"POLITEHNICA" UNIVERSITY OF BUCHAREST
Doctoral School of Applied Chemistry and Materials Science
Department of Chemical and Biochemical Engineering

DOCTORAL THESIS

OPTIMIZATION OF DRINKING WATER QUALITY MANAGEMENT

(Summary of the doctoral thesis)

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Keywords: drinking water quality, monitoring, risk, forecast, multilayer neural networks

INTRODUCTION

Water is the essential factor for the development of all vital processes, being indispensable for metabolic processes.

Water supply is essential for public health, quality of life, environmental protection, economic activity and sustainable development. In this context, it is important to ensure the continuous improvement of all processes in order to guarantee water quality and safety. The development of know-how and growing concerns about public health and the environment have contributed to positive developments in the water sector in many countries. (Roeger and Tavares, 2018).

The main objective of the thesis is to make original contributions through the presented studies aimed at identifying, analyzing and assessing the risks of drinking water quality, as well as forecasting the evolution of pollutants in drinking water.

Achieving the main goal is possible by pursuing secondary goals as follows:

- study and analysis of research in the literature
- establishing the stages of water treatment and presenting them through a flow chart
- identification and assessment of drinking water quality risks at each stage
- quantitative and qualitative analysis of water using Analytica software
- treatment of raw water for drinking purposes
- forecast of the evolution of the concentration of a pollutant in a drinking water source using multilayer neural networks.

The doctoral thesis is structured in two parts: literature data and original contributions.

PART I. LITERATURE DATA

In the first part is detailed the study of specialized literature in which they are presented: in chapter 2 the risk management of the quantity and quality of drinking water (evaluation of the drinking water supply system, importance of using flow charts, drinking water quality parameters, identification, assessment and analysis of hazards and risks), and in Chapter 3 monitoring of water sources and identification of risk factors.

Expressed in quantifiable terms, risk can be defined as a function of the probability that an undesirable event will occur, with a certain periodicity or in specific circumstances. (Maria, 2007). In order to achieve an acceptable level of risk, it is crucial to analyze the risk and, based on the identified level of risk and the causes of its occurrence, to establish security actions to reduce the risk. (Lindhe et al, 2009).

Thus, the risk analysis is a combination of the following elements, which must be contained (Table 2.9):

- the probability of occurrence of consequences (danger, accident), of an unwanted event, with a certain periodicity or in certain circumstances;
- the severity of the potential consequences (Maria, 2007; Woinaroschy and Iordache, 2019).

Table 2.9 Analysis of the severity and probability of consequences (Șchiopu, 2011; Mosse and Murray, 2015; Maria, 2007; Woinaroschy and Iordache, 2019)

GRAVITY		**GRAVITY OF POTENTIAL CONSEQUENCES**
1	**NEGLIGIBLE**	Consequences: no impact
2	**SMALL**	Consequences: minor lesions and/or sickenings, the absence of effects or minor effects, or consequences that appear only after exposure to high value doses in long periods of time
3	**MEDIUM**	Consequences: minor diseases
4	**LARGE**	Consequences: substantial prejudice and/or rarely serious disease
5	**SERIOUS**	Consequences: fatal, serious diseases, incurabile prejudice, that manifest themselves immediately or after a long period
PROBABILITY OF APPEARANCE		**PROBABILITY OF APPEARANCE OF CONSEQUENCES**
1	**VERY RARE**	Negligible: P < 1/year
2	**RARE**	Small: P = 1/year
3	**MODERATE PROBABILITY**	Medium: P = 1/month
4	**PROBABILE**	Large: P ≥ 1/month
5	**FREQUENT**	Serious: P > 1/week

The risk level identification method (Șchiopu, 2011; Mosse and Murray, 2015) (gravity function and appearance probability) is the following:

NR = P x G

Table 2.10 The risk level identification (Șchiopu, 2011; Mosse and Murray, 2015; Woinaroschy and Iordache, 2019)

Gravity (G)	**Risk level**				
Serious	5	10	15	20	25
Large	4	8	12	16	20
Medium	3	6	9	12	15
Small	2	4	6	8	10
Negligible	1	2	3	4	5
Probability of appearance (P)	Negligible	Small	Medium	Large	Serious

Table 2.11 Description of the risk level (Șchiopu, 2011; Mosse and Murray, 2015; Woinaroschy and Iordache, 2019)

Risk level	**Risk class**
1 - 2	No action required
3 - 5	Keep under observation / consider the water source control or water treatment measures
6 - 10	It is necessary to control the water collection or the treatment process / a possible intervention is necessary if the treatment is not appropriate
12 - 16	Emergency control of catchments or treatment and investments if treatment is not adequate
20 - 25	Emergency control of catchments or treatment and investments if treatment is not appropriate

It is good to identify the risks regardless of whether their source is under the control of the organization or not, even if the source or cause of the risk may not be obvious. It is recommended that the risk identification include an examination of the side effects of the specific consequences, including cascading and cumulative effects. It is also recommended to consider a wide range of consequences, even if the source or cause of the risk may not be obvious. Once identifying what could happen, it is necessary to consider possible causes and scenarios that show the consequences that may occur. It is recommended that all significant causes and consequences be considered (Moldovan, 2018).

PART II ORIGINAL CONTRIBUTIONS

The second part presents the scientific research on the identification and assessment of risks in drinking water and the forecast of the evolution of pollutants in drinking water, presenting the experimental results obtained using Analytica software and artificial neural networks, as well as the interpretation and statistical processing of these data.

Chapter 4 includes the study on the risk analysis of insufficient drinking water using Analytica software. The case study presents the ability of Analytica software to analyze and anticipate water demand in a seasonal tourist city, where economic activities and population numbers are quite different between the cold season (October - April) and the hot season (May - September).

Chapter 5 studies the analysis of the effectiveness of the chlorine water treatment process and the identification of risk factors. Based on the results of this study, regular monitoring of the concentration of free residual chlorine and microbiological indicators at the outlet of the treatment plant and in the water distribution system is recommended to ensure that chlorine residues of 0.1–0.5 mg/L are available.

Chapter 6 includes the analysis of the risk of contamination of raw water with nitrates using Analytica software. This study exposes the ability of Analytica software to analyze the evolution of the nitrate indicator in Mangalia, an analysis that can be used as input to management analyzes and for the analysis of emergency procedures for water contamination with nitrates.

The scientific research in Chapter 7 presents the forecast of the evolution of pollutants through the use of multilayer neural networks, a promising way for forecasts in the field of drinking water quality management. The advantages and disadvantages of regression models and artificial neural networks for predicting the evolution of pollutants in drinking water are also presented.

CHAPTER 4
RISK ANALYSIS REGARDING INSUFFICIENT QUANTITY OF DRINKING WATER USING ANALYTICAL SOFTWARE

4.1. Flow diagram of the Eforie Nord Water Supply System

The water supply of the Eforie Nord supply area is ensured from the Eforie Nord storage-pumping complex.

In this tank is stored water from the deep springs Cişmea I, Cişmea II and from the surface water source Galeşu, having as intermediaries the Palas and Constanța Sud water storage complexes.

The figure below (Fig. 4.1) shows the flow diagram for the Eforie Nord water supply system.

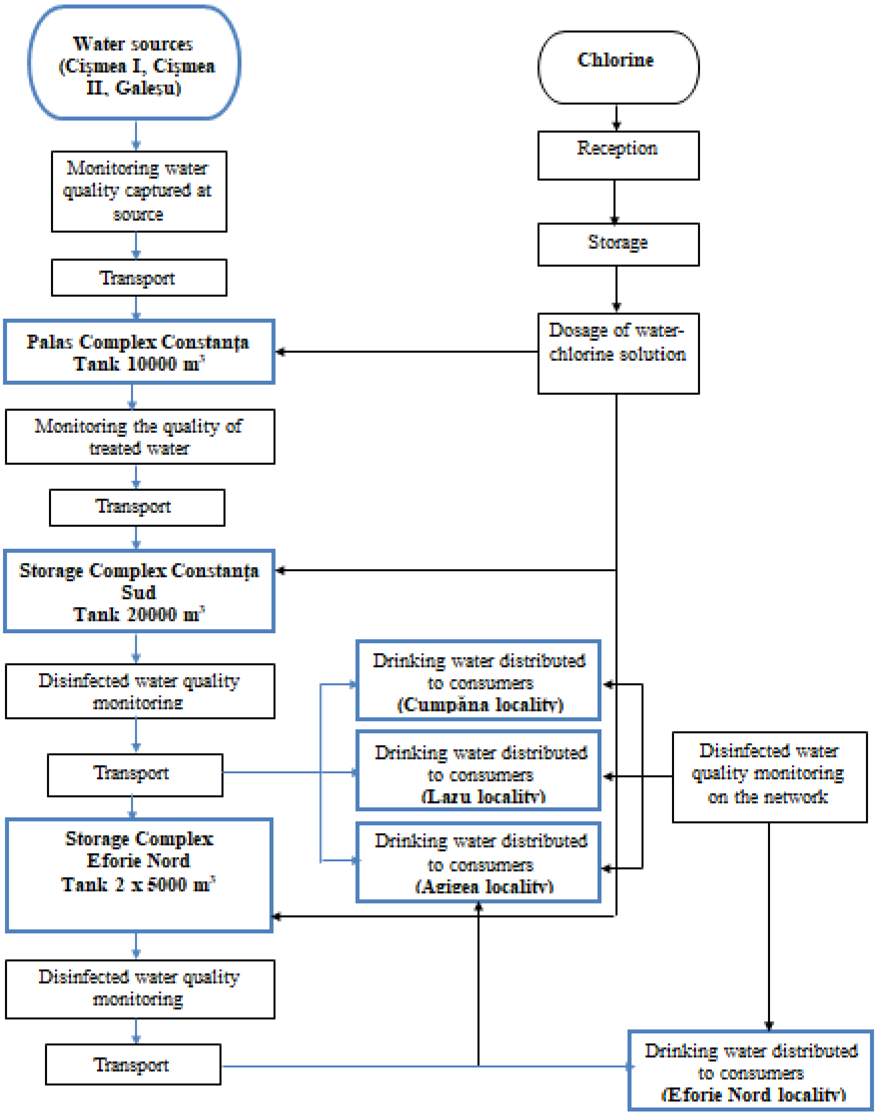

Fig. 4.1 Flow diagram of the Eforie Nord Water Supply System (Woinaroschy and Iordache, 2019)

4.2. Risk analysis for the Eforie Nord water supply system

Identifying potential hazards and risks to both the water source and the water treatment and distribution system, growing public health and environmental concerns are contributing to recent positive developments in the water sector in many countries. (Roeger A. and Tavares A.F., 2018).

Risk analysis is the next step in identifying hazards in the water flow. The risks are related to the supply to users of water of unacceptable quality, which can lead to serious consequences for the health of users. Risks are assessed according to the causes of the occurrences, the potential consequences and the safety actions taken to prevent water contamination (Table 4.1).

Table 4.1 Risk analysis regarding the insufficient amount of drinking water supplied from the Eforie Nord Water Supply System (Woinaroschy and Iordache, 2019; Bostian et al., 2015; Janmaat, 2017; Fornib et al., 2016; Sandu and Racovițeanu, 2002; Cavalierea et al., 2017)

Potential risk	Causes of risk appearance	Potential consequences	Risk level	Security measures	Proposed residual risk level
PROCESS: CAPTURE AND TRANSPORT OF RAW WATER					
Stage: Capture and transport of surface raw water/ groundwater					
Insufficient drinking water distributed to consumers	- Filling of water sources - Decrease in surface water due to drought	- Lower users' health and hygiene	G = 3 P = 1 RL = 3	- Ensuring the quantity of drinking water required in relation to the variation in the number of consumers - Permanent monitoring of water sources	3

4.3. Quantitative risk analysis using Analytica software

Analytica provides an integrated risk and sensitivity analysis for the analysis of models with uncertain inputs and powerful facilities for time-dependent dynamic simulations.

Analytica is a software for risk assessment in various applications. Using a visual, point-and-click approach, by drawing nodes and arrows to describe the relationships between the components of the model, allows the description of the essential qualitative nature of the problem without getting lost in the details. As the model develops and the understanding of the problem becomes clear, the exact quantitative details of the model can be defined. (Lumina, 2015)

Ideally, in times when raw water has a constant quality and quantity, a water supply system will operate continuously, without changes in flow or other operating conditions for individual treatment processes. In this way, an optimized system will have the best opportunity to constantly produce safe drinking water. However, ideal conditions do not always apply with various factors that influence the quality and quantity of water required. (fig. 4.2). (Mosse and Murray, 2015; Woinaroschy and Iordache, 2019)

Drinking water distributed in Eforie Nord is derived from the underground sources of Cișmea I and II and from the surface water source Galeşu, so the risk of insufficient drinking water distributed to consumers is due to the clogging of water sources or the decrease of the surface water level due to drought, lack of precipitation. (Xie et al., 2016; Lanz and Provins, 2016) A potential consequence of this risk may be the lowering of the level of health and hygiene of the users and the security actions that can be taken are: ensuring the quantity of drinking water required in relation to the variation of the number of consumers and the permanent monitoring of the water sources.

At present, the amount of surface water used is up to 20% of the total amount of water. (Woinaroschy and Iordache, 2019).

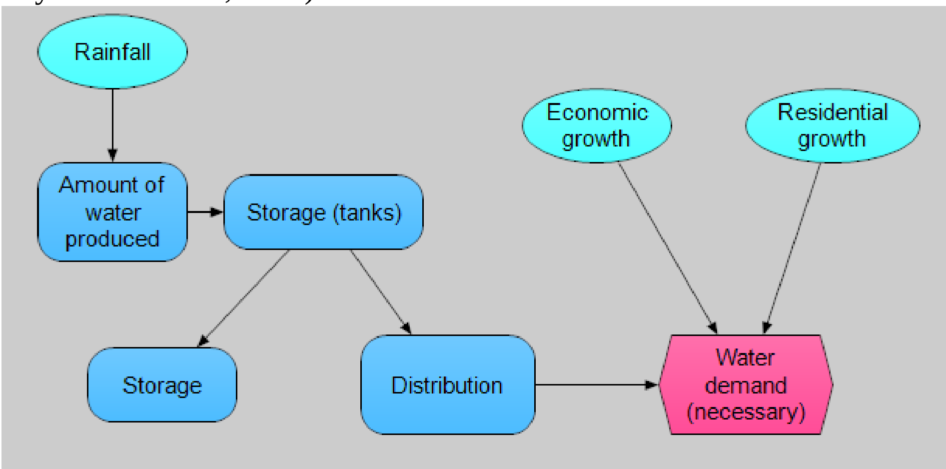

Fig. 4.2 Analytica model on the factors that influence the amount of drinking water

Drinking water supply is a continuing concern, and if underground water supply is relatively stable, in the case of surface water an important factor that influences the amount of water is precipitation. (fig. 4.3).

Supply of surface water is vulnerable to decreasing the amount of water during periods of low rainfall. In this case, the uncertain key variable is rainfall, which varies with the season. (www.vremea.ro, 2018; Woinaroschy and Iordache, 2019)

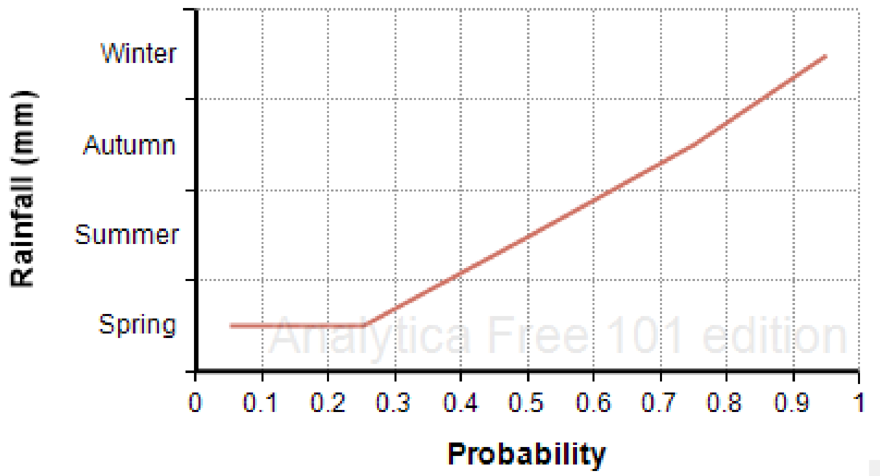

Fig. 4.3 Analytica model regarding the variation of precipitations

Water storage is provided in a tank of 20000 mc (Storage Complex Constanța Sud) and in a tank of 10000 cubic meters (2 cuvettes of 5000 mc of Eforie Nord).

An important issue to keep in mind is economic growth (fig. 4.4) through the development of area tourism and automatic residential growth (fig. 4.5) (www. primăriaeforie.ro, 2018). Typically, during the summer season, the number of users is four times higher than during the cold season, and the drinking water requirement is four times higher (Woinaroschy and Iordache, 2019).

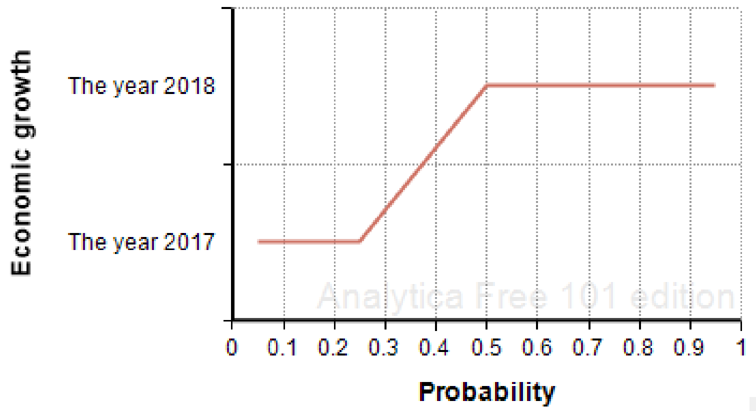

Fig. 4.4 Analytica model on economic growth

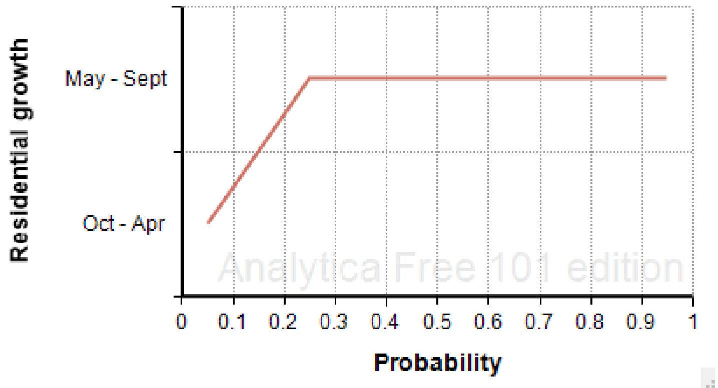

Fig. 4.5 Analytica model on residential growth

If during the cold season (October - April) the volume of water billed is about 41000 mc per month, during the summer season (May - September) at the level of 2017 it was about 184000 mc per month and it is expected to increase to 2018 up to 200,000 mc per month thanks to the development of the area's tourism. (fig. 4.6) (Woinaroschy and Iordache, 2019).

Fig. 4.6 Analytica model regarding the variation of water demand depending on residential growth

The presente analysis can allow water operators to understand probabilities and potential impacts on water resources. It can be used as input to manage analyses, to analyse water storage emergency procedures, and to create a new water allocation process and monitorise in real-time water resources conditions. (Woinaroschy and Iordache, 2019; Roebeling, 2014).

4.4 Conclusions

We need to treat risk assessment as a preventive management to ensure safe drinking water quality and quantity, taking into account the following main elements:

- Evaluation of the management system,
- Establishing as the primary objective of user health concerns,
- Operational phased monitoring, from raw water abstraction to the distribution of drinking water to users, control measures (security actions) established,
- Elaborating, documenting, communicating and periodically reviewing management system monitoring plans, risk assessment plans, describing actions, measures to be taken under normal operating conditions and potential incidents, including upgrading and improving.

By developing and following compliance with a risk assessment plan, we ensure that distributed drinking water complies with the legal requirements in force.

Drinking water quality can be controlled by combining the protection of water sources, the control of treatment processes and the management of water distribution. The guidelines must be appropriate for national, regional and local circumstances, which require adaptation to environmental, social, economic and cultural circumstances and the setting of priorities.

Control measures (Security actions) must have a clearly defined monitoring regime that validates efficiency and monitors performance against established limits. Following periodic evaluations, non-compliance reports should be initiated, corrective action taken to eliminate the causes of non-compliance. Operational monitoring actions shall be performed at planned intervals and at the time of planned or unplanned changes to the water supply system.

Developing a risk assessment plan is not an end of itself but a means for a goal. A risk assessment plan is only useful if it is implemented, monitored and reviewed periodically (WHO, 2009).

The case study presented the ability of Analytica software to analyze and anticipate water demand in a seasonal tourist city, where economic activities and population numbers are quite different between the cold season (October - April) and the hot season. (May - September) (Woinaroschy and Iordache, 2019).

CHAPTER 5
ANALYSIS OF THE EFFECTIVENESS OF THE WATER TREATMENT PROCESS AND IDENTIFICATION OF RISK FACTORS

5.1 Description of the water supply system Constanța, Litoral

The Palas Constanța treatment, storage, pumping complex is located in the industrial area of the city of Constanța, on Aurel Vlaicu Boulevard, Palas neighborhood, with an area of about 7.8 ha. The complex can take over the entire flow captured from the Galeșu surface source, as well as the water collected from the underground sources Cișmea I and II. The volume of water stored within the complex is repurposed in the distribution network of the city of Constanța, as well as in the Litoral water supply system. (Oglindă, 2019)

In fig. 5.1 is presented the flow chart of the Palas Constanța Treatment, Storage, Pumping Complex

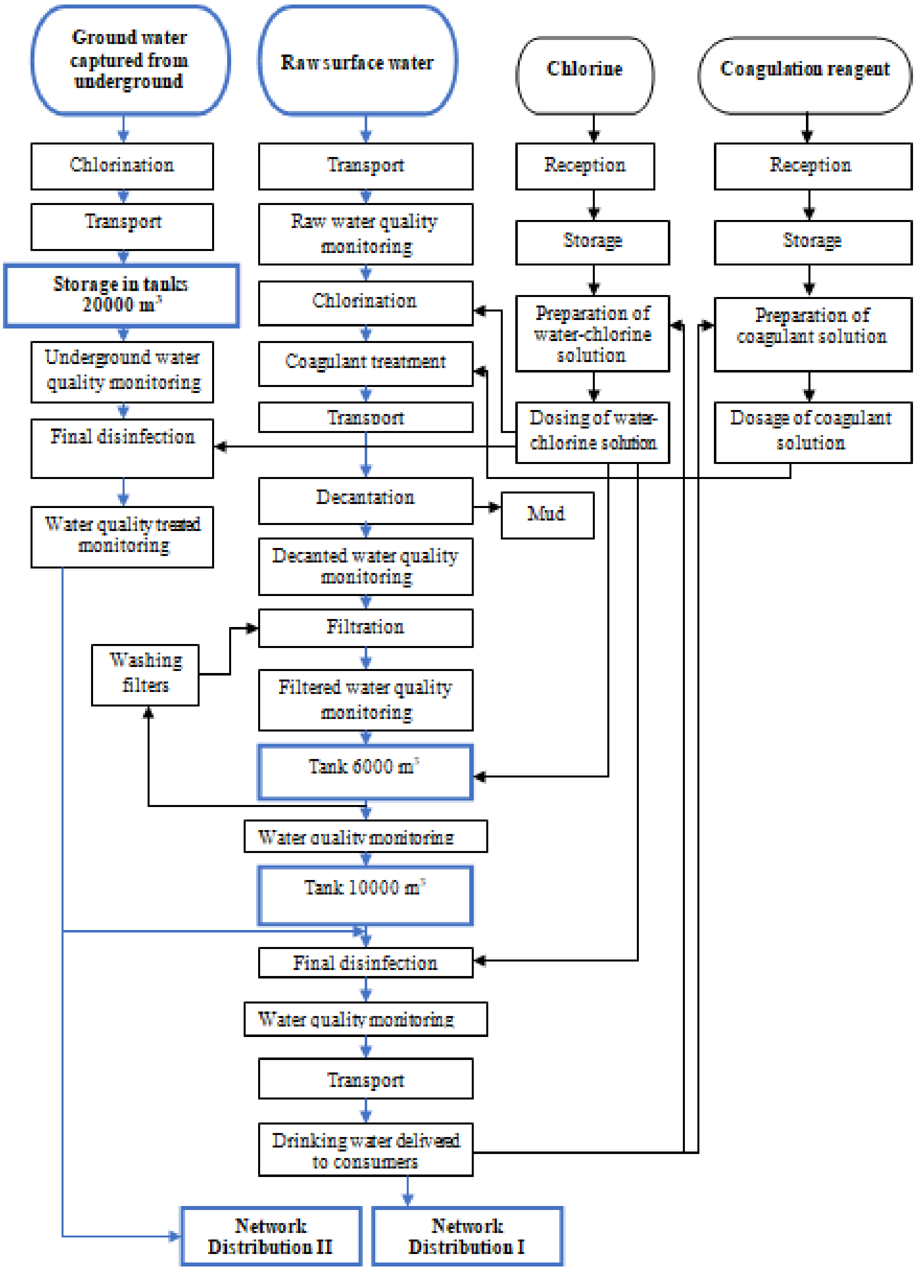

Fig. 5.1 Flow diagram of the Treatment, Storage Complex, pumping Palas Constanța

The flow diagram (fig. 5.1) provides a graphical representation of the water treatment process.

The flow diagram shown in fig. 5.1 includes:

- the succession and the interaction of the treatment stages
- points of entry into flux of raw materials (raw groundwater and surface water), ingredients (chlorine and coagulant solution)
- the stage where the water treatment takes place
- stages of water quality monitoring
- the final stage of water distribution

5.2 Risk factors identified in the chlorine water treatment process at the Palas Constanța complex

The cheapest and most efficient method of obtaining safe drinking water for consumption is to maintain a risk management, based on prevention, along with a proper monitoring of the functioning of the water supply system. As each stage of the water supply system may be subject to contamination, it is important to identify the risk factors, the causes of their occurrence and the security actions that need to be applied to keep them under control (WHO, 2014).

Table 5.1 identifies the risk factors in the chlorination phase of the water, the potential causes of the occurrence of the risks and the possible control measures/ security actions that must be taken to be able to control the risks.

Table 5.1 Identification of risk factors in the chlorination stage (ESA, 2018; Ioniță, 2018; Mosse and Murray, 2015)

STAGE	RISK FACTORS	THE CAUSES OF RISKS	SAFETY MEASURES/ ACTIONS
Chlorination	- Inefficiency of water disinfection due to chlorine concentration underdose - Excess residual chlorine content due to chlorine overdose	- Insufficient staff awareness and training - Unreported defects in chlorine dosing equipment - Improper maintenance of the chlorine appliance - Failures in the distribution network and lack of washing and disinfection of the water pipe at the end of the work	- Monitoring of water quality - Compliance with the established chlorine concentration - Periodic verification of chlorine dosing equipment - Staff training and awareness - Washing and disinfecting the water pipe following a failure in the distribution network

The greatest risk involved in the chlorination activity of the water is the insufficient amount of residual chlorine for the destruction of the microorganisms in the water.

In order to minimize the risks to the health of users, activities should be periodically undertaken to monitor the quality of drinking water, to verify chlorination facilities and to train staff (WHO, 2014).

5.3 Analysis of the effectiveness of the chlorine water treatment process

In recent years, water has become a subject of international policy and maintaining the quality parameters of drinking water supplied to consumers, within the range specified by the legal and regulatory requirements in force, is certainly a priority.

The chemical processes of water disinfection are characterized by the use of bactericidal chemicals such as: chlorine, chlorine dioxide, sodium hypochlorite, ozone, ultraviolet rays. Chlorine and ozone are among the most commonly used disinfectants worldwide (Water RA, 2015).

Drinking water quality varies throughout the system, so the assessment should aim to verify the quality of drinking water at the consumer's tap, by comparing it with the limit values set by the legal requirements in force. (Sandu and Racovițeanu, 2002)

Each of the disinfection agents has a specific spectrum of action that is variable in time and conditioned by the quality of the raw water (Farooq S. et al., 2008).

Table 5.2 shows the advantages and disadvantages of using the most common disinfection agents.

Table 5.2 Disinfectants used in the water treatment process (Sandu M. and Racovițeanu G., 2002; American Chemistry Council, 2018)

Disinfection agent	Advantages	Disadvantages
Chlorine	It is remnant (residual) in the distribution network. High microbiological efficiency of high disinfection. Low costs. High validity term (1 year).	Requires long contact time. Potential for rapid decomposition.
Sodium hypochlorite	It is remnant (residual) in the distribution network High microbiological efficiency of high disinfection. Low costs.	Requires long contact time. Potential for rapid decomposition. Short validity term (45 days).
Chlorine dioxide	It is remnant (residual) in the distribution network. They do not form trihalomethane by-products. It has good oxidizing power, oxidizes phenols and is very effective at pH over 8,5.	Requires instant preparation and dosing. At too high a dose it can form chlorates. Higher costs in relation to chlorine. It is unstable and explosive at temperatures above 40^0C.
Ozone	It has the highest oxidation capacity. Total elimination of biological, microbiological and micropollutant compounds. Eliminate pesticides.	Requires instant preparation and dosing. High energy consumption. It can form bromates or aldehydes by-products. There is no remnant (residual) in the distribution network.
Ultraviolet radiation	UV sterilization is safe and effective. It does not change the taste, smell, pH and color of the water. High microbiological efficiency of disinfection. Disinfection is done immediately (3-5 seconds).	Only effective for short water supply networks, not suitable for large systems.

Chlorine is commonly used for water disinfection, due to its high efficiency and relatively low cost compared to other disinfectants. Throughout the distribution system the quality of the water must be constantly monitored to verify the presence of free residual chlorine. Loss of chlorine residues makes the distribution system vulnerable to microbial contamination (Water RA, 2015; Farooq S. et. al., 2008).

When the chlorine is introduced into the raw water, hypochlorous acid (HOCl) and hydrochloric acid (HCl) are formed. Hypochlorous acid (HOCl) dissociates into hydrogen ions (H +) and hypochlorite ions (ClO-) which represent the active element.

Chlorine, introduced into the water, acts in several stages. In the first stage, the mineral substances are oxidized (salts of iron, magnesium, nitrates, nitrites, etc.). In the next step, the remaining amount of chlorine acts on the ammonia (NH_4) to form chloramines (NH_2Cl, $NHCl_2$, NCl_3). They give the water a non-compliant taste and smell. Continued introduction of chlorine into water leads to the oxidation of chloramines. After this stage, an increase of free residual chlorine is recorded which is destined for disinfection (Gibbs M.S. et. al., 2006; American Chemistry Council, 2018).

The stages of disinfection and the necessary doses of chlorine are always established on the basis of laboratory analyzes. Water samples are taken from both the treatment station, during the treatment stages, at the exit from the station and from the distribution network (Water RA, 2015; WHO, 2014).

The study on the capacity of the water treatment process for water purification consists of monitoring the free residual chlorine, coliform bacteria, E. Coli and Enterococci between 01.2013 - 12.2018 for two sampling points: at the entrance to the water supply network (the Palas Constanța water treatment complex) and towards the end of the supply network (Eforie Nord network). The legislation in force, respectively Law 458/2002 republished on 03.09.2017 regarding the quality of drinking water, specifies the limit allowed for the indicator Free residual chlorine of 0.1 - 0.5 mg / L in the distribution network (connection, end of the network), and for bacteriological indicators the allowed limit is 0.

Chlorine is used to disinfect water and thus decrease, eliminate bacteriological indicators: coliform bacteria, fecal coliforms, E. coli, etc.

A number of 576 water samples were monitored between 01.2013 - 12.2018 regarding the free residual chlorine, coliform bacteria, E. Coli and Enterococci, the values obtained of the indicators being presented in table 5.3.

Table 5.3 Values of the indicators Free residual chlorine, Coliform bacteria, E. Coli and Enterococci monitored in the period 2013 - 2018

No.	**Year/ Month**	**Indicators drinking water departure Complex Palas Constanța**				**Eforie Nord network drinking water indicators**			
		Free residual chlorine mg/L	Col. Bact., no. /100 ml	E. Coli, no./ 100 ml	Enterococci, no./100 ml	Free residual chlorine mg/L	Col. Bact., no./100 ml	E. Coli, no./100 ml	Enterococci no./100 ml
1.	**2013** Jan	0.5	0	0	0	0	0	0	0
2.	Feb	0.51	0	0	0	0	0	0	0
3.	Mar	0.74	0	0	0	0.2	0	0	0
4.	Apr	0.56	0	0	0	0.1	0	0	0
5.	May	0.65	0	0	0	0	0	0	0
6.	Jun	0.47	0	0	0	0	16	14	17
7.	Jul	0.44	0	0	0	0.1	0	0	0
8.	Aug	0.51	0	0	0	0.3	0	0	0
9.	Sep	0.25	0	0	0	0.2	0	0	0
10.	Oct	0.73	0	0	0	0.3	0	0	0
11.	Nov	0.73	0	0	0	0.4	0	0	0
12.	Dec	0.55	0	0	0	0	0	0	0
13.	**2014** Jan	0.46	0	0	0	0	0	0	0
14.	Feb	0.54	0	0	0	0	0	0	0
15.	Mar	0.43	0	0	0	0	0	0	0
16.	Apr	0.59	0	0	0	0	0	0	0
17.	May	0.39	0	0	0	0	0	0	0
18.	Jun	0.51	0	0	0	0.1	0	0	0
19.	Jul	0.29	0	0	0	0.2	0	0	0

No.	Year/ Month	Indicators drinking water departure Complex Palas Constanța				Eforie Nord network drinking water indicators			
		Free residual chlorine mg/L	Col. Bact., no. /100 ml	E. Coli, no./ 100 ml	Enterococci, no./100 ml	Free residual chlorine mg/L	Col. Bact., no./100 ml	E. Coli, no./100 ml	Enterococci no./100 ml
20.	Aug	0.48	0	0	0	0.3	0	0	0
21.	Sep	0.51	0	0	0	0.1	0	0	2
22.	Oct	0.64	0	0	0	0	0	0	0
23.	Nov	0.54	0	0	0	0	0	0	0
24.	Dec	0.5	0	0	0	0	0	0	0
25.	**2015** Jan	0.46	0	0	0	0	0	0	0
26.	Feb	0.63	0	0	0	0	0	0	0
27.	Mar	0.45	0	0	0	0	0	0	0
28.	Apr	0.39	0	0	0	0	0	0	0
29.	May	0.56	0	0	0	0	0	0	0
30.	Jun	0.29	0	0	0	0.2	6	5	0
31.	Jul	0.47	0	0	0	0.1	0	0	0
32.	Aug	0.54	0	0	0	0.3	0	0	0
33.	Sep	0.5	0	0	0	0.2	0	0	0
34.	Oct	0.56	0	0	0	0.3	0	0	0
35.	Nov	0.65	0	0	0	0.1	0	0	0
36.	Dec	0.56	0	0	0	0.1	0	0	0
37.	**2016** Jan	0.6	0	0	0	0.1	0	0	0
38.	Feb	0.6	0	0	0	0.1	0	0	0
39.	Mar	0.4	0	0	0	0.1	0	0	0
40.	Apr	0.5	0	0	0	0.4	0	0	0
41.	May	0.5	0	0	0	0.2	0	0	0
42.	Jun	0.4	0	0	0	0.4	0	0	0
43.	Jul	0.6	0	0	0	0.4	0	0	0
44.	Aug	0.23	0	0	0	0.1	0	0	0
45.	Sep	0.5	0	0	0	0.4	0	0	0
46.	Oct	0.5	0	0	0	0.2	0	0	0
47.	Nov	0.6	0	0	0	0.5	0	0	0
48.	Dec	0.4	0	0	0	0.5	0	0	0
49.	**2017** Jan	0.6	0	0	0	0.2	0	0	0
50.	Feb	0.4	0	0	0	0.3	0	0	0
51.	Mar	0.4	0	0	0	0.1	0	0	0
52.	Apr	0.5	0	0	0	0.4	0	0	0
53.	May	0.3	0	0	0	0.2	0	0	0
54.	Jun	0.5	0	0	0	0.2	0	0	0
55.	Jul	0.4	0	0	0	0.3	0	0	0
56.	Aug	0.3	0	0	0	0.2	0	0	0
57.	Sep	0.4	0	0	0	0.2	0	0	0
58.	Oct	0.5	0		0	0.1	0	0	0
59.	Nov	0.3	0	0	0	0.1	0	0	0
60.	Dec	0.6	0	0	0	0.1	0	0	0
61.	**2018** Jan	0.5	0	0	0	0.1	0	0	0
62.	Feb	0.4	0	0	0	0.1	0	0	0

No.	Year/ Month	Indicators drinking water departure Complex Palas Constanța				Eforie Nord network drinking water indicators			
		Free residual chlorine mg/L	Col. Bact., no. /100 ml	E. Coli, no./ 100 ml	Enterococci, no./100 ml	Free residual chlorine mg/L	Col. Bact., no./100 ml	E. Coli, no./100 ml	Enterococci no./100 ml
63.	Mar	0.6	0	0	0	0.2	0	0	0
64.	Apr	0.4	0	0	0	0,1	0	0	0
65.	May	0.5	0	0	0	0,2	0	0	0
66.	Jun	0.2	0	0	0	0.1	0	0	0
67.	Jul	0.4	0	0	0	0.3	0	0	0
68.	Aug	0.3	0	0	0	0.2	0	0	0
69.	Sep	0.3	0	0	0	0.1	0	0	0
70.	Oct	0.5	0	0	0	0.4	0	0	0
71.	Nov	0.6	0	0	0	0.5	0	0	0
72.	Dec	0.5	0	0	0	0.3	0	0	0

Fig. 5.2 shows the evolution of the free residual chlorine indicator at the departure of the Complex of treatment, storage, pumping Palas Constanța (blue) and in the network of Eforie Nord (orange).

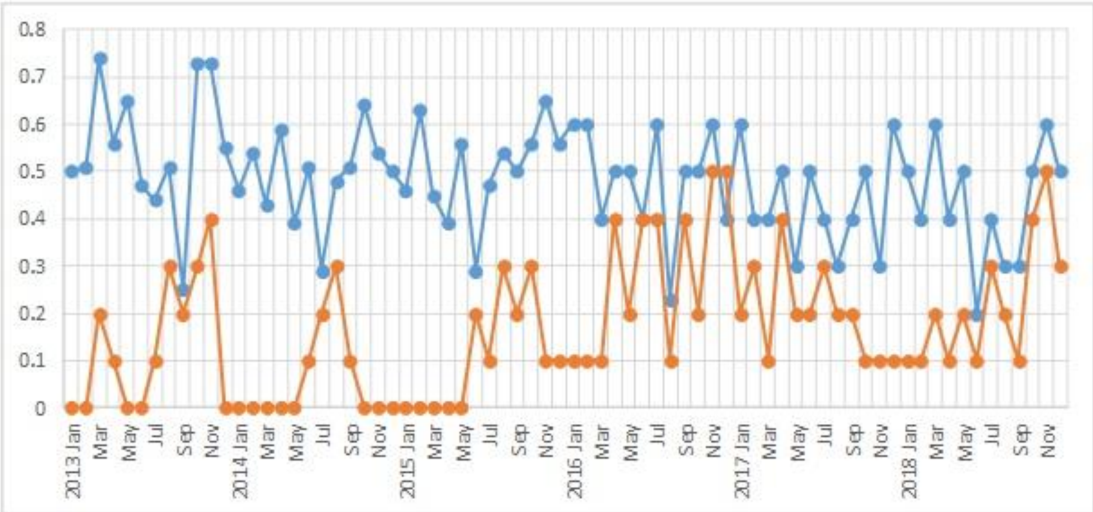

Fig. 5.2 Evolution of the free residual chlorine indicator in the period 2013 - 2018

It can be observed that in the period 2013 - 2015 the residual free chlorine indicator in the network has frequently reached the value 0, which means firstly the risk of the population's illness by increasing the values of the bacteriological indicators and secondly the non-compliance with the legal regulations in force.

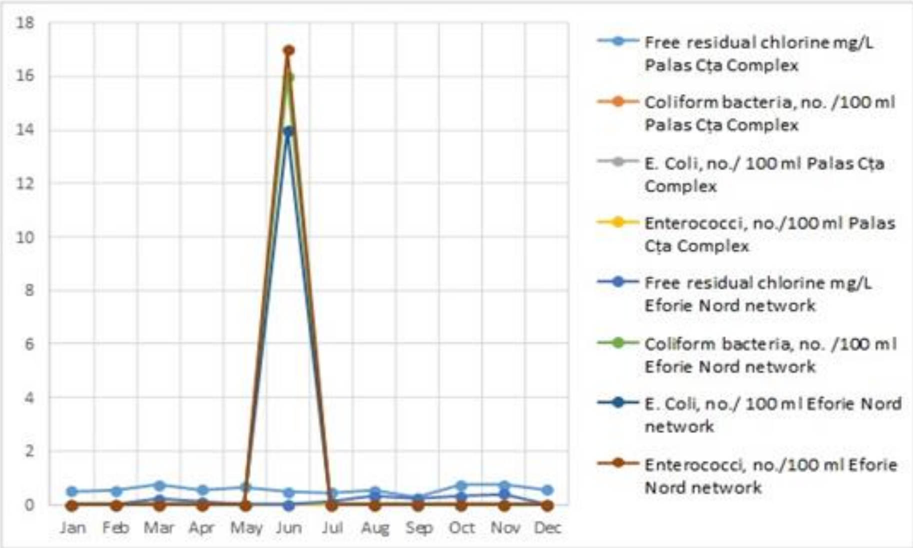

Fig. 5.3 Evolution of indicators of free residual chlorine, Coliform Bacteria, E. Coli and Enterococci at the level of 2013

Fig. 5.3 shows the evolution of the free residual chlorine indicator from the treatment, storage, pumping complex Palas Constanța, in the network of Eforie Nord and the bacteriological indicators monitored: coliform bacteria, E. Coli and Enterococci in the network of Eforie Nord in 2013.

It is noted that in June 2013, exceedances of the permissible limit concentrations of the coliform bacteria indicators, E. Coli and Enterococci, were identified due to the lack of chlorine in the water which could have caused the users to become ill.

The control measures should be identified both at the point where the nonconformity is detected and downstream so that their effect can be appreciated as a whole.

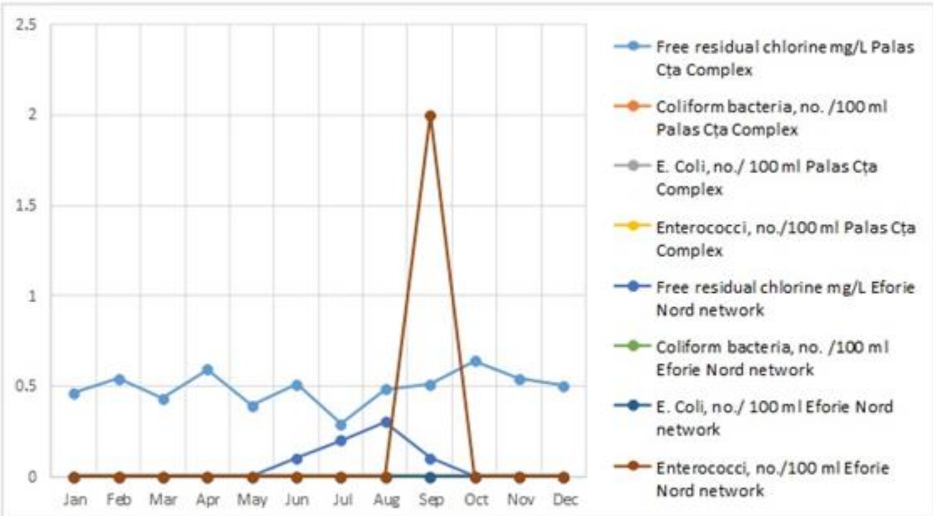

Fig. 5.4 Evolution of indicators of free residual chlorine, Coliform Bacteria, E. Coli and Enterococci at the level of 2014

Fig. 5.4 shows the evolution of the free residual chlorine indicator upon leaving the Palas Constanța treatment, storage, pumping complex, in the network of Eforie Nord, and the bacteriological indicators monitored: coliform bacteria, E. Coli and Enterococci in the network of Eforie Nord in 2014.

Also, it is noted that at the level of September 2014, there was an exceedance of the permissible limit concentrations at the Enterococi indicator in the network of Eforie Nord, which could have caused the users sickness.

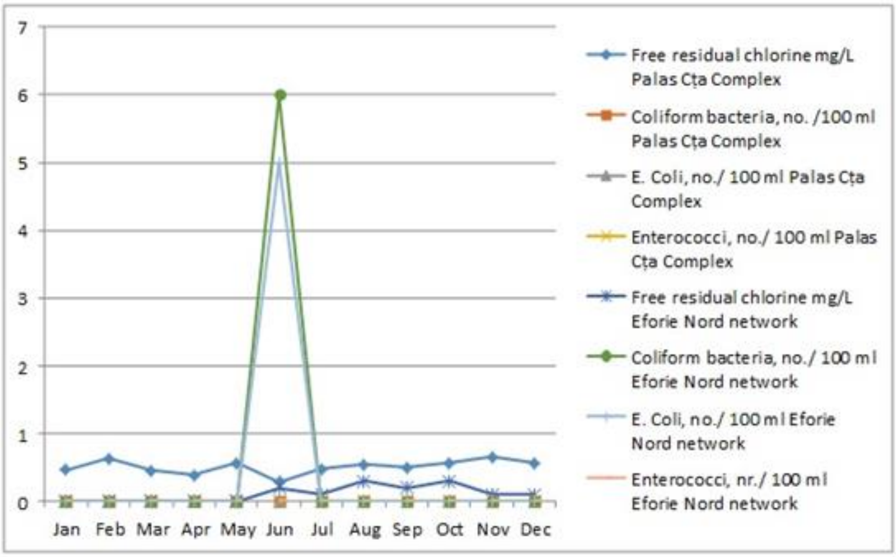

Fig. 5.5 Evolution of indicators of free residual chlorine, Coliform Bacteria, E. Coli and Enterococci at the level of 2015

Fig. 5.5 shows the evolution of the free residual chlorine indicator upon leaving the Palas Constanța treatment, storage, pumping complex, in the network of Eforie Nord, and the bacteriological indicators monitored: Coliform Bacteria, E. Coli and Enterococci in the network of Eforie Nord in 2015.

At the level of June 2015, there was an exceedance of the allowable limit concentrations for the Coliform bacteria and E. Coli indicators in the network of Eforie Nord.

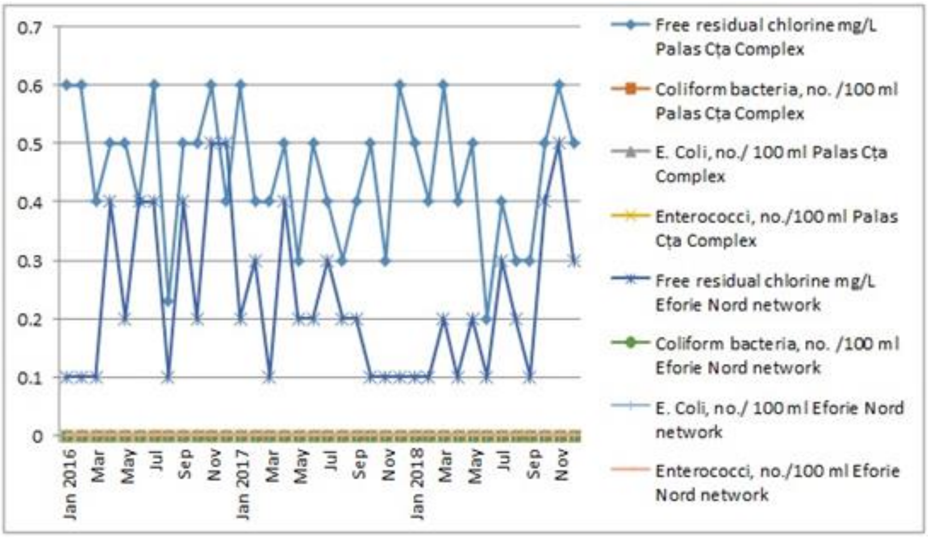

Fig. 5.6 Evolution of indicators of free residual chlorine, Coliform Bacteria, E. Coli and Enterococci at the level of 2016 - 2018

Fig. 5.6 shows the evolution of the free residual chlorine indicator upon leaving the Palas Constanța treatment, storage, pumping complex, in the network of Eforie Nord, and the bacteriological indicators monitored: Coliform bacteria, E. Coli and Enterococci in the network of Eforie Nord at the level of 2016-2018. In the period 2016-2018 there were no exceedances of the bacteriological indicators.

5.4 Conclusions

The value of the free residual chlorine for the water samples taken ranged from the lowest value of 0 mg/L in the network of Eforie Nord, to the highest value of 0.74 mg/L at the exit of the Palas Constanța treatment complex. Microbiological analyzes indicated exceedances of the indicators of coliform bacteria, E. Coli and Enterococci in the years 2013-2015, mainly due to the lack of free residual chlorine in the distribution network.

As a result of the reaction of chlorine with the substances present in the water and with the deposits on the walls of the pipes, its concentration may decrease as the water passes through the distribution network. This phenomenon is known as chlorine degradation. The amount of chlorine with which the water is treated is very important. If the dose of chlorine used is too low, residual chlorine may not remain at the end of the distribution network to protect against recontamination. If the dose of chlorine is too high, it may lead to customer complaints due to taste and odor, corrosion of the distribution network or the formation of by-products, including trihalomethanes (THM) (Gibbs M.S. et. al., 2006; American Chemistry Council, 2018; Nescerecka A. et al., 2014).

As surface or ground water, used as a source for water supply systems, must meet quality conditions corresponding to the category of use, according to the legal norms and debit necessary to ensure a continuous supply, regardless of the daily, seasonal or development trends of the localities, it is necessary to follow both the indicators of potability and the operating parameters.

In order to be able to distribute safe drinking water for consumption, it is necessary that the raw water comes from a source that complies both qualitatively and quantitatively. It is much more convenient to ensure the protection of the water source and its proper maintenance than it is to be contaminated and the costs of water treatment to be much higher. In addition to the cost disadvantage, there are also the risks of chemical, bacteriological nature that lead to diseases (Vinod K. and Imran A., 2013).

The distribution system through which drinking water is transported to the consumer must be safe against contamination after treatment. The presence of the residual disinfectant in the distribution network provides protection of the microbiological quality of the water. Only chlorine-based disinfectants can provide residual protection. The deficiencies that appear in the distribution system due to the degradation of the infrastructure, the damages appeared in the network, make the residual disinfectants to be even more important for the protection of the public health.

An important advantage of using chlorine in water treatment for drinking is the very long-lasting chlorine residue compared to other disinfectants used. Chlorine is effective in eliminating bacteria, costs are relatively low compared to other disinfectants, and the shelf life is long (1 year).

During the monitored period it was possible to observe the presence of the risk of illness of the population due to the presence in the drinking water network of the Coliform bacteria, E. Coli and Enterococci indicators in concentrations that exceeded the limits allowed according to the legal regulations in force. The main factor in the occurrence of this non-compliance was the inefficiency of water disinfection due to chlorine overdose.

As possible causes may be:

- Failures of chlorine dosing devices;
- Improper maintenance of chlorine dosing devices;
- Insufficient staff awareness and training;
- Damages in the water network and lack of washing and disinfection of the water pipe at the end of the work.
-

The control measures / security actions that can be taken in such situations are:

- Periodic verification of chlorine dosing devices;
- Staff training and awareness;
- Compliance with the established chlorine concentration;
- Washing the water pipe after a network failure;
- Monitoring of water quality.

Based on the results of this study, it is recommended to periodically monitor the concentration of free residual chlorine and the microbiological indicators at the exit of the treatment station and in the water distribution system to ensure that the chlorine residues of 0.1-0.5 mg/L are available.

The minimum residual chlorine level at the end user should be at least 0.1 mg / L to ensure quality water for consumers.

CHAPTER 6
RISK ANALYSIS REGARDING RAW WATER CONTAMINATION WITH NITRATES USING ANALYTICAL SOFTWARE

6.1. Description of Mangalia Water Supply System

Mangalia is a tourist town and a port on the Black Sea, situated near the southern end of the Romanian seaside.

The water captured from the Vârtop and Albești sources is chlorinated in the Mangalia storage-pumping complex. The water is treated in the Mangalia Complex, with chlorine gas at a dose of 0.5 mg/ L.

The water captured from the Tatlageac, Dulcești and Pecineaga springs is chlorinated in the Tatlageac storage-pumping complex. The water is treated in the Tatlageac Complex, with chlorine gas in a dose of 0.5 mg/ L (Oglindă, 2018).

6.2. Flow diagram

An important aspect when analyzing the risks of drinking water systems is that the entire water supply system, from the water source to the consumer's tap, must be considered. This means that the water supply as well as the disinfection / treatment system and the distribution system to the consumer's tap must be taken into account.

The main elements for adopting an integrated strategy are:

(1) the existence of interactions between stages/ events (flow diagrams);

(2) the failure at one stage of the system can be offset by other steps / events.

If these circumstances are not taken into account, important information may be overlooked. The objective of water treatment is to produce an adequate and continuous supply of water that is chemically, bacteriologically and aesthetically acceptable. (Lindhe et al., 2009)

Fig. 6.1 shows a Flow Diagram for the Mangalia Water Supply System. The water disinfection system is made with chlorine, and water quality monitoring is done both the source (raw water), at the tank and in the distribution network (drinking water).

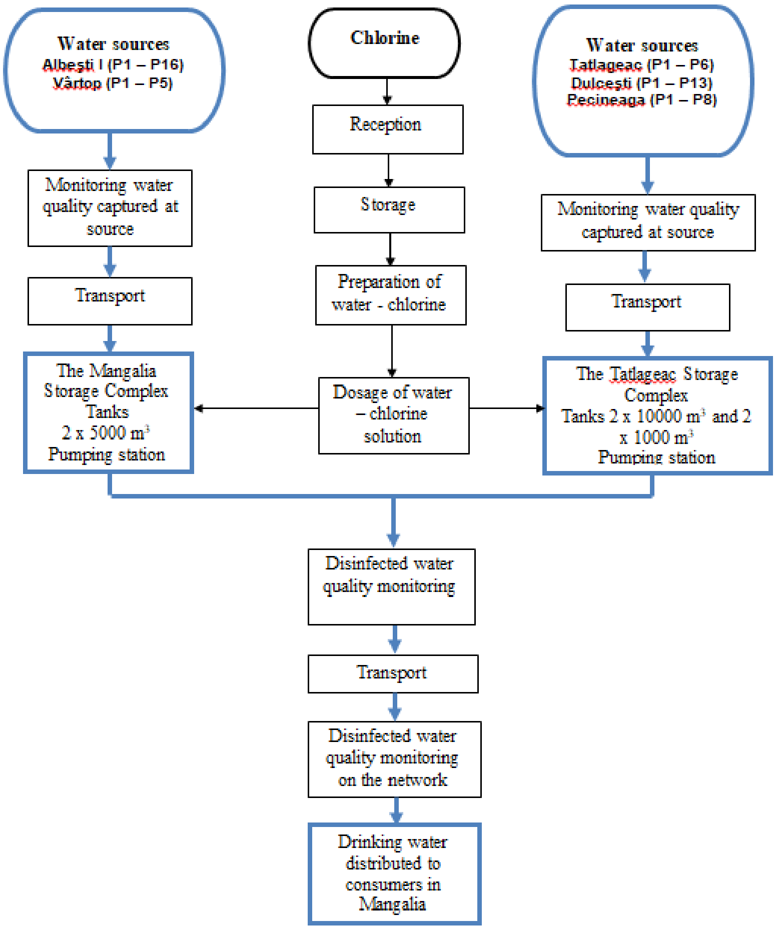

Fig. 6.1. Flow diagram of Mangalia Water Supply System

6.3. Risk analysis

Table 6.1 presents the analysis of the risks regarding water contamination with nitrates at the level of the Mangalia water supply system.

Table 6.1 Risk analysis for the Mangalia water supply system (Cavalierea et. al, 2017; Sandu and Racovițeanu, 2002; Lucaciu et. al., 2011; Nescerecka, 2014)

Potential Risk	**Causes of risk appearance**	**Potential consequences**	**RL**	**Security measures**	**Residual RL proposed**
PROCESS: CAPTURE AND TRANSPORT OF RAW WATER					
Stage: Capture and transport of groundwater					
Underground groundwater contaminated with nitrates	Inappropriate disposal of waste	Contamination of raw water	G = 3 P = 5 RL = 15	- Monitoring the quality of raw water - Stopping water supply from contaminated drilling and exclusive water supply from uncontaminated drilling - Stopping water supply if total source contamination is found and an imminent epidemiological risk - Informing authorities and population - Training and awareness of staff	6

The risk level for the water supply system is calculated as a weighted average of the risk levels established for the identified stages and processes (Ministry of Health, 2012)

$$Nr = \frac{\sum_{i=1}^{n} ri \times Ri}{\sum_{i=1}^{n} ri}$$

Nr = the level of risk to the water supply system;
r_i = the rank of the risk factor 'i';
R_i = the level of risk for the risk factor 'i';
n = the number of risk factors identified.

Thus, the level of partial risk, in stages, is as follows:

Stage: Storage of raw materials and equipment

$$Nrp = \frac{\sum_{i=1}^{n} ri \times Ri}{\sum_{i=1}^{n} ri} = \frac{2x2+2x3}{4} = 2.5$$

Stage: Capture and transport of raw groundwater

$$Nrp = \frac{\sum_{i=1}^{n} ri \times Ri}{\sum_{i=1}^{n} ri} = \frac{3x3+1x6}{4} = 3.75$$

Stage: Water treatment – Chlorination

$$Nrp = \frac{\sum_{i=1}^{n} ri \times Ri}{\sum_{i=1}^{n} ri} = \frac{2x2+1x4}{3} = 2.66$$

Stage: Water storage – Sanitation

$$Nrp = \frac{\sum_{i=1}^{n} ri \times Ri}{\sum_{i=1}^{n} ri} = \frac{1x3+2x4}{3} = 3.66$$

Stage: Water distribution - Transport of drinking water through the distribution network

$$Nrp = \frac{\sum_{i=1}^{n} ri \times Ri}{\sum_{i=1}^{n} ri} = \frac{1x4+1x5}{2} = 4.5$$

Following the identification of the partial risk levels on each stage of the risk analysis, we can determine the global risk level for the entire Mangalia water supply system:

$$Nr = \frac{\sum_{i=1}^{n} ri \times Ri}{\sum_{i=1}^{n} ri} = \frac{4x2+6x3+4x4+1x5+1x6}{16} = 3.31$$

Thus, it is found that the overall level of risk for the Mangalia water supply system falls into the category 3-5 = To be observed/ to consider the control of the water source or measures related to water treatment.

6.4. Qualitative risk analysis of raw water contamination with nitrates

Analytica offers an integrated risk and sensitivity analysis for uncertainty-entry models and powerful facilities for time-dependent dynamic simulations. (Lumina, 2015)

The main objectives of the study are:

(1) development of an integrated method and probabilistic risk analysis for a drinking water supply system;

(2) risk assessment of contamination of raw water with nitrate.

The analysis (fig. 6.2) includes situations where the amount of water required for the consumer is delivered, but there is a risk that it does not meet the drinking water quality standards (failure to ensure the optimum quality of drinking water) (Lindhe ş.a., 2009).

The risk of nitrate-contaminated groundwater being improperly disposed of.

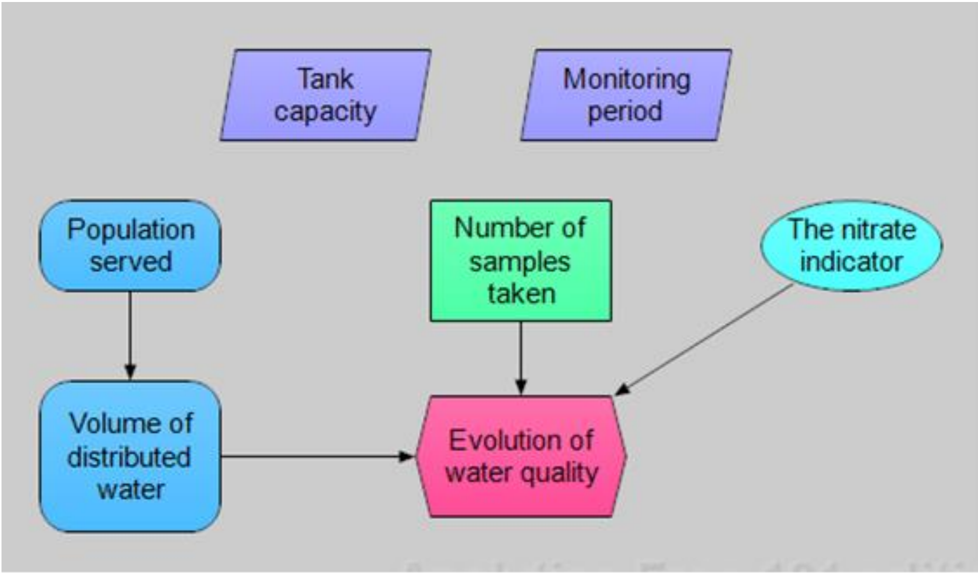

Fig. 6.2 Analytica chart for the evolution of the nitrate indicator at the Mangalia Water Supply System

The water storage is ensured in a tank of 10000 m3 (2 tanks of 5000 m3 each) at the Mangalia Complex, one of 20000 m3 (2 tanks of 10000 m3 each) and in a tank of 2000 m3 (2 tanks of 1000 m3 each) at the Tatlageac Complex.

Table 6.2 Centralization of records corresponding to the Mangalia water supply system

YEAR	POPULATION PROVIDED (number of users)	VOLUME WATER DISTRIBUTED (m^3/ day)	NUMBER OF ANNUAL SAMPLES	NITRATE INDICATOR (mg/ L)
2014	41770	7820	19	47
2015	41980	7405	14	53
2016	41980	8405	36	44
2017	36400	8348	19	42
2018	33310	8355	15	41

According to the census and exploitation data, the population served by the Mangalia water supply system is presented in table 6.2. A significant decrease in the number of users can be observed in the last 2 years.

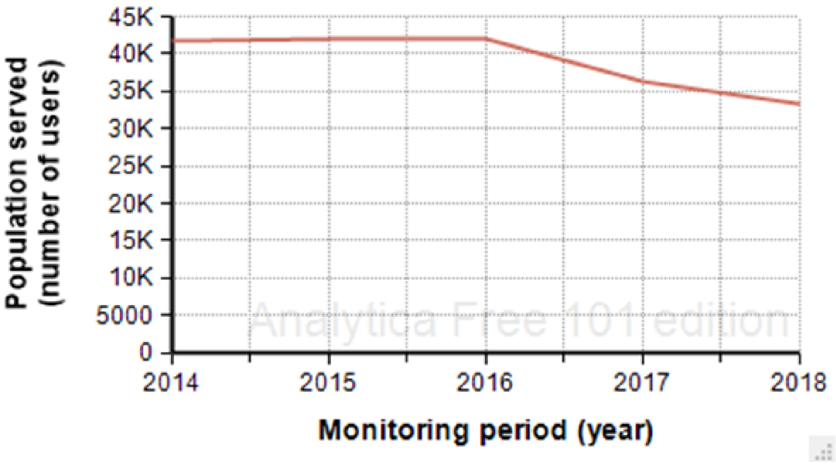

Fig. 6.3 Population served (number of users) over a 5-year monitoring period in the Mangalia Water Supply System

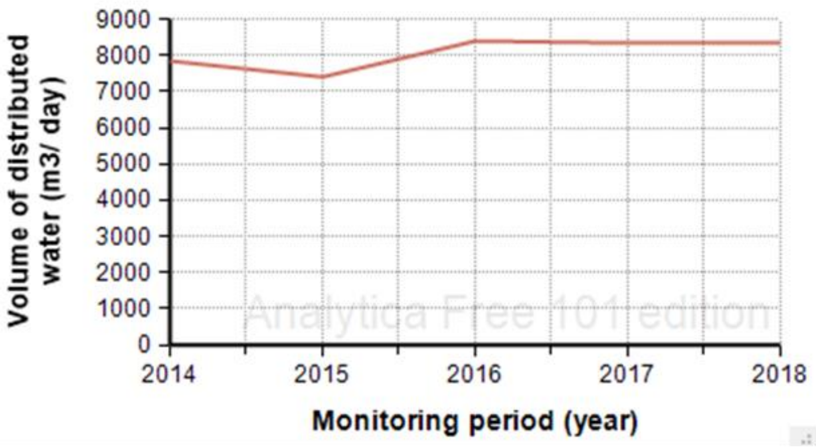

Fig. 6.4 Volume of water distributed over a 5-year monitoring period in the Mangalia Water Supply System

The number of samples taken annually for the nitrate indicator is established at the beginning of each year according to the evolution of the indicator in the previous year and is presented in Table 6.2.

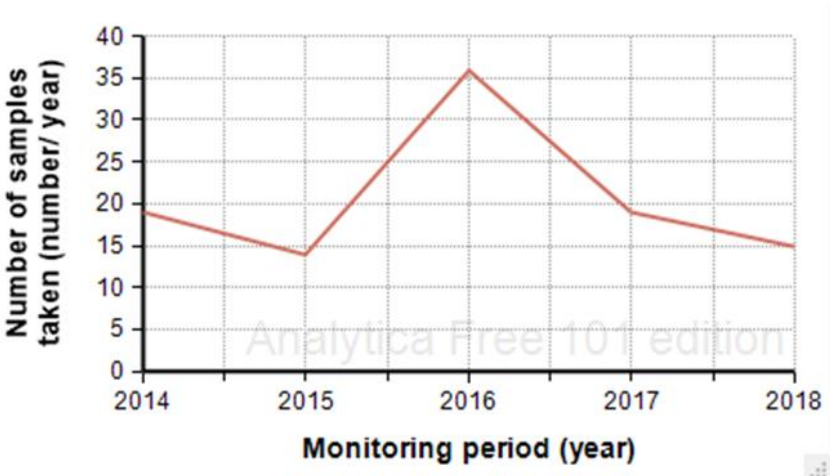

Fig. 6.5 Number of samples taken over a period of 5 years from the supply area of Mangalia Food Supply System

Table 6.2 shows the evolution of the nitrate indicator over a period of 5 years. According to Law 458/2002, the maximum allowed value of the chemical parameter nitrate is 50 mg/ L.

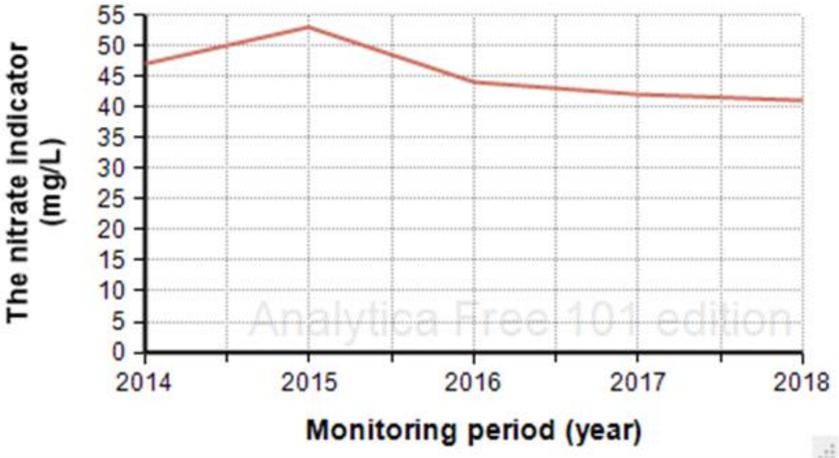

Fig. 6.6 Evolution of the nitrate indicator (mg/ L) over a 5-year monitoring period in the Mangalia Water Supply System

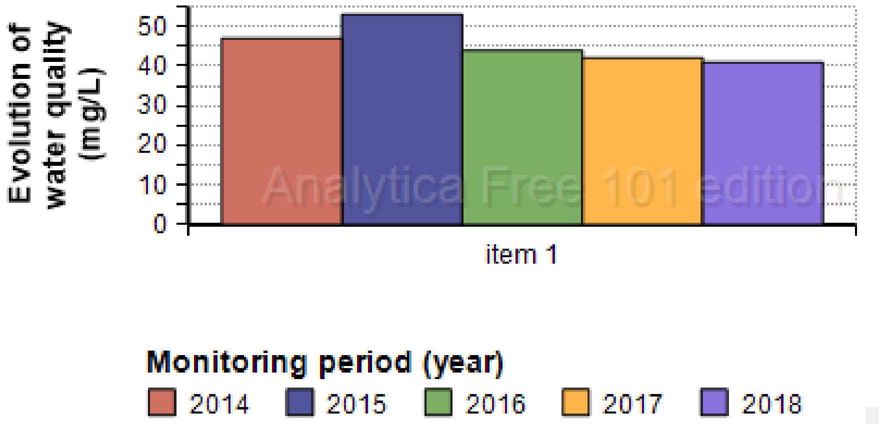

Fig. 6.7 Evolution of water quality over a 5-year monitoring period in the Mangalia Food Supply System

An evolution of the nitrate indicator is quite noticeable in the year 2015.

The concentration and frequency of the presence of a contaminant in water are important and necessary to evaluate the health risk. Where there are exceedances of legal limit values, risk assessment is required to determine the security actions to be taken to reduce it. This is an important step because it is necessary to find a compromise between the provision of chemically contaminated water at values higher than the Maximum Admissible Concentration (CMA) and the risk of not distributing water or using alternative sources that may be microbiologically inappropriate.

Thus, once the maximum admissible limit has been exceeded, the water sampling system for monitoring the nitrate indicator has been intensified, the supply of water from the contaminated source has ceased and water has been supplied from the chemically appropriate sources of water.

6.5 Conclusions

Drinking water quality can be kept under control by combining the protection of raw water sources, controlling disinfection / treatment processes and managing the water distribution system.

There is a wide range of chemical and microbiological contamination agents that may be present in drinking water, some of which can adversely affect consumer health. Contaminants can come from a range of sources, and in some cases from the actual treatment process. Understanding the nature of hazards, sources of contamination and how they can enter the water supply system is an important aspect in achieving sanogenic and clean drinking water quality.

The most advantageous and effective means of producing safe drinking water is the application of risk management, supported by proper monitoring of the functioning of the supply system. As each stage of the water supply system can be susceptible to contamination, it is important that risk management represents a permanent approach throughout the water supply chain, from the raw water source to the consumer's tap.

Quality assurance and risk assessment systems provide an additional guarantee that consistently supplied drinking water is of good quality. Implementing a water safety plan integrated with existing water quality management practices is a means of demonstrating that this approach is viable, has advantages and would facilitate the acceptance of this new method of risk management at critical points. (Mosse and Murray, 2015; Roebeling, 2014).

Good communication throughout the technological flow is essential to ensure that all significant hazards and risks to the quality of drinking water quality are adequately identified and controlled. This involves both internal communication and external communication (with customers, suppliers of products and services, and authorities).

The established security actions must have a clearly defined monitoring regime that validates efficiency and monitors performance against established limits.

In this case study the Analytica software was exposed to analyze the evolution of the nitrate indicator at Mangalia city level.

The presented analysis can allow water operators to understand probabilities and potential impacts on water resources. It can be used as input for management analysis and for the analysis of emergency procedures for contamination of nitrate water.

CHAPTER 7
FORECAST OF THE EVOLUTION OF POLLUTANTS

7.1 Time series, forecast

Time series modelling in the original literature involves the analysis of a dynamic system characterized by a series of inputs and outputs, which refers to a function. The various techniques in this field aim to reproduce the output series reliably and accurately based on the input series and possibly a transfer function. (Maçaira et al., 2018).

Time series modelling can be essentially divided into two classes of methods: univariable and multivariable. Univariable methods correspond to a series of seasonal outputs and/ or trends over time. Multivariable methods use the influence of other variables on the behaviour of the output series to obtain the best possible results in the representation of a transfer function.

A major area of application of these methods is that of environmental sciences. For example, Nunnari et al. (2004) used several statistical techniques to model SO2 concentration using as information a database distributed over time containing wind direction and speed, solar radiation, temperature and relative humidity. Andriyas and McKee (2013) based on the biophysical conditions on the lands of some farms, as well as the irrigation delivery system during the plant growth period, made anticipations of the water orders for irrigation. Lima et al. (2014) developed a flood forecasting model that incorporates the effect of variable climate, such as precipitation amounts. Sfetsos and Coonick (2000) approached the forecast of solar radiation, and Porporato and Ridolfi (2001) approached that of river flows.

Maçaira et al., (2018) established that in 2018 the field of environmental sciences had as number of published articles the first share (12%) of the total of 10 fields of application of time series modelling. It is also evident the increase in the number of forecast applications, from 49 in the period 1967-1998, to 142 in the period 2013-2016 (Maçaira et al., 2018). The two main methods of approaching these applications are regression models and artificial neural networks. A confrontation of regression models with artificial neural networks is presented by Maçaira et al., (2018):

Advantages of regression models:

- Does not require high computing power;
- The relationship between input and response variables is explicit and often interpretable.

Disadvantages of regression models:

- They are sensitive to high numerical values;
- Assumes that the model errors are independent and follow a normal distribution with zero mean and constant variation.

Advantages of artificial neural networks:

- High data processing power due to its massively distributed structure and its ability to learn and therefore generalize, producing adequate outputs for inputs that were not present during the learning stage;

Disadvantages of artificial neural networks:

- Requires high computing power and a large amount of data in the training process;
- It is a black box model, because the relationship between input and response variables is impossible to interpret.

In the field of environmental sciences, two types of artificial neural networks were mainly involved (Ye et al., 2020):

- Multilayer neural networks;
- Radial-based neural networks.

The performance of the two types of networks is comparable. Implementing multilayer networks is easier.

7.2 Forecast of the evolution of the concentration of a pollutant in a source of drinking water

The possibility of predicting the evolution of the concentration of a pollutant in a source of drinking water is particularly important: if it indicates the future increase of that concentration above the legally allowed limits, appropriate measures must be taken to prevent this undesirable phenomenon. That study requires a historical database, which consists of a series of measurements of the concentration of the pollutant at different time intervals in a given period.

The forecast of the nitrate concentration in the drinking water from the Mangalia tank is presented as an application. The historical database includes monthly measurements of the respective concentration for the period January 2013 - October 2019, being presented in tab. 7.1

Table 7.1. Monthly measurements of the nitrate indicator.
The historical database

Month	**Nitrate concentration (mg/L)**						
Year	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**	**2019**
January	31.80	40.20	50.50	54.80	43.00	37.40	38.50
February	58.80	42.00	43.10	74.50	37.10	34.10	39.80
March	51.80	44.00	41.20	72.70	43.50	34.60	38.40
April	51.40	45.10	40.80	82.00	47.10	38.30	39.70
May	60.90	47.50	39.40	37.50	35.80	35.80	39.00
June	60.00	48.20	40.60	36.10	39.40	40.10	43.50
July	61.60	46.80	52.30	35.80	40.10	46.60	45.40
August	61.90	66.70	66.60	38.00	46.30	42.30	47.20
September	45.10	38.40	54.30	36.20	42.30	40.00	42.00
October	41.80	42.00	51.80	31.00	41.02	44.20	47.40
November	38.40	44.50	48.40	34.60	39.80	42.60	
December	37.90	44.30	52.40	31.10	37.60	40.20	

The maximum permitted limit (Law 458/2002 and Law 311/2004) of nitrate concentration is 50 mg / L. It should be noted that this was exceeded in January, July, September and October in 2015 and in January - April in 2016.

7.2.1. Forecast based on regression model

The best correlation using a regression model was obtained based on a polynomial of degree 10 and is represented in Figure 7.5.

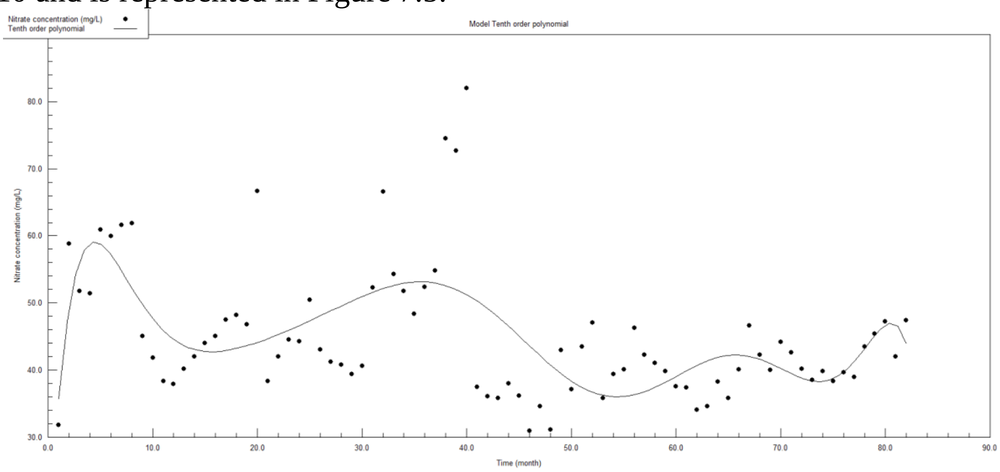

Fig. 7.5. Regression model using a tenth order polynomial

It is also observed from figure 7.5, the fact that the respective correlation cannot be considered satisfactory to be used in a prognosis study. As a result, the prediction based on artificial neural networks was used.

7.2.2. Forecast based on multilayer neural networks

The prediction of the evolution of nitrate concentration over time was made with a neural network with 16 input neurons, an inner layer (hidden) containing 10 neurons and an output layer with 4 neurons. The learning dataset corresponds to a dynamic "window" (Refenes et al., 1993, Woinaroschy, 1993). The center of the window corresponds to the reference time t_0. As network inputs are 8 previous values and 8 future values (in relation to the reference time t_0) of the nitrate concentration. The desired answers correspond to the following 4 values of nitrate concentration, after the next 8 values. It should be noted that because the database is "historical", future values (relative to the center of the window) are known when used in the learning algorithm. The dynamic window scrolls through the data set with a step Δt of one month. When the end of the database is reached, its exploration is resumed from the beginning until the maximum number of learning iterations is exhausted, or an error limit value is reached between the “target” values and those calculated by the network.

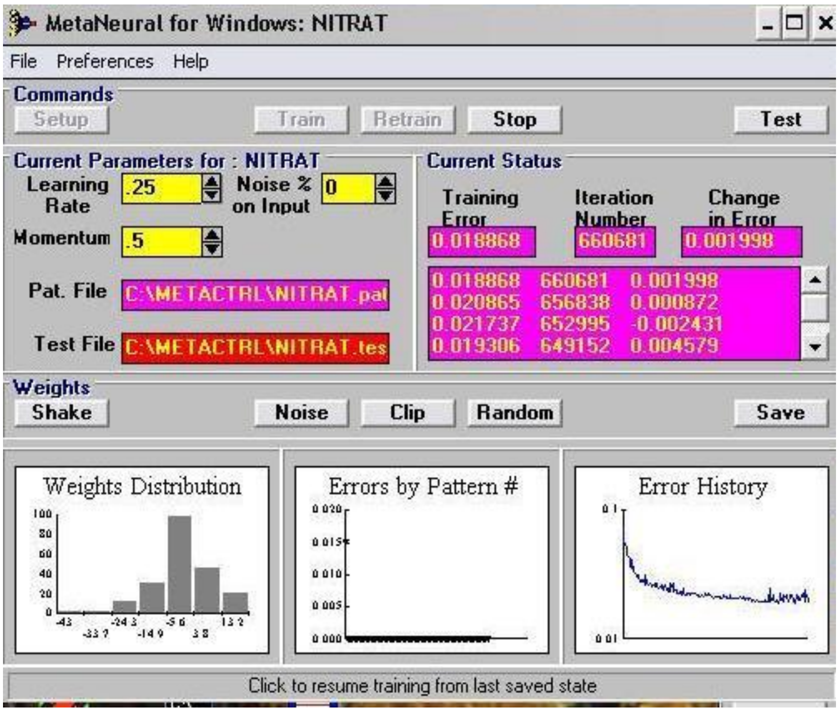

Fig. 7.6. METANEURAL software application

The METANEURAL software application was used (fig. 7.6.), with a sigmoid activation function, a learning rate of 0.25 and a moment of 0.5, the maximum number of iterations being 1 000 000, and the learning limit error of 0.01. At the end of 1 000 000 learning iterations the error is 0.0209.

The predictions for 2019 of the learned network were analyzed. The respective results are set out in tab. 7.2.

Table 7.2 Measured and predicted values of nitrate concentration

Month, Year	Measured nitrate conc. (mg/L)	Predicted nitrate conc. (mg/L)	Error %
January 2019	38.5	42	9.09
February 2019	39.8	39.6	-0.5
March 2019	38.4	43.5	13.28
April 2019	39.7	45.4	14.35
May 2019	39	47.2	21.02
June 2019	43.5	42.2	-2.99
July 2019	45.4	43.3	-4.63
August 2019	47.2	45.6	-3.39
September 2019	42	43.3	3.09
October 2019	47.4	47.2	-0.42

The errors between the measured and the predicted values are reasonable, the maximum value being for May 2019 (21.02%), and the average value is 4.89%. Both the measured and predicted values are below the legal limit of 50 mg/ L, so no measures were needed to limit the increase in nitrate concentration (Woinaroschy and Iordache, 2020).

The approached application demonstrates that the use of multilayer neural networks is a promising way for forecasts in the field of drinking water quality management.

CHAPTER 8
GENERAL CONCLUSIONS, MAIN CONTRIBUTIONS AND OPENINGS OF THE DOCTORAL THESIS

8.1. General conclusions

The doctoral thesis entitled "Optimizing the management of drinking water quality" is the result of analysis and research conducted at the Polytechnic University of Bucharest, Faculty of Applied Chemistry and Materials Science, Department of Chemical and Biochemical Engineering, and within RAJA S.A. Constanța.

The presented studies aimed at identifying, analyzing and assessing the risks regarding the quality of drinking water, as well as the forecast of the evolution of pollutants in drinking water.

Water supply is essential for public health, quality of life, environmental protection, economic activity and sustainable development. Continuous improvement of all processes can guarantee water quality and safety. The development of technical knowledge and growing public health and environmental concerns are contributing to positive developments in the water sector in many countries.

The research paper met the main objective proposed, namely to make original contributions through the presented studies aimed at identifying, analyzing and assessing the risks of drinking water quality, as well as forecasting the evolution of pollutants in drinking water.

The achievement of the main objective was possible by fulfilling some secondary objectives as follows:

- study and analysis of research in the literature
- establishing the stages of water treatment and presenting them through a flow chart
- identification and risk assessment of drinking water quality at each stage
- quantitative and qualitative analysis of water using Analytica software
- treatment of raw water for drinking
- forecasting the evolution of the concentration of a pollutant in a source of drinking water using multilayer neural networks.

Based on the experimental results obtained and the partial conclusions presented at the end of each chapter, a number of general conclusions are highlighted, as follows:

✓ By developing and monitoring compliance with a risk assessment plan, we ensure that the drinking water distributed complies with the legal regulations in force.

We must treat the risk assessment as a preventive management in order to ensure safe drinking water in terms of quality and quantity, taking into account the following main elements:

- Evaluation of the management system,
- Setting users' health concerns as the main objective

- Operational monitoring in stages, from the capture of raw water to the distribution of drinking water to users, of the control measures (security actions) established
- Development, documentation, communication and regular evaluation of management system monitoring plans, risk assessment plans, describing actions, measures to be taken under normal operating conditions and potential incidents, including modernization and improvement.

Drinking water quality can be controlled by combining protection of water sources, control of treatment processes and management of water distribution. Analytica software has the ability to analyze and anticipate water demand in a seasonal tourist city, where economic activities and population numbers are quite different between the cold season (October - April) and the hot season (May - September).

✓ In order to be able to distribute safe drinking water, it is necessary that the raw water comes from a source that complies both qualitatively and quantitatively. An important advantage of using chlorine in water treatment for drinking is the very long-lasting chlorine residue compared to other disinfectants used. Chlorine is effective in eliminating bacteria, costs are relatively low compared to other disinfectants, and the shelf life is long (1 year). The presence of residual disinfectant in the distribution network ensures a protection of the microbiological quality of the water.

The value of free residual chlorine for the water samples taken varied from the lowest value of 0 mg/ L in the network of Eforie Nord locality, to the highest value of 0.74 mg/ L at the exit of the Palas Constanța Treatment Complex. Microbiological analyzes indicated exceedances of the coliform bacteria, E. Coli and Enterococci indicators at the level of 2013-2015, mainly due to the lack of free residual chlorine in the distribution network.

Based on the results of this study, regular monitoring of the concentration of free residual chlorine and microbiological indicators at the outlet of the treatment plant and in the water distribution system is recommended to ensure that chlorine residues of 0.1–0.5 mg/ L are available.

The minimum residual chlorine level at the end user should be at least 0.1 mg/ L, to ensure quality water for consumers.

The distribution of water to consumers must be done safely, the water must be protected against contamination after treatment. The presence of free residual chlorine in the distribution network ensures the protection of the microbiological quality of the water.

Only chlorine-based disinfectants can provide residual protection. The deficiencies that appear in the distribution system due to the degradation of the infrastructure, the damages appeared in the network, make the residual disinfectants to be even more important for the protection of the public health.

✓ There is a wide range of chemical and microbiological contaminants that may be present in drinking water, some of which have negative effects on consumer health. Contaminants can come from a number of sources, and in some cases even from the treatment process itself.

The cheapest and most efficient way to produce safe drinking water is to apply risk management, supported by proper monitoring of the operation of the water supply system. As each link in the supply system may be susceptible to contamination and / or damage, it is important that risk management is a consistent approach throughout the causal chain, from the capture outlet to the consumer tap. The established security actions must have a clearly defined monitoring regime that validates the efficiency and monitors the performance according to the established limits.

In this case study was exposed the ability of the Analytica software to analyze the evolution of the nitrate indicator in Mangalia.

The analysis presented can allow water operators to understand the probabilities and potential impacts on water resources. It can be used as an input in management analyzes and for the analysis of emergency procedures regarding water contamination with nitrates.

✓ The possibility of predicting the evolution of the concentration of a pollutant in a source of drinking water is very important: if it indicates the future increase of that concentration above the legally allowed limits, appropriate measures must be taken to prevent this undesirable phenomenon.

The errors between the measured and predicted values are reasonable, the maximum value being for May 2019 (21.02%), and the average value is 4.89%. Both the measured and predicted values are below the legal limit of 50 mg/ L, so no measures were needed to limit the increase in nitrate concentration.

The case study demonstrates that the use of multilayer neural networks is a promising way for forecasts in the field of drinking water quality management.

8.2. Openings of the doctoral thesis

The studies carried out have the value of fundamental and applied research, the data obtained being able to constitute reference elements for the probabilities and potential impacts on water resources.

The implementation of a risk assessment plan integrated with the already existing water quality management practices is a means to demonstrate that the drinking water distributed to users is of quality and respects the limits imposed by the legal regulations in force.

Analytica software has the ability to analyze the risks of both the amount of water needed to meet user demand and the quality of drinking water distributed, depending on various predetermined factors.

The information obtained from the use of multilayer neural networks can be used for the analysis of water quality risks, as inputs to management analyzes and for the analysis of emergency procedures regarding water contamination.

SCIENTIFIC PAPERS ELABORATED DURING THE DOCTORAL INTERNSHIP

During the doctoral internship, the results of scientific research were published in journals and expressed in communications of scientific papers as follows:

a) Papers published in ISI listed journals

1. A. Woinaroschy, A. Iordache: *Drinking Water Quantity and Quality Risk Management*, în U.P.B. Sci. Bull., Series B, Vol. 81, no. 1, 2019, p. 29 – 40, ISSN 1454-2331.
2. A. Iordache, A. Woinaroschy: *Drinking Water Quality Risk Management. Risk Analysis of Nitrogen Groundwater Contamination Using Analytica Software*, în Rev. Chim. Vol. 70, no. 11, 2019, p. 3971 – 3976, ISSN 0034-7752, Impact Factor: 1,755.
3. A. Iordache, A. Woinaroschy: *Analysis of the Efficiency of the Water Treatment Process with Chlorine*, în Environmental Engineering and Management Journal, Vol. 19, no. 8, 2020, ISSN 1582 – 9596, Impact factor: 1,186.

b) Paper published in a journal type B database

1. A. Woinaroschy, A. Iordache: *Forecast of the Evolution of a Polluant Concentration from a Groundwater Source*, Journal of Engineering Sciences and Innovation, Vol. 5, no. 2, 2020, p. 141-148, ISSN 2360 - 4697.

c) Communications at scientific events

1. A. Iordache, C. Singureanu, A. Woinaroschy: *Safety Management of Drinking Water Quality*, la International Conference CHIMIA 2018 – ”New trends in applied chemistry”, Constanța, Romania, May 24 – 26, 2018
2. A. Woinaroschy, A. Iordache: *Drinking Water Quantity Risk Management. Risk Analysis of the Incomplete Quantity of Potable Water Distributed to Consumers Using Analytica Software*, la International Symposium of Chemical Engineering and Materials, SICHEM 2018, Faculty of Applied Chemistry and Materials Science, Bucharest, Romania, September 6-7, 2018.
3. A. Iordache, A. Woinaroschy: *Analysis of the Effectiveness of the Water Treatment Process Within the Palas Constanta Storage and Water Treatment Plant and the Identification of Risk Factors*, la Romanian International Conference in Chemistry and Chemical Engineering, RICCCE 21, Constanța, Romania, September 4 – 7, 2019.

SELECTIVE BIBLIOGRAPHY

1. American Chemistry Council, (2018), Drinking Water Chlorination a Review of U.S. Disinfection Practices and Issues, On line at: www.americanchemistry.com/

2. Analytica Tutorial, (2015), Lumina Decision Systems, p. 2-110

3. Andriyas, S., McKee, M., (2013), “Recursive partitioning techniques for modeling irrigation Behavior”, Environ. Model. Software, 47, p. 207–217.

5. Bostian M., Whittaker G., Barnhart B., Fare R., Grosskopf S., (2015), ”Valuing water quality tradeoffs at different spatial scales: An integrated approach using bilevel optimization”, Water Resources and Economics, 11, p. 1-12

7. Cavalierea A., Maggib M., Stroffolinic F., (2017), ”Water losses and optimal network investments: Price regulation effects with municipalization and privatization”, Water Resources and Economics, 11, p. 1-19

8. Chen, C.H., (1996) “Fuzzy Logic and Neural Network Handbook”, McGraw- Hill, New York. ISBN 0-07-011189-8.

13. Farooq S., Hashmi I., Qazi I.A., Qaiser S., Rasheed S., (2008), ”Monitoring of Coliforms and Chlorine Residual in Water Distribution Network of Rawalpindi”, Pakistan, Environmental Monitoring Assess, 140, p. 339-347

15. Fornib G., Medellín-Azuarac J., Tanseyd M., Youngb C., Purkeyb D., Howitta R., (2016), ”Integrating complex economic and hydrologic planning models: An application for drought under climate change analysis”, Water Resources and Economics, 16, p. 15-27

16. Gibbs M.S., Morgan N., Maier H.R., Dandy G.C., Nixon J.B., Holmes M., (2006), ”Investigation into the relationship between chlorine decay and water distribution parameters using data driven methods”, Mathematical and Computer Modelling, 44, p. 485-498

22. http://www.vremea.ro/gt/clima_constanta, last access on 25.02.2018

24. Ioniță A., (2019), Operational procedure “Planning and implementation of safe water” RAJA S.A. Constanța, p. 20-26

25. Ioniță A., (2018), Water safety plan within RAJA S.A. Constanța, p. 1-13

26. Janmaat J., (2018), ”Drought risk and water conservation expenditures as a household production problem”, Water Resources and Economics, 22, p. 32-49

27. Lanz B., Provins A., (2016), ”The demand for tap water quality: Survey evidence on water hardness and aesthetic quality”, Water Resources and Economics, 16, p. 52-63
28. Lima, L.M.M., Popova, E., Damien, P., (2014), “Modeling and forecasting of Brazilian reservoir inflows via dynamic linear models”, Int. J. Forecast., 30, p. 464–476.
29. Lindhe A., Rosen L., Norberg T., Bergstedt O., (2009), ”Fault tree analysis for integrated and probabilistic risk analysis of drinking water systems”, Water Research, 43, p. 1641-1653
30. Lucaciu I., Cruceru L., Cosma C., Nicolau M., Gheorghe S., Dinu L., Patroescu V. Hem L.J., Hafskjold L.S., Eikebrokk B, (2011), ”Monitoring the quality of water intended for human consumption”, Rom Aqua, 75, p. 26-30
31. Maçaira, P., M., Tavares Thomé, A., M., , Oliveira F., L. , Carvalho Ferrer, A., L., (2018), “Time series analysis with explanatory variables: A systematic literature review”, Environ. Model. Software, 107, p. 199-209.
32. Maria G., (2007), ”Evaluarea cantitativă a riscului proceselor chimice și modelarea consecințelor accidentelor”, Editura Printech, București, p. 19-25
33. Metoda I.N.C.D.P.M. de evaluare a riscurilor de accidentare și îmbolnăvire profesională la locurile de muncă, (2012), Ministerul Sănătății și Ministerul Muncii și Solidarității Sociale, On line la: https://legislatiamuncii.manager.ro/
34. Moldovan D., (2018), ”Aspects regarding risk management in the process of transportation and distribution of drinking water”, Rom Aqua, 125, p. 42-45
35. Mosse P. and Murray B., (2015), ”Good Practice Guide to the Operation of Drinking Water Supply Systems for the Management of Microbial Risk”, Water Research Australia Limited, Final Report – WaterRA Project 1074, p. 23-33
36. Nescerecka A., Rubulis J., Vital M., Juhna T., Hammes F., (2014), ”Biological Instability in a Chlorinated Drinking Water Distribution Network”, Catalan Institute for Water Research (ICRA), On line at: https://doi.org/10.1371/journal.pone.0096354
37. Nunnari, G., Dorling, S., Schlink, U., Cawley, G., Foxall, R., Chatterton, T., (2004), “Modelling SO2 concentration at a point with statistical approaches”, Environ. Model. Software 19, p. 887–905.
38. Oglindă N., (2019), Memoriu tehnic – Sistemul de alimentare cu apă a orașului Constanța, RAJA S.A. Constanța, p. 2-7
39. Oglindă N., (2018), Memoriu tehnic – Sistemul de alimentare cu apă Mangalia, RAJA S.A. Constanța, p. 2-7
41. Porporato, A., Ridolfi, L., (2001), “Multivariate nonlinear prediction of river flows”, J. Hydrol 248, p. 109–122.
42. Refenes, A., N., Azema-Barac, M., Chen, I., Karoussos, S., A., (1993), “Currency exchange rate prediction and neural network design strategies”, Neural Computing & Applications, 1, p.46-58.
43. Roebeling P., (2014), ”Economics of trans-boundary water resources management”, Water Resources and Economics 8, p. 1-3
44. Roeger A., Tavares A. F., (2018), ”Water safety plans by utilities: A review of research on implementation”, Utilities Policy, 53, p. 15 – 24
45. Sandu M., Racovițeanu G., (2002), ” Manual pentru inspecția sanitară și monitorizarea calității apei în sistemele de alimentare cu apă”, Editura Conspress, București, p. 194-207
46. Sfetsos, A., Coonick, A.H., (2000), “Univariate and multivariate forecasting of hourly solar radiation with artificial intelligence techniques”, Sol. Energy 68, p. 169–178.
49. Şchiopu E. C., (2011), “Monitorizarea indicatorilor de calitate a apei potabile din localitatea Polovragi”, Analele Universităţii “Constantin Brâncuşi” din Târgu Jiu, Seria Inginerie, 2, p. 166
52. WHO, (2009), ” Water Safety Plan Manual - Step-by-step risk management for drinking-water suppliers”, World Health Organization, Geneva, Switzerland, On line at: www.who.int.

53. WHO, (2014), ”Water safety in distribution systems”, World Health Organization Document Production Services, Geneva, Switzerland, On line at: www.who.int.
54. Woinaroschy, A., (1993), “Reţele neurale”, U.P.B.
55. Woinaroschy, A., Iordache, A., (2019), ”Drinking water quantity and quality risk management”, U.P.B. Sci. Bull, 81, p. 3
56. A. Woinaroschy, A. Iordache: ”Forecast of the evolution of a polluant concentration from a groundwater source”, Journal of Engineering Sciences and Innovation, Vol. 5, Iss. 2, 2020, p.141-148.
57. Xie Y., Zilberman D., (2016), ”Theoretical implications of institutional, environmental, and technological changes for capacity choices of water projects”, Water Resources and Economics, 13, p. 19-29
58. Ye Z., Jiaqian Yang J., Zhong N., Tu X., Jia J., Wang J., (2020), “ Tackling environmental challenges in pollution controls using artificial intelligence: A review”, Science of the Total Environment, 699, 134279.