in the Region of Murcia (southeastern Spain), as shown in Fig. 2, and are designed to reuse their treated water for agriculture and/or irrigation of green areas. The first plant is located at region inland receiving water from the municipalities Molina de Segura (MO) and its districts, where the water is mainly originating from industrial and public domain. The other two WWTPs are located in the

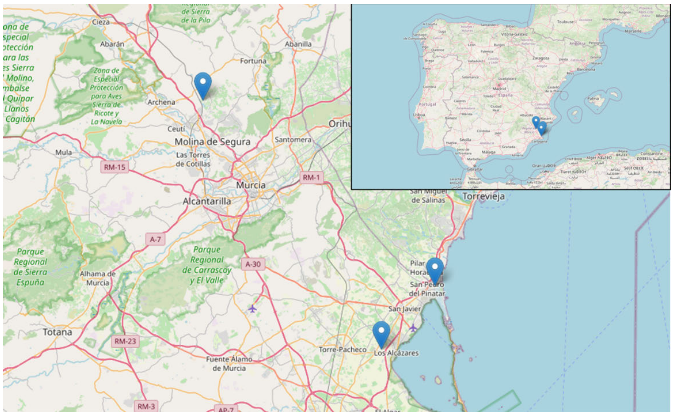


Fig. 2. IoT devices deployment sites in Murcia, SE Spain.

TABLE I
LIBRARIES AND SOFTWARE VERSIONS

Software Environment	Version
On-Premise	R version 4.3.2 called "Eye Holes"
AMD Ryzen 7 5800X 8-Core Processor 3.80 GHz with 32 GB RAM with GPU Nvidia GTX 3050 8GB GDDR6.	
Cloud	R version 4.3.3 called "Angel Food Cake"
Posit Cloud Server	
Library	**Version**
dplyr	1.1.4
tidyr	1.3.0
ggplot2	3.4.4
hrbrthemes	0.8.7
ggpmisc	0.5.5
MASS	7.3-60
zoo	1.8-12
imputeTS	3.3

coastal area adjacent to the agricultural lands of Cartagena, Los Alcázares (LZ), and San Pedro (SP), near the Mar Menor coastal lagoon, where the population grows during summer period.

D. Data Collection

This section describes the methods used for the collection and analysis of the samples taken during the campaign using both laboratory and the IoT device-based procedures.

1) Laboratory Data Collection: These nonautomated manual data collection operations consisted of physically going to the plant to collect samples and measure the required parameters in laboratory. Samples were taken at the water inlet and outlet points and taken to the laboratory for analysis. This sampling was performed on weekdays, daily at MO WWTP and Monday, Wednesday, and Friday at LZ and SP WWTPs, from March 2019 to January 2021. Water samples were taken from the same influent and effluent in 500-mL amber glass bottles from the WWTP to analyze nitrate and nitrite levels, together with other water quality parameters, in laboratory tests. Water samples were collected in acid-washed glass bottles, rinsed with deionized water and sterilized, and then stored in a portable refrigerator at 4 °C for proper preservation until arrival at the laboratory. Then, nitrate and nitrite contents were measured using a procedure following an official international method recommended by the Association of Official Analytical Chemists (AOAC) [33].

2) IoT Device Data Collection: The same parameters were measured in situ using an IoT device with integrated IC, described in Section II-B, deployed at the same location where the manual samples were taken. All necessary data were collected remotely using the IoT platform for data logging that is accessible online from a web interface. The IoT device transmits the water quality data, using GPRS mobile connectivity, to the IoT platform in the cloud, where it is decoded, stored, and further processed.

E. Statistical Analysis Software

The data preparation, transformation, analysis, and modeling processes were executed utilizing the Statistical Programming Language R [34], following the configurations outlined in Table I for both on-premise and cloud environments. The cloud environment [35] was leveraged to parallelize several analyses and tasks.

III. RESULTS AND DISCUSSION

This section consolidates the findings from the comparative analysis of the IoT devices and traditional laboratory methods in monitoring nitrate and nitrite concentrations at wastewater treatment facilities during a long-term measurement. As it has been previously enunciated, data have been gathered from March 2019 to January 2021 at three WWTPs for both procedures.

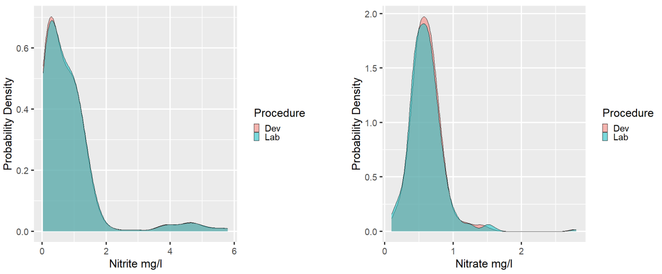
The study's sections sequentially address the statistical agreement between the IoT and laboratory data (Section III-A), the accuracy of the IoT measurement data across different settings (Section III-B), the stability of these statistics over time (Section III-C), and their resilience to seasonal variations and irregular events (Section III-D). Collectively, these analyses show the reliability, accuracy, and operational efficiency of the IoT devices, advocating their integration into real-time water quality monitoring systems.

A. Exploratory Data Analysis (EDA)

To allow analyzing and comparing both procedures, the data from the remote system devices have been subset to match the laboratory samples. Next, an exploratory analysis has been conducted, encompassing both graphical representations and statistical methods, which facilitates the examination and comparison of data distributions from the three WWTPs for both influents and effluents regarding nitrate and nitrite.

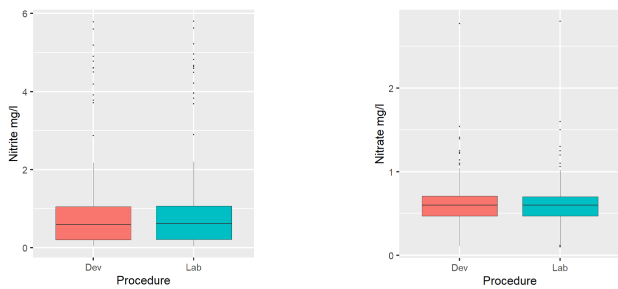
Figs. 3–5 illustrate the examples of the distribution comparisons between device-based and laboratory procedures for nitrite and nitrate influents at the SP WWTP, using box plots, violin plots, and density plots. Although the distributions of nitrates and nitrites differ between each other and depend on the specific treatment plant and whether it is an influent or effluent, the distributions of the data extracted through the laboratory procedure and the IoT device significantly coincide in shape for every WWTP, stream, and nutrient.

Table II provides comprehensive summary statistic of central tendency, including both robust (median) and nonrobust



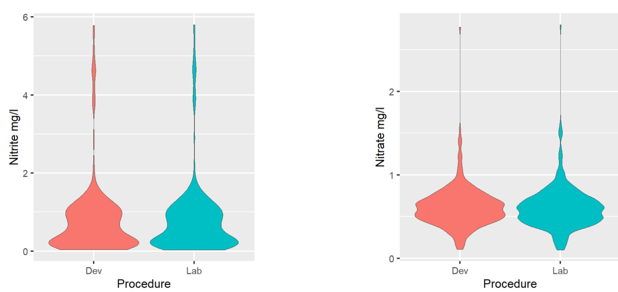
(a) (b)

Fig. 3. Distribution comparison using density plot, in particular, for (a) nitrite (NO_2^-) and (b) nitrate (NO_3^-) influents in SP WWTP using laboratory (Lab) and the IoT device (Dev) procedures.



(a) (b)

Fig. 4. Distribution comparison using box plot for (a) nitrite (NO_2^-) and (b) nitrate (NO_3^-) influents in SP WWTP using laboratory (Lab) and the IoT device (Dev) procedures.



(a) (b)

Fig. 5. Distribution comparison using violin plot for (a) nitrite (NO_2^-) and (b) nitrate (NO_3^-) influents in SP WWTP using laboratory (Lab) and the IoT device (Dev) procedures.

measures (mean), as well as dispersion metrics, such as the standard deviation (SD), and positional statistics, including the minimum (Min), maximum (Max), and the first and third quartiles (Q1 and Q3, respectively) for each WWTP for both nitrite and nitrate at the influent and effluent stages. N represents the number of instances. MO WWTP has more instances due to five samples per week instead of three samples per week at LZ and SP WWTPs.

The statistics shown in the values of Table II and the graphical charts presented in Figs. 3–5 indicate that, although there are some differences in measurement between different WWTPs, there are not significant differences in measurement outcomes between the IoT devices and traditional laboratory methods in each WWTP. The overall data distributions for nitrate and nitrite in both influent and effluent streams are statistically comparable across the different treatment plants. This consistency supports the potential for the IoT devices to provide reliable, real-time monitoring of water quality parameters, which could enhance operational efficiencies and environmental compliance in wastewater management.

B. Accuracy Analysis of Laboratory Versus the IoT Device Procedures

To identify different accuracy behaviors, a descriptive analysis was conducted separately for influent and effluent streams, considering differences and absolute differences between laboratory and the IoT device measurements for nitrate and nitrite for each WWTP. Mean and SDs of the differences were calculated to assess measurement consistency across different settings.

The results shown in Table III indicate variability in measurement accuracy between influent and effluent streams and among different WWTPs, distributed across various streams and chemical elements. The data gathered by the IoT devices exhibit similar behavior across nitrate and nitrite. Larger SDs in effluent streams, in 13 over 16 comparisons, suggest higher variability in effluent measurements. The average of the differences is always negative, suggesting that devices underestimate laboratory calculated values.

In addition, to measure the accuracy between laboratory and remote systems procedures, a linear regression analysis has been carried out for each stream (influent and effluent) and each WWTP. Also, a general comparison considering the combined data of the WWTP has been done.

Fig. 6 represents the scatter plots comparing laboratory (y-axis) and the IoT device (x-axis) procedures for influent and effluent streams of nitrate and nitrite considering all WWTPs. The blue line represents the linear regression of both procedures, and the estimated formula and the coefficient of determination are presented.

To evaluate numerically the fitting of both procedures, coefficient of determination (R^2) has been calculated for the combined data and for each WWTP.

Table IV shows that the average of the coefficient of determination for an individual WWTP is 96.7%, reaching the minimum at 88.8% (influent nitrite at MO) and the maximum at 99.9% (effluent nitrate at LZ and influent nitrite at SP). Nitrate presents, in average, higher coefficient of determination (98.4%) than nitrite (95.0%). Influent and effluent streams present the same coefficient of determination average (97.0%).

C. Analysis of Stability Difference Over Time

To identify instability over time, several time-series representations have been created and analyzed to identify stability over time for influent and effluent streams considering weekly mean and SD of differences and absolute differences between laboratory and the IoT device measurements for nitrate and nitrite for each WWTP and aggregated WWTP. Fig. 7 displays an example.

After examining all the mean and SD time series, a total of 32, no increase in the discrepancies over time was observed that would indicate a temporal deterioration of the IoT devices.

TABLE II
SUMMARY STATISTICS OF NITRITE AND NITRATE IN WWTPS OF MOLINA (MO), LOS ALCÁZARES (LZ), AND SAN PEDRO (SP)

			Nitrite $NO_2^-(mg \times l^{-1})$				**Nitrate** $NO_3^-(mg \times l^{-1})$			
			Influent		**Effluent**		**Influent**		**Effluent**	
WWTPs	**N**	**Statistic**	**Lab**	**IoT Dev**	**Lab**	**IoT Dev**	**Lab**	**IoT Dev**	**Lab**	**IoT Dev**
MO	472	Mean	0.083	0.104	0.976	1.027	0.673	0.680	2.663	2.680
MO	472	SD	0.160	0.173	1.026	1.040	0.414	0.409	1.934	1.929
MO	472	Min	0.020	0.010	0.010	0.020	0.000	0.000	0.120	0.160
MO	472	Q1	0.040	0.050	0.200	0.225	0.480	0.480	1.100	1.082
MO	472	Median	0.050	0.060	0.605	0.660	0.580	0.600	2.350	2.350
MO	472	Q3	0.080	0.090	1.500	1.552	0.710	0.720	3.800	3.812
MO	472	Max	2.100	2.170	5.200	5.150	4.650	4.600	11.400	11.350
SP	290	Mean	0.828	0.813	0.153	0.177	0.605	0.614	1.904	1.907
SP	290	SD	0.981	0.979	0.217	0.236	0.262	0.250	0.702	0.711
SP	290	Min	0.030	0.040	0.010	0.020	0.100	0.110	0.400	0.380
SP	290	Q1	0.210	0.200	0.070	0.080	0.470	0.470	1.400	1.385
SP	290	Median	0.610	0.570	0.100	0.110	0.600	0.600	1.900	1.890
SP	290	Q3	1.070	1.042	0.150	0.170	0.700	0.710	2.340	2.370
SP	290	Max	5.800	5.780	2.500	2.580	2.800	2.770	3.900	3.930
LZ	288	Mean	0.209	0.216	0.106	0.126	0.561	0.564	1.111	1.123
LZ	288	SD	0.305	0.299	0.151	0.159	0.569	0.568	0.740	0.736
LZ	288	Min	0.010	0.020	0.000	0.000	0.100	0.090	0.300	0.320
LZ	288	Q1	0.100	0.100	0.020	0.030	0.400	0.367	0.800	0.810
LZ	288	Median	0.130	0.130	0.040	0.050	0.490	0.455	1.000	1.010
LZ	288	Q3	0.172	0.180	0.120	0.140	0.530	0.550	1.200	1.212
LZ	288	Max	3.020	3.000	0.940	0.980	5.400	5.430	9.200	9.140

TABLE III
DIFFERENCES AND ABSOLUTE DIFFERENCES IN mg/L BETWEEN THE IOT DEVICE AND LABORATORY PROCEDURES FOR NITRITE AND NITRATE IN EACH WWTP AND AGGREGATE WWTPS (THE VALUES FARTHEST FROM ZERO ARE REPRESENTED IN RED BOLD, WHILE THOSE CLOSEST TO ZERO ARE REPRESENTED IN BLUE BOLD FOR EACH STATISTIC IN WWTPS OF MOLINA (MO), LOS ALCÁZARES (LZ), AND SAN PEDRO (SP)

			Differences (Dev-lab)		**Absolute Differences**	
Variable	**Stream**	**N**	**Mean**	**SD**	**Mean**	**SD**
MO WWTP						
NO_2^-	Influent	472	0.020	0.058	**0.024**	0.056
NO_2^-	Effluent	472	**0.051**	**0.186**	**0.069**	**0.180**
NO_3^-	Influent	472	**0.007**	**0.032**	0.026	**0.020**
NO_3^-	Effluent	472	0.018	0.159	0.052	0.151
LZ WWTP						
NO_2^-	Influent	288	0.007	**0.060**	0.024	**0.056**
NO_2^-	Effluent	288	**0.019**	**0.017**	**0.019**	**0.016**
NO_3^-	Influent	288	**0.003**	0.030	**0.026**	0.017
NO_3^-	Effluent	288	0.012	0.026	0.021	0.019
SP WWTP						
NO_2^-	Influent	290	-0.016	**0.037**	0.031	**0.025**
NO_2^-	Effluent	290	**0.024**	0.077	**0.028**	0.076
NO_3^-	Influent	290	0.009	0.050	**0.044**	**0.025**
NO_3^-	Effluent	290	**0.002**	**0.149**	0.040	**0.144**
Aggregated WWTPs						
NO_2^-	Influent	1050	0.007	0.056	**0.026**	0.050
NO_2^-	Effluent	1050	**0.035**	0.132	**0.044**	**0.130**
NO_3^-	Influent	1050	**0.006**	**0.038**	0.031	**0.022**
NO_3^-	Effluent	1050	0.012	**0.133**	0.040	0.127

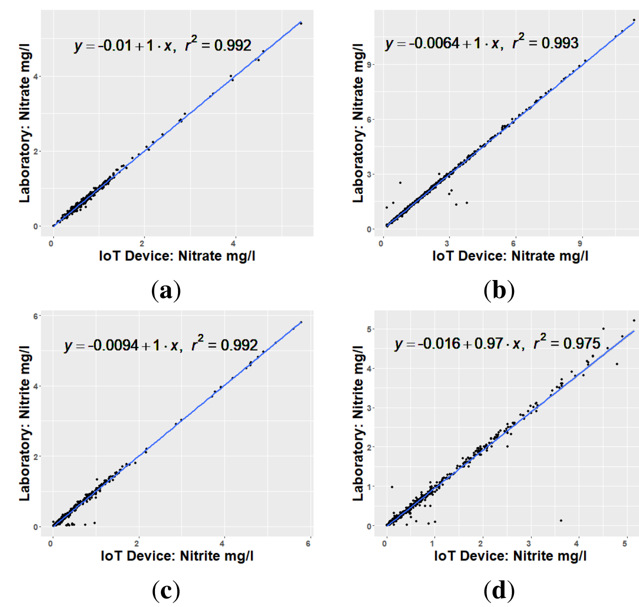
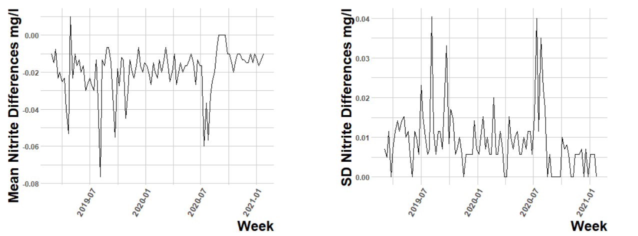


Fig. 6. Linear regression estimation between laboratory (y-axis) and the IoT devices (x-axis) gathered data for nitrate and nitrite in influent or effluent stream. (a) NO_3^- influent. (b) NO_3^- effluent. (c) NO_2^- influent. (d) NO_2^- effluent.

TABLE IV
COEFFICIENT OF DETERMINATION (R^2) BETWEEN DATA GATHERED BY THE IOT DEVICE AND LABORATORY PROCEDURES FOR NITRITE AND NITRATE IN WWTPS OF MOLINA (MO), LOS ALCÁZARES (LZ) AND SAN PEDRO (SP), AND AGGREGATED WWTPS

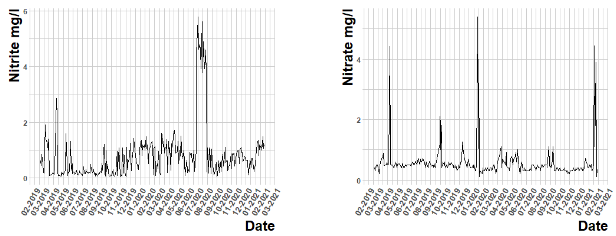
	Nitrite NO_2^-		**Nitrate** NO_3^-	
WWTPs	**Influent**	**Effluent**	**Influent**	**Effluent**
MO	0.888	0.968	0.994	0.993
SP	0.999	0.894	0.964	0.956
LZ	0.961	0.992	0.997	0.999
Aggregated	0.992	0.975	0.992	0.993

However, to quantify the stability over time, two linear regression analysis were conducted to examine the relationship of differences between the laboratory and the IoT device measurements for nitrite and nitrate concentrations in effluent and influent streams over time. Note that, for first regression analysis, the dependent variable is the mean of the differences between the measurements, and the independent variable is time, measured in weeks. The results are shown in Table V.



(a) (b)

Fig. 7. Laboratory versus the IoT device absolute difference time series for LZ WWTP. (a) NO_2^- effluent difference mean *y*. (b) NO_2^- effluent difference SD.



(a) (b)

Fig. 8. Time-series behavior. (a) Influent nitrite data evolution in SP WWTP with laboratory procedure. (b) Influent nitrate data evolution in MO WWTP with laboratory procedure.

TABLE V
LINEAR REGRESSION PARAMETERS AND PERFORMANCE METRICS FOR NITRITE AND NITRATE DIFFERENCES BETWEEN PROCEDURES ALONG TIME IN EFFLUENT AND INFLUENT STREAMS IN AGGREGATED WWTPS

Variable	Stream	R^2	Intercept Estimate	Slope Estimate	Slope StdError	Slope T-value	Slope P-value
NO_2^-	Influent	0.0030	-0.103	5.25E-06	9.64E-06	0.544	0.587
NO_2^-	Effluent	0.0002	-0.083	2.66E-06	1.96E-05	0.135	0.893
NO_3^-	Influent	0.0078	-0.136	7.07E-06	7.99E-06	0.885	0.378
NO_3^-	Effluent	0.0001	-0.059	2.63E-06	2.19E-05	0.120	0.905

R^2: Determination coefficient, **Estimate**: Linear regression coefficient estimation, **StdError**: standard error of the coefficient estimation, **T-value**: T-statistic of the t-test of the null hypothesis that a coefficient equals zero, **P-value**: Probability of obtaining a t-value with an absolute value at least as large as the one we actually observed in the sample data if the null hypothesis is actually true.

TABLE VI
LINEAR REGRESSION PARAMETERS AND PERFORMANCE METRICS FOR SD OF NITRITE AND NITRATE DIFFERENCES BETWEEN PROCEDURES ALONG TIME IN EFFLUENT AND INFLUENT STREAMS IN AGGREGATED WWTPS

Variable	Stream	R^2	Intercept Estimate	Slope Estimate	Slope StdError	Slope T-value	Slope P-value
NO_2^-	Influent	0.0255	-0.541	3.16E-05	1.97E-05	1.601	0.112
NO_2^-	Effluent	0.0013	0.433	-2.01E-05	5.72E-05	-0.351	0.726
NO_3^-	Influent	0.0224	0.164	-7.10E-06	4.74E-06	-1.499	0.137
NO_3^-	Effluent	0.0011	-0.287	1.93E-05	5.81E-05	0.332	0.740

R^2: Determination coefficient, **Estimate**: Linear regression coefficient estimation, **StdError**: standard error of the coefficient estimation, **T-value**: T-statistic of the t-test of the null hypothesis that a coefficient equals zero, **P-value**: Probability of obtaining a t-value with an absolute value at least as large as the one we actually observed in the sample data if the null hypothesis is actually true.

For the second regression analysis, the dependent variable is the SD of the differences between the measurements, and the independent variable is time, measured in weeks. The results are shown in Table VI.

The goodness of fit of the models (via coefficient of determination) is lower than 3% in each case, showing that there is no evidence of relationship between time and procedures' differences for nitrates and nitrites at influent and effluent streams. In the same manner, the p-values shown in Tables V and VI are significantly high (greater than 0.05), suggesting that there is not statistical evidence to assert a temporal trend in the average or variability of the differences between the laboratory and the IoT device measurements for any of the analyzed nutrients or streams. In summary, these results indicate that the evaluated IoT devices maintain consistent accuracy relative to laboratory procedure for nitrite and nitrate concentrations over the studied period.

Although this study validates the accuracy and stability of the sensors in these particular configurations by not detecting significant discrepancies over time, it is important to note that, in general, the sensors may be affected by performance under operational or environmental conditions other than those evaluated in the WWTP facilities. Therefore, it would be interesting for future work to validate the reliability of these sensors in other environments, such as seawater, which can affect factors, such as sensor drift or gradual wear.

D. Analysis of Seasonality and Irregularities

The concentration of nitrate and nitrite in wastewater may exhibit nonhomogeneous behavior, with periods of elevated levels, as depicted in Fig. 8(a), which shows an increase in nitrite levels during the period of July and August 2020 or periodically peaks, such as Christmas, Easter, or Summer, as shown in Fig. 8(b).

For this reason, a seasonality analysis has been conducted to evaluate the stability of the measurement differences between the laboratory and the IoT device in relative terms, with the goal of identifying moments of greater discrepancy. A total of 24 seasonality analysis, both additive and multiplicative, were performed on the nitrate and nitrite time series for influent and effluent flows from all WWTPs. These analyses did not identify significant seasonal components. Although nitrate and nitrite values show a variability over time for both influent and effluent waters, see Table II, this variability is not periodic and, as the results show, is not related to any seasonal factor.

In Fig. 9, box plot diagrams are presented, showing the absolute differences between the laboratory and the IoT device measurements of nitrate and nitrite for both influent and effluent streams, combining data from all WWTPs. The data have been grouped by month to assess whether significant differences are identified across different time periods.

The monthly distributions of the absolute differences do not show statistically significant differences between months, confirming that the IoT device performance is not affected by seasonality behavior or irregular events, such as the ones shown in Fig. 9.

In addition, some F-tests were conducted to assess statistical significance differences between any regression model comparing sensor data with laboratory data, and the other

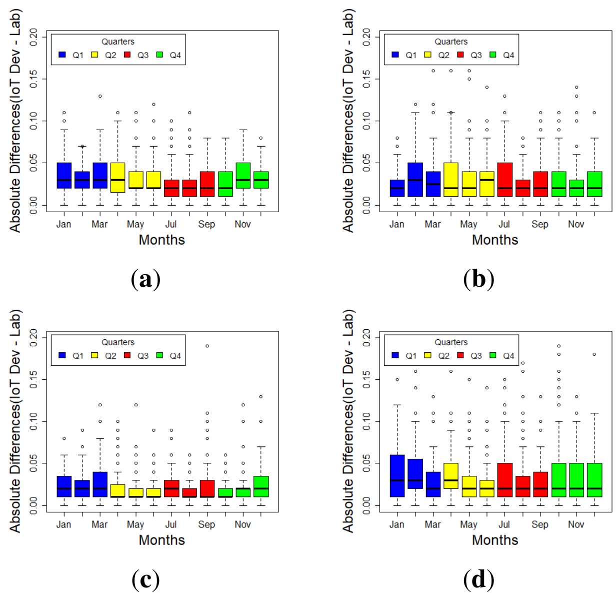


Fig. 9. Laboratory versus the IoT device monthly absolute differences box plot considering all WWTPs for (a) NO_3^- influent, (b) NO_3^- effluent, (c) NO_2^- influent, and (d) NO_2^- effluent.

regression model comparing sensor data with laboratory data alongside environmental factors (temperature, dew point, humidity, wind speed, pressure, and precipitation) for both influents and effluents regarding nitrate and nitrite. Null hypothesis was not rejected; therefore, it is shown that there is no evidence that environmental factors significantly impact the performance of the monitoring system.

IV. Conclusion

This article addresses the important issue of water quality monitoring applying the IoT system that benefits from up-to-date technologies. In this work, an evaluation of an IoT device for long-term monitoring of water quality parameters has been done. This evaluation has been carried out by comparing the results obtained, in a long-term campaign, with a standardized laboratory procedure and with the values provided by several IoT devices that have been deployed in three WWTPs, located in the region of Murcia, Spain.

In general, real-time monitoring of nitrate and nitrite in wastewater using this IoT device based on the IC method has offered analytical performance comparable to standard laboratory instruments, reducing the cost of obtaining water quality data and helping control on-site contamination. The values obtained by the IoT devices show a precise approximation with little difference in relation to the standard method.

Specifically, statistical analyses reveal that the coefficient of determination of the regression between laboratory and device procedures reaches 96.7% on average in the three WWTPs for both nitrate and nitrite and influent and effluent streams, indicating high consistency and low variability in the IoT measurements relative to laboratory standards. More evidences have been presented from the absolute differences t-tests and linear regression analyses, which confirm the reliability of the IoT devices over time and across various operational conditions within the plants, showing a satisfactory validation against standardized laboratory values.

Moreover, no significant trend in measurement variability or bias over time was observed, suggesting that the IoT devices maintain their calibration and accuracy throughout the study periods, demonstrating the long-term measurement capability of the system. This is crucial for the long-term implementation of automated monitoring systems in dynamic and sometimes unpredictable environments, such as WWTPs.

The absence of evidence for seasonal variations or irregularities in measurements reinforces the capability of the IoT devices to operate effectively unaffected by environmental fluctuations or atypical events. This demonstrates their suitability for integration into real-time monitoring applications, providing a reliable tool for environmental management and surveillance.

In conclusion, the findings of this study support the use of these IoT devices for water quality monitoring at treatment facilities, offering a viable and efficient alternative to traditional laboratory methods. By addressing nutrient pollution in wastewater with the IoT devices, this approach not only optimizes resources but also enhances responsiveness and enables timely interventions in wastewater treatment facility management.

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