

INVESTIGATING RESIDUAL CHLORINE IN WATER STREAMS AT LOW FLOW CONDITIONS USING 2D WATER QUALITY MODEL

Amaal Osama

Numerical Modelling department, Hydraulics Research Institute, National Water Research Center, Qaluiobya, Egypt.

*Corresponding Author E-mail: moolausama@yahoo.com

ABSTRACT

This study's aim is using Delft3d software to simulate a chlorine containing water source to study the residual chlorine in a water stream. Cooling water of power plants is disinfected by chlorine. Although chlorine concentration is relatively low, its effect is major at low flow conditions. Effluent chlorine is subjected to different operations, dispersion, decomposition and ultraviolet decay. It also works as an oxidant on nitrogen containing organics such as ammonia to form chloramines components. In order to research the forms of chlorine, a 2d numerical model is used to simulate these various operations. A hydrographic survey is performed to measure the bed levels. Water quality parameters are measured through in-situ and in lab measurements. Dairout thermal power plant in Beheira governorate at Rosetta branch is chosen to be studied due to its low flow conditions. Delft3d software is used to create a 2d hydro-dynamic simulation of the study area. FLOW module is coupled to water quality module DELWAQ. Finally, chlorinated water effluent was analyzed according to the concentration threshold in the standards and regulations.

KEYWORDS: Residual chlorine, Rosetta branch, water quality, Delft3d, cooling water.

بحث الكلور المتبقي في المجارى المائية في حالات التصرف المنخفض باستخدام نموذج نوعيه مياه ثنائي الأبعاد

أمال أسامة فتحي

قسم النماذج الرياضيه , معهد بحوث الهيدروليكا , المركز القومي لبحوث المياه, القليوبيه, مصر

*البريد الإلكتروني للباحث الرئيسي: moolausama@yahoo.com E-mail

المخلص

تهدف هذه الدراسة إلى استخدام برنامج Delft3d لمحاكاة مصدر مياه يحتوي على الكلور لدراسة الكلور المتبقي في مجرى مائي. يتم تعقيم مياه التبريد لمحطات الطاقة بالكلور. على الرغم من أن تركيز الكلور منخفض نسبيًا، إلا أن تأثيره يكون كبيرًا في ظروف التدفق المنخفض. يتعرض الكلور المتدفق لعمليات مختلفة؛ التشتت والاضمحلال والتحلل نتيجة التعرض لأشعة الشمس فوق بنفسجية. كما أنه يعمل كمؤكسد على المواد العضوية المحتوية على النيتروجين مثل الأمونيا لتشكيل مكونات الكلورامين. من أجل البحث في أشكال الكلور، تم استخدام نموذج رقمي ثنائي الأبعاد لمحاكاة العمليات المختلفة. يتم إجراء مسح هيدروغرافي لقياس التغيرات في مناسيب القاع. وبعد ذلك يتم قياس معايير جودة المياه من خلال القياسات في الموقع وفي المعمل. تم اختبار محطة كهرباء ديروط الحرارية بمحافظة البحيرة بفرع رشيد لدراستها بسبب ظروف التدفق المنخفض. يتم استخدام برنامج Delft3d لإنشاء محاكاة ديناميكية مائية ثنائية الأبعاد لمنطقة الدراسة. تقترن وحدة FLOW بوحدة جودة المياه DELWAQ. أخيرًا، تم تحليل المياه المتدفقة المخلوطة بالكلور وفقًا لمحددات التركيز في المعايير واللوائح القانونية.

الكلمات المفتاحية: الكلور المتبقي، فرع رشيد، جودة المياه، دلفت ثلاثي الأبعاد، "مياه التبريد".

1. INTRODUCTION

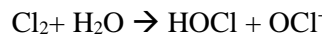
The Nile River in Egypt is the main source of fresh water and is used for many activities. It is important to maintain its freshness and characteristics within the standard limits to ensure healthy usage and environmental preservation. Thermal power plants on the Nile consume its water for cooling purposes and discharge it back. For disinfection purposes, power plants use chlorine to disinfect cooling pipes. When water is discharged back to the river, it contains a certain concentration of chlorine which might affect the environment if not studied and controlled.

In the winter season, the Nile flows - released from the High Aswan Dam - are low due to the low requirements of irrigation and the other purposes of consuming water. During this season, the effects of concentrations of different substances increase. In this study, we focus on chlorine concentrations from cooling water effluents of power plants.

Power plants commonly use chlorine in their cooling system for disinfection. Chlorine is dosed in one of two main sources in common; dissolution of chlorine gas or addition of a Na-hypochlorite solution. The chlorine concentration in the effluents depends on the dosing rates used in chlorination [1]. Increasing the concentration of residual chlorine may affect the water quality of the ambient water and hence, the ecological system[2]. When the cooling water containing chlorine discharged into nearby waters, it will affect the ecological environment of water [3].It is important to study residual chlorine from cooling water of power plants as it might cause severe effects on the environment as previously studied[4], [5]and [6].

2. CHLORINE CHEMISTRY IN FRESH WATER

Chlorine oxidizes and eliminates organic compounds and converts some soluble metallic impurities into insoluble solids. Ammonia is an organic compound that is oxidized by chlorine, forming chloramine compounds. Chlorine concentration at the effluent discharge is affected by many factors such as alkalinity. PH of the surrounding media affects the decomposition of chlorine according to its form. Chlorine is soluble in water and reacts with it forming hypochlorite acid (HOCl) by hydrolysis. In alkali solutions (PH above 8), hypochlorite acid dissociates forming hypochlorite ion (OCl⁻) while in the range between (PH 5 and 8) it prefers hypochlorite acid (HOCl) [7]. Chlorine, hypochlorite acid, and hypochlorite ion exist together in equilibrium.



Increasing pH →

(EQN 1)

Fig. 1 below shows the effect pH has on the equilibrium.

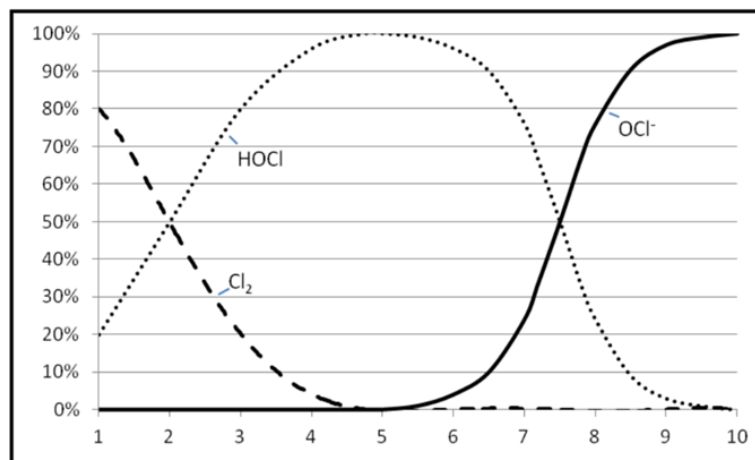
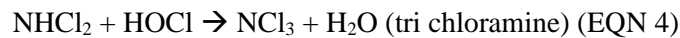
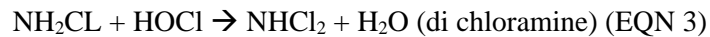
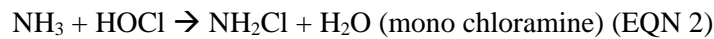


Fig. 1: Chlorine speciation profile as a function of pH

When PH is 2 or less, the equilibrium favors chlorine. Between pH 2 and 7.4 hypochlorite acid predominates and above pH 7.4 hypochlorite predominates. This means that when alkalinity increases above 7.4, the chlorine compound decomposes into a hypochlorite.

The other major factor that affects chlorine is the ultraviolet radiation of sunlight. It catalyzes the chlorine. Ultraviolet is even used in dechlorination in wastewater treatment plants. UV dechlorination is believed to outperform other dechlorination technologies since there no mixing or contact tanks required, no chemical addition required, and only minimum operation and maintenance involved. It leaves no impact on the taste, odor, color, and pH of water as well. Chlorinated effluents that are subjected to sunlight are affected by ultraviolet.

Chlorine also is a strong oxidant. It reacts with ammonia and nitrogen containing organic compounds to form halamines, chloramines, and bromines [8]. The reaction with ammonia proceeds by sequential substitution of the hydrogen atoms as follows:



The chlorine when discharged is subjected to water kinetics that affects its distribution and dissipation. Residual chlorine is the persisting chlorine after achieving chlorine demand. The residual chlorine in non-uniform flow in 2D convection-diffusion equation [9] can be expressed as (EQN 5)

$$\frac{\partial \rho}{\partial t} + u \frac{\partial \rho}{\partial x} + v \frac{\partial \rho}{\partial y} = \frac{\partial}{\partial x} (E_x \frac{\partial \rho}{\partial x}) + \frac{\partial}{\partial y} (E_y \frac{\partial \rho}{\partial y}) - K_p + S$$

(EQN 5)

Where ρ is the concentration of chlorine, t is time, x & y are distances, u & v are horizontal and vertical average velocities, E_x & E_y are diffusion coefficient, K is attenuation coefficient and S is the pollutant source concentration .

In this study, a numerical two-dimensional convection-diffusion model is used to solve the above equations using Delft3d software.

3. STUDY AREA

A case study of Dairout power plant on Rosetta Branch of the Nile River is chosen as one which has a chlorinated effluent to be studied. The vacancy location of the power plant is interesting to be studied. The following satellite image describes the study location in **Fig. 2**.



Fig. 2: Satellite image describes study area

As shown, there's a vast meandering from south to west direction which affects the velocities indeed. Also, there's a regulator 10 km downstream farther from this location which's closed most of the year. These factors were taken into consideration when choosing this area. To study the most extreme case, the area was studied during the closure in the winter season. The kinematics during this season has Lake Regime characteristics; the velocities are relatively low which causes a high concentration of any discharge effluent spatially and temporally [4].

4. METHODOLOGY

As previously mentioned, this article studies the diffused chlorine, the factors affecting it, and affected by it as well. To achieve this purpose, a CFD and environmental model is applied. Bathymetric data of the selected area is collected by the Hydraulics research institute survey team. Hydrographic data is collected. Archival data regards the discharges is aggregated from the ministry of water resources and irrigation. Another team from Central Laboratories for Environmental Quality Monitoring (CLEQM) in corporation with Hydraulics research institute collected the environmental water quality parameters.

4.1. Model set up:

The bathymetric data were applied to the Delft3D numerical software. The grid creating tool – RGFGRID- was used to schematize a 4*4 m² curvilinear grid covering the study area. **Fig. 3** shows the grid used for hydrodynamics.

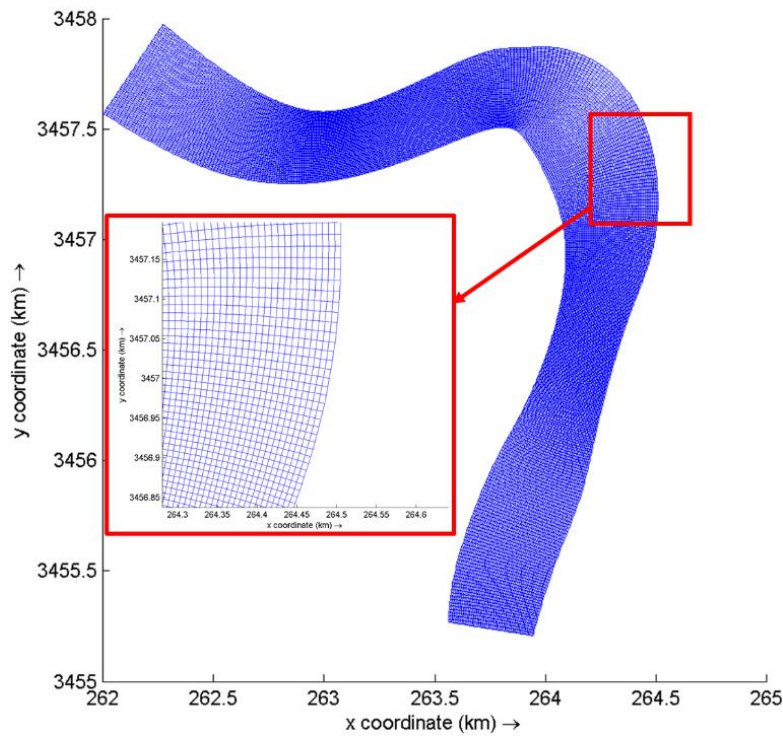


Fig. 3: Schematization grid for hydrodynamics

QUICKIN tool is used to add and interpolate the collected bathymetry along the study area. Numerical requirements for the model are achieved and the hydrodynamic simulation for the area is performed. **Fig. 4** is the bed levels variation of the study area.

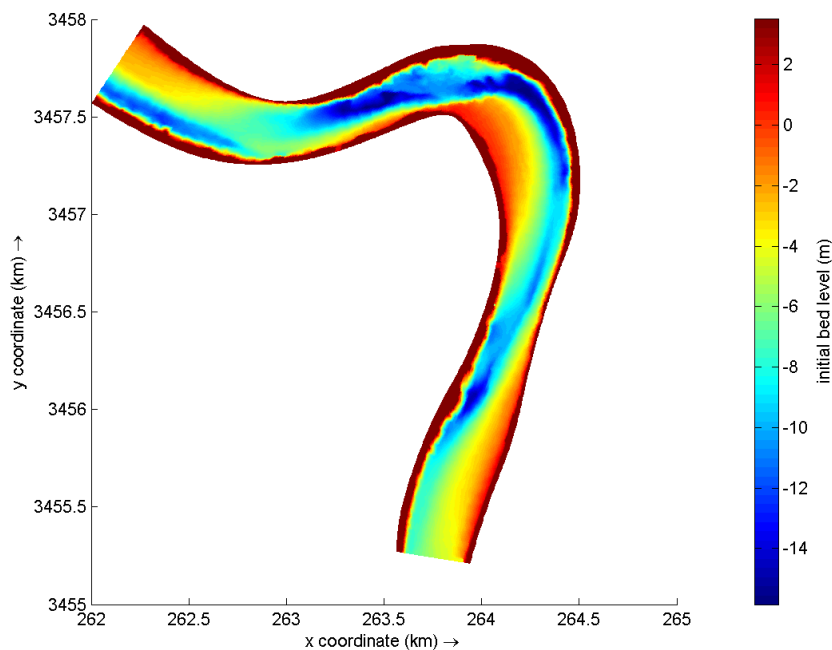


Fig. 4: Bathymetry of study area

4.2. Model Calibration:

The model is calibrated afterward to achieve a reasonable similarity in results. Calibration was achieved along five velocity cross-sections and water level along the study area. **Fig. 5** illustrate calibration of velocity along a cross section 100m downstream the first boundary and **Fig. 6** describes

velocity along the meandering cross section. Manning co-efficient values were changed along the area according to vegetation zones.

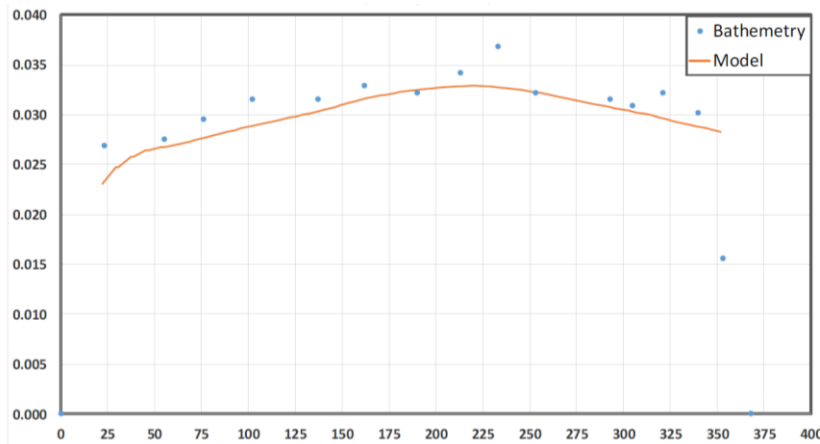


Fig. 5: Velocity cross section (1) calibration

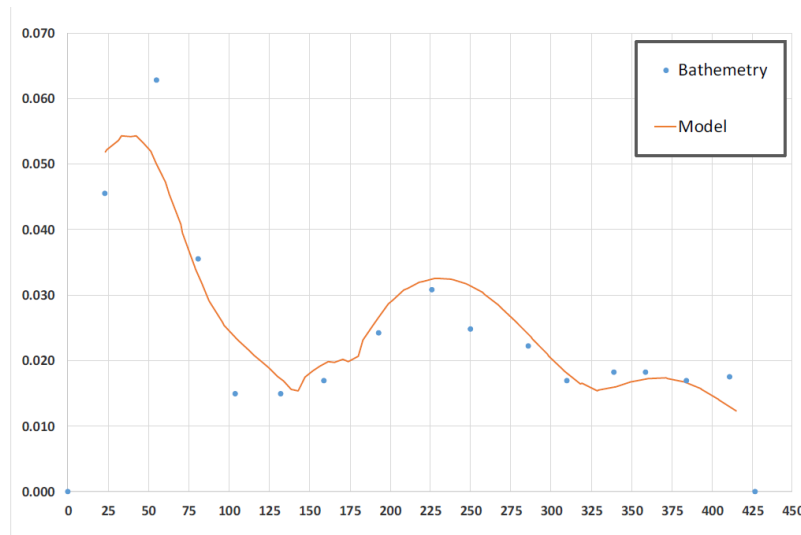


Fig. 6: Velocity cross section (3) calibration

Also, this area contains many fish cages in stochastic order. Locations of fish cages corners were located using GPS. **Fig. 7** shows these locations. Fish cages in this area played a major role in selecting this area specifically because of its negative effect on the area kinetics which is considered to be an extreme case due to the very low velocities. Cages walls were simulated as thin dams that are not connected to each other which allows water to pass through it to simulate nature as possible. These locations were given high manning co-efficient, model resulted velocity values were then compared to those that are measured in field. Many model runs were simulated until high similarity was satisfied. **Fig. 8** is the resulted water level from model versus measured water level.

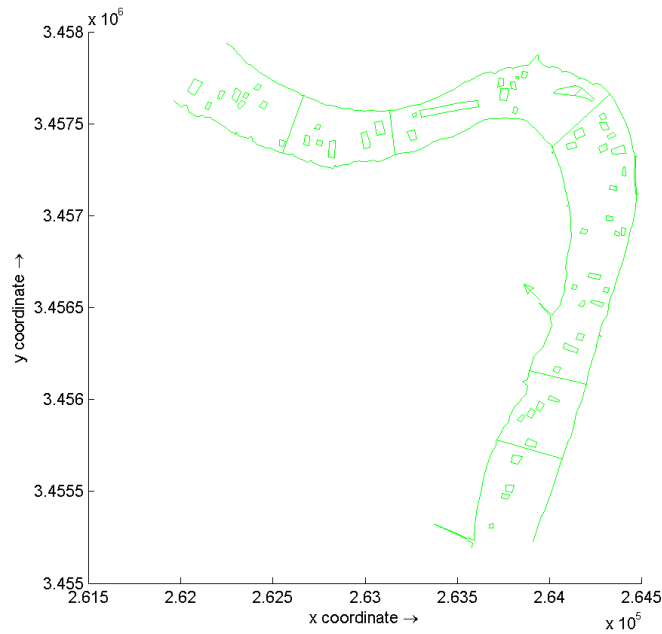


Fig. 7: Fish cages locations

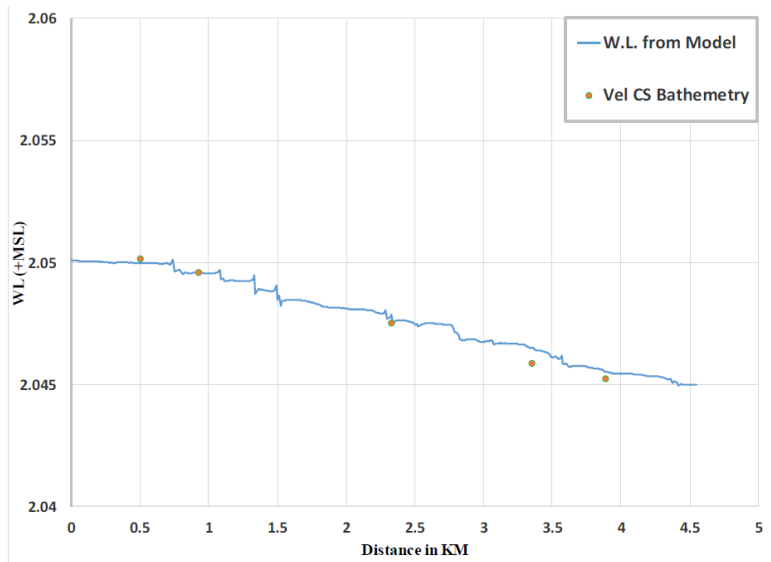


Fig. 8: Water level calibration

After calibration, another tool (DIDO) was used to aggregate the grid used in the hydrodynamic simulations into a less fine grid to ease the calculations. The 2D hydrodynamic fine grid was aggregated into a coarser grid water quality model. These results were applied to the DELWAQ module to create an input file. Flow module of the model was coupled to simulate the water quality parameters in the area. “Cascade” process is used to simulate the different forms of chlorine as follows:

Cascade 1: mimics sodium hypochlorite.

Cascade 2: mimics hypochlorite acid.

Cascade 3: mimics chloramine.

Cascade 1 is subjected to a transformation process into the second substance (sodium hypochlorite decomposes into hypochlorite acid)

Cascade 2 is subjected to a transformation process into the third substance (hypochlorite acid oxidizes ammonia into chloramine). It is also subjected to a decay process (hypochlorite acid decays due to ultraviolet radiation).

The exact values of transformation factor were calculated according to the weight of compounds in reactions of **Eqn 2, 3 and 4**. The same Tanique is applied in calculating the transformation factor of oxidation of ammonia to be applied in the DELWAQ module. One year data of ultraviolet is downloaded from the ECMWF datasets of metrological data then processed. Different calculations are performed to calculate the decay factor of hypochlorite acid [10]. The decay factor varies according to fluence. To study the most critical case for UV radiation, we applied the used disinfection dose – regular 3 times a day- to be once at 4 am and the second to be noon and the third is 8 pm. Each dose is continuous for 30 min. This method uses the least radiation at 4 am and 8 pm so only decay occurs once a day at noon. In this method, the least decay is studied to discuss the highest concentration as a critical case. The decay factor is entered into the model as a time series. Each hour of the day has its calculated value according to its fluence.

A 2D model of 3 days of the study area with the thermal power plant as an effluent source of sodium hypochlorite (every 8 hours) is schematized. Total reactions of sodium hypochlorite, hypochlorite acid, and the total concentration of chloramine are applied in the model using cascade processes. Measured PH and UV fluence are taken into consideration in the reactions. The flow model is 1.5 seconds time step and 1 minute for the Water Quality module. As for discharges and water levels as boundary conditions, they were taken from hydrographic survey same as any other related data to the study area; fish cages, intakes, dry islands, etc.

5. RESULTS AND ANALYSIS

Model was schematized on the low flow scenario. Upstream boundary is discharge with a value of $2.38 \text{ Mm}^3/\text{d}$ and downstream boundary is water level 1.98 m above sea level. Power plant has three units, each consumes $13.6 \text{ Mm}^3/\text{d}$ cooling water, totally $40.8 \text{ Mm}^3/\text{d}$. Study area's kinetics are very close to a lake. Shows the area's velocities. As shown, the values tend to be almost stagnant which cause any pollutant to have a severe influence on water body. **Fig. 9** clarifies resulted depth averaged velocities in the area.

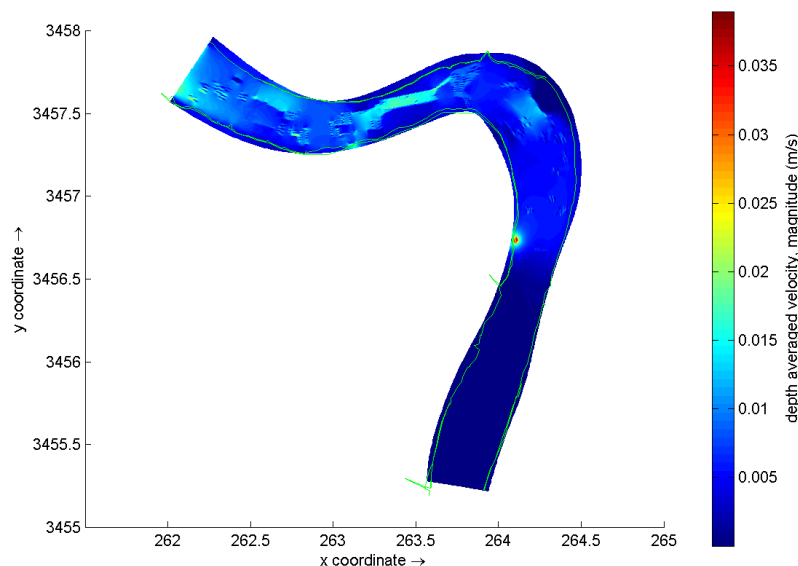


Fig. 9: Depth averaged velocities

A significant change has occurred in the study area starting from discharging the effluent chlorine source. Residual chlorine values started to increase due to the accumulation. Low flow conditions affect the hydrodynamics in the area, such as slight velocities. Fig. 10 shows the dispersion of residual chlorine after the first dose. Apparently, the concentration is relatively high after discharging and values reach 1 ppm. However, chlorine mixes quickly due to its high solubility in water. While the solubility of chlorine increases with temperature[11], the effluent is at a higher temperature than the ambient due to its usage in cooling requirements. Because of this solubility, dissipation occurs very

quickly, causing the higher concentration to be lowered in a few hours. Dissipation of residual chlorine after first, second, and third dose appears in **Fig. 10**, **Fig. 11** and **Fig. 12**.

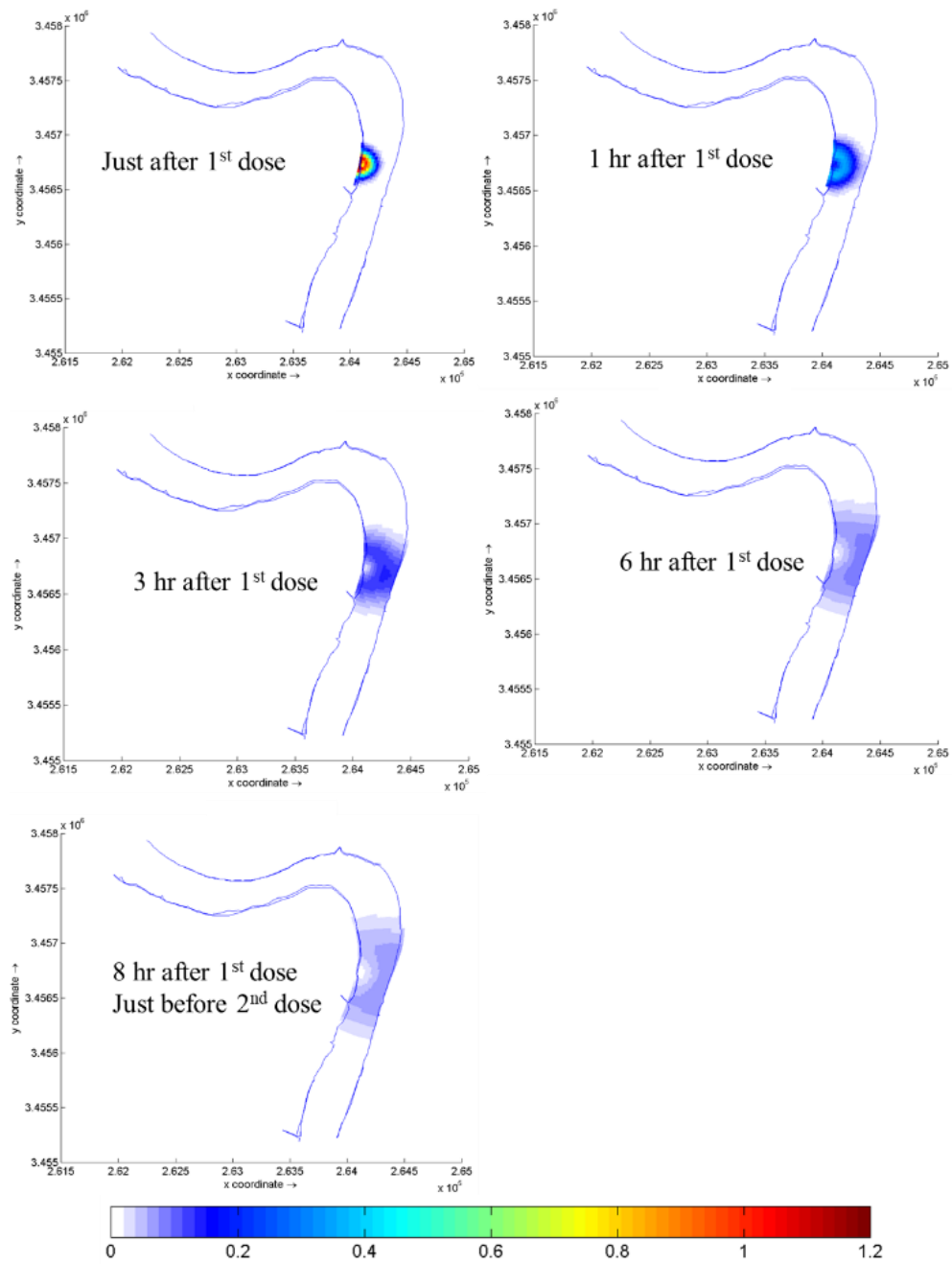


Fig. 10: Spatial and temporal Resident chlorine from the effluent source after 1st dose

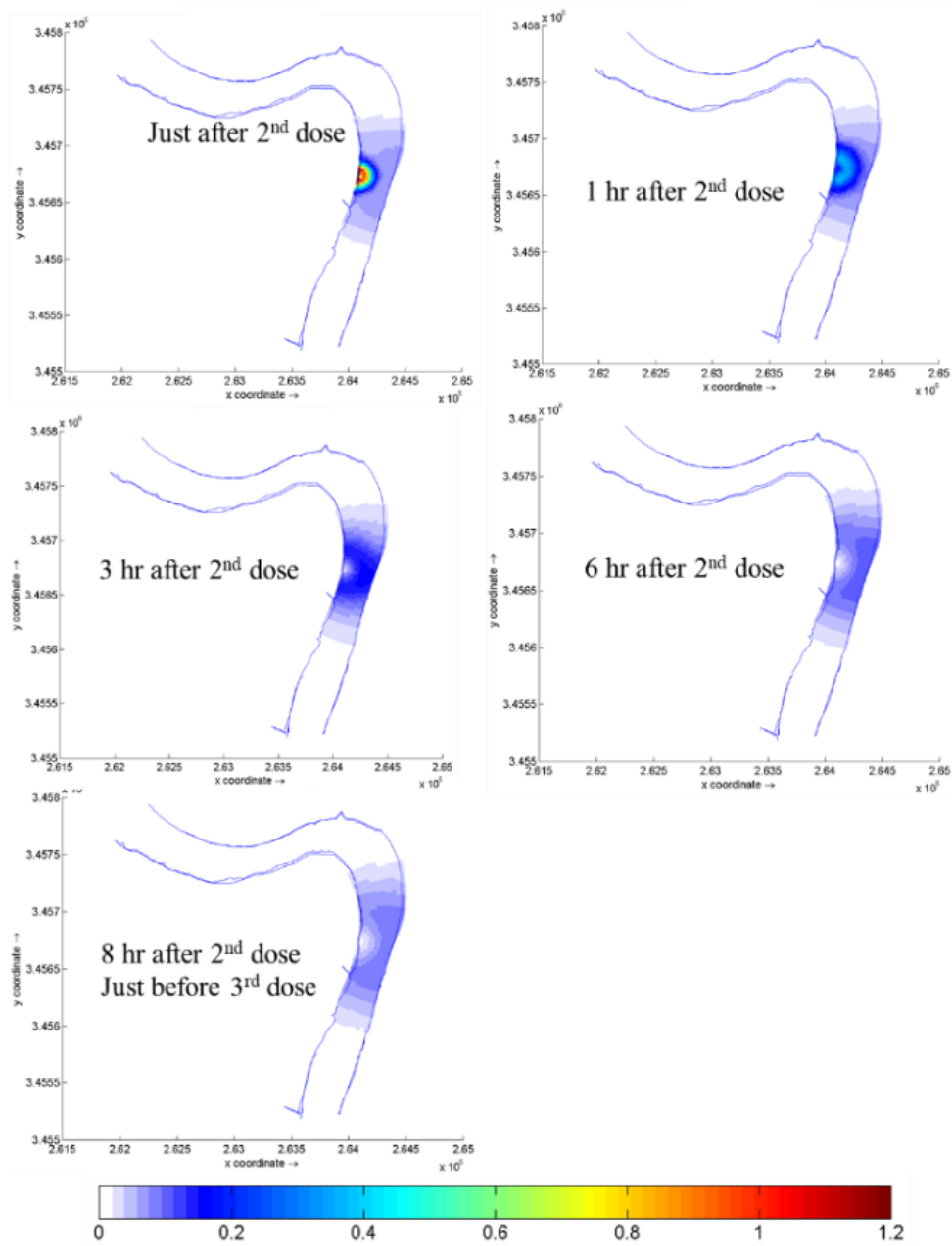


Fig. 11: Spatial and temporal Residual chlorine from the effluent source after 2nd dose

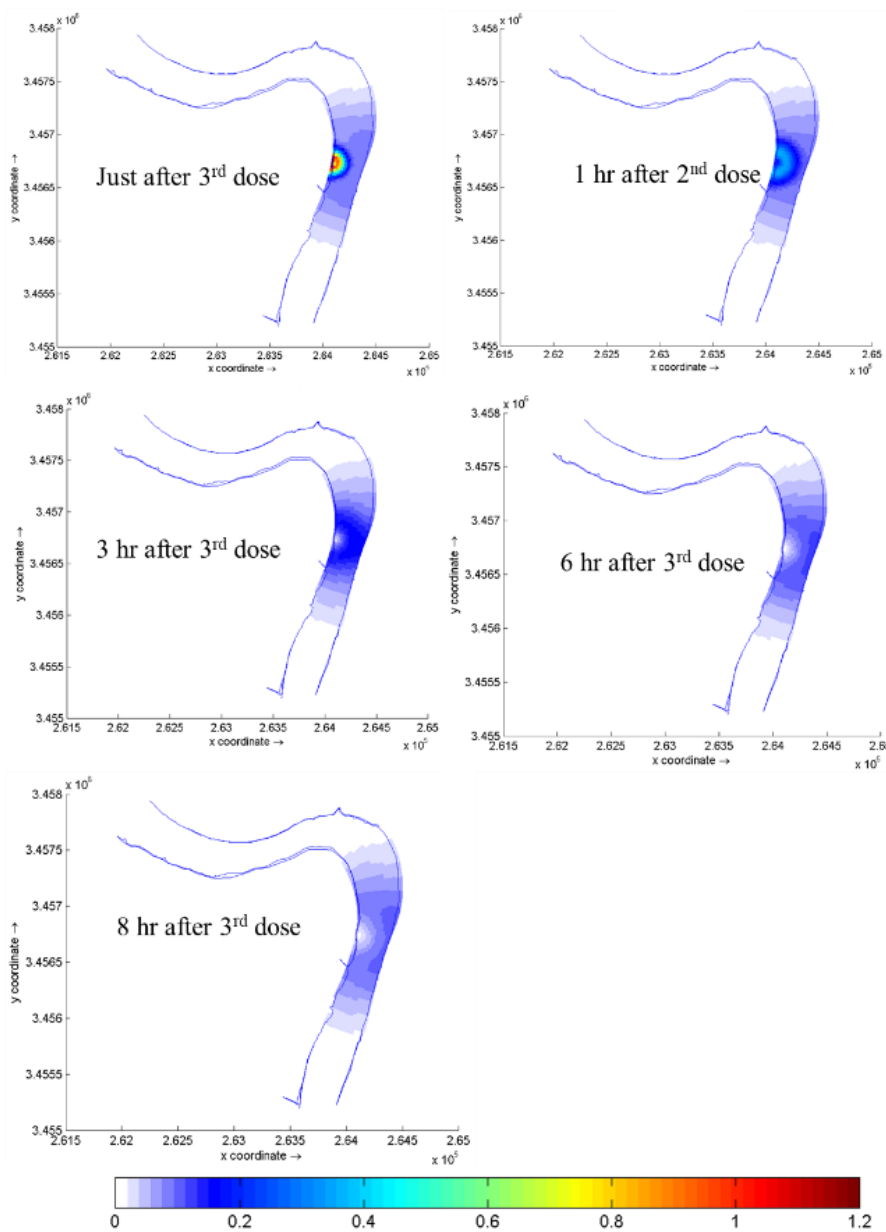


Fig. 12: Spatial and temporal Residual chlorine from the effluent source after 3rd dose

Fig. 13 shows hypochlorite acid values after dosing sodium hypochlorite for 3 days. Chlorine modelled is in forms of sodium hypochlorite and hypochlorite acid that oxidize ammonia to form chloramines. Residual chlorine is the persisting chlorine after chlorine demand has been met in its decomposition and oxidation of ammonia. Noticing the residual chlorine values for three days, each of three times dosing a day, **Fig. 14** shows the residual chlorine after 8 hours of the third dose of the third day of dosing.

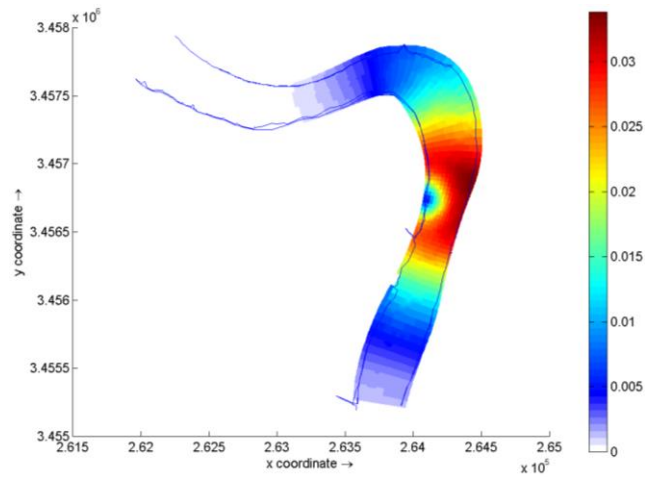


Fig. 13: hypochlorite acid after 3 days of dosing

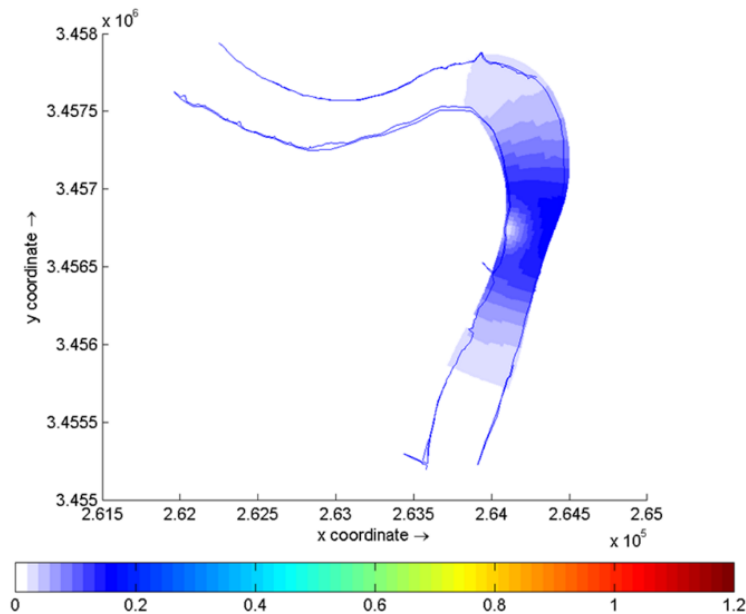


Fig. 14: Residual chlorine after 3 days of dosing

It is noticed that the mixing zone widens but the values of residual chlorine within it does not increase. Mixing zone is affected by kinetics of the low flow stream which means that it doesn't transfer for long distance with time, although, it quickly expands since chlorine dissipates. Chlorine concentration decreases to 0.05 ppm after 8 hours until the next dose. The next dose increases the concentration at the mixing zone once again but decreases afterwards because of dissipation. Very limited accumulation of concentration occurs. To consider accumulation, the model is run for three days with 3-ppm sodium hypochlorite concentration for 30 minutes in each dose 3 times a day, controlling two doses to be at night to have minimum UV decay effect. By comparing the resulted values to World Bank Group EHS Guidelines for Thermal Power Plants, values of free available chlorine or total residual chlorine did not exceed the limit although the extreme cases of the rate of dosing and the UV radiation were applied.

6. DISCUSSION

There are different major factors that affect residual chlorine values, such as media alkalinity, water temperature, and water quality of stream and disposed UV at the studied location. PH or alkalinity affects decomposition of discharged chlorinated solution either into hypochlorite acid or hypochlorite ion. Water temperature affects solubility of sodium hypochlorite –or any other form of chlorine- into

water. Water quality in the stream, specifically, ammonia values plays a significant role as it is consumed in reaction with hypochlorite acid to produce chloramines. One other factor that affects decomposition of hypochlorite acid is the ultraviolet radiation. In this study, a chlorinated water discharge into a water stream at low flow conditions is investigated. Results from simulating previous mentioned operations in a numerical model –Delft3d- , showed that instant transformation from sodium hypochlorite into hypochlorite acid has a high rate. Transformation factor was calculated from EQN 1 by weight transformation to be 0.703. This factor means that almost 70% of sodium hypochlorite is transformed into hypochlorite acid. The rest is easily dissipated with a high rate due to the high solubility of chlorine in hot water. Hypochlorite acid itself reacts with ammonia in water to form chloramines.

One major factor that controls the mixing zone is the flow discharge of the power plant's cooling water. The plant consumes 40.8 Mm³/d and discharges it back to the stream. Meaning that the discharged water is 17 times the running water in the stream. This was not a weakness point on residual chlorine distribution, contrariwise, the high values of discharge increased the velocities of discharged cooling water which enlarged the mixing zone and enhanced the distribution.

A previous study was performed in this area to study thermal effect on water quality parameters – including ammonia- [12]. The study concluded that there's a positive effect of thermal effluent on ammonia as it was lowered since ammonium solubility decreases with increasing temperature for the same PH [13], So, hypochlorite acid reacts with low concentrated ammonia –after being lowered from high temperature- and produce chloramines. Hypochlorite acid is decayed due to UV exposure.

CONCLUSION AND RECOMMENDATIONS

This study aimed to investigate the chlorine residual in a low-flow freshwater stream. The chlorine source in this study is the effluent of a thermal power plant cooling system. The power plant cooling system is once-through. This means that the water enters the cooling system for cooling then it is discharged back to the water source. Chlorine is used in the disinfection system of the cooling water in the form of sodium hypochlorite. This compound is subjected to many processes that affect it. PH of the water affects its decomposition into hypochlorite acid, which in turn is decayed according to the fluence of ultraviolet at the water surface. Hypochlorite acid itself affects the ammonia in water since it is a strong oxidant. It also is a decayable substance, which means that it is decayed with time. 1 year data of ultraviolet is collected and different calculations are performed to calculate the decay factor of hypochlorite acid. The decay factor varies according to fluence, maximum month of uv is selected with its hourly fluence.

In this paper, a numerical modeling approach is used to simulate all these different operations and interactions to detect the different forms of chlorine after being discharged into the stream. Delft3D software package is used in the simulation of the study area. Field data collection is performed. A hydrographic survey covered the bed levels of the study area. Water quality sampling is performed to collect different water quality parameters used in the numerical modelling process. FLOW module is used to simulate the hydrodynamics of the stream and the results are calibrated and coupled to the DELWAQ module for water quality parameters simulation. The results were satisfactory compared to the environmental standards.

It is concluded that, for low flow streams, it is environmentally safe to discharge chlorine doses for different purposes if the doses considered the studied operations. Finally, the methodology used in this study was successful to track the chlorine disposal. So, it is recommended to investigate the impacts of any chlorine disposal on a low-flow stream following the same methodology.

ACKNOWLEDGMENTS

The author gives many appreciations to Arjen Markus in Numerical Simulation Software, Deltares, for his guidance and valuable help.

REFERENCES

- [1] A. Areiqat and K. A. Mohamed, "Optimization of the negative impact of power and desalination plants on the ecosystem," *Desalination*, vol. 185, no. 1–3, pp. 95–103, May 2005, doi: 10.1016/j.desal.2005.04.038.
- [2] J. Yi, J. Lee, M. A. Fikri, B. I. Sang, and H. Kim, "Application of computational fluid dynamics in chlorine-dynamics modeling of in-situ chlorination systems for cooling systems," *Appl. Sci.*, vol. 10, no. 13, 2020, doi: 10.3390/app10134455.
- [3] Y. Zhang, M.-Y. Sun, and L.-X. Han, "Numerical simulation of the effects on residual chlorine water discharge from LNG on the ocean water environment," 2017, doi: 10.2991/eesed-16.2017.102.
- [4] G. LI, H. CAO, X. YANG, and M. TIAN, "Effect of Residual Chlorine on Marine Organisms for Huarun Caofeidian Power Plant," *DEStech Trans. Environ. Energy Earth Sci.*, no. gmee, Dec. 2017, doi: 10.12783/dteees/gmee2017/16582.
- [5] C. E. Nash, "Residual Chlorine Retention and Power Plant Fish Farms," *Progress. Fish-Culturist*, vol. 36, no. 2, pp. 92–95, 1974, doi: 10.1577/1548-8659(1974)36[92:RCRAPP]2.0.CO;2.
- [6] R. E. Basch and J. G. Truchan, "Toxicity of chlorinated power plant condenser cooling waters to fish. Final report," Michigan, 2000. Accessed: Jun. 02, 2021. [Online]. Available: <https://nepis.epa.gov/Exe/ZyNET.exe/9101Y99D.TXT?ZyActionD=ZyDocument&Client=EP A&Index=1976+Thru+1980&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A%5Czyfiles%5CIndexData%5C76thru80%5CTxt%5C00000035%5C9101Y99D.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=hpfr&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Resul ts page&MaximumPages=1&ZyEntry=1&SeekPage=x&ZyPURL>.
- [7] L. Wang *et al.*, "Hypochlorous acid as a potential wound care agent: part I. Stabilized hypochlorous acid: a component of the inorganic armamentarium of innate immunity.," *J. Burns Wounds*, vol. 6, 2007.
- [8] S. Rajagopal, H. A. Jenner, and V. P. Venugopalan, *Operational and environmental consequences of large industrial cooling water systems*, vol. 9781461416982. 2012.
- [9] D. P. Loucks and E. van Beek, "Water Quality Modeling and Prediction," in *Water Resource Systems Planning and Management*, Springer International Publishing, 2017, pp. 417–467.
- [10] M. P. Astuti, R. Xie, and N. S. Aziz, "Laboratory and pilot plant scale study on water dechlorination by medium pressure ultraviolet (UV) radiation," in *MATEC Web of Conferences*, 2017, vol. 101, doi: 10.1051/mateconf/201710102003.
- [11] R. P. Whitney and J. E. Vivian, "Solubility of Chlorine in Water," *Ind. Eng. Chem.*, vol. 33, no. 6, 1941, doi: 10.1021/ie50378a014.
- [12] A. Osama, M. H. ElNadi, N. A. H. Nasr, and M. B. Ezzat, "Determination of Thermal Pollution Effect on End Part of Stream," *Int. J. Innov. Technol. Explor. Eng.*, vol. 9, no. 3, 2020, doi: 10.35940/ijitee.b6280.019320.
- [13] J. M. Hales and D. R. Drewes, "Solubility of ammonia in water at low concentrations," *Atmos. Environ.*, vol. 13, no. 8, 1979, doi: 10.1016/0004-6981(79)90037-4.