Using of Green Oxidant for Treatment of Drinking Water

Emerging Micro-pollutant

By

Alaa Mohamed Fareed Mahmoud Farrag

(M.Sc. in chemistry, Ain Shams University, 2013)

A Thesis Submitted

For Ph.D. Degree in Chemistry

To

Chemistry Department

Faculty of Science

Ain Shams University

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APPROVAL SHEET

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ABSTRACT

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Name: Alaa Mohamed Fareed Mahmoud Farrag

Title of thesis: Using of Green Oxidant for Treatment of Drinking Water Emerging Micro-pollutant

Degree: **(Ph.D.)** Doctor in Science Thesis, Faculty of Science, Ain Shams University, 2018.

In recent years, because of the advanced analytical instrumentation and new analytical techniques, scientists have been able to detect very low concentrations of many chemicals in natural and drinking waters. These low levels of emerging micropollutants in raw waters and drinking water may not cause the immediate lethal effect to humans but may promote disastrous impacts on human health in a long term. While the risk that low concentrations of emerging contaminants pose to humans and the environment requires further investigation, it is important to identify the concentrations of these compounds in water streams and drinking water thereby, an effective technique could be developed to treat these contaminants. An investigation of the emerging micropollutants was done along the Rosetta branch, the founded results demonstrated an adverse effect of 5 drains along the branch those drains reserve untreated wastewater from unserved villages located in the domain of the branch watershed. 18 sampling points were investigated by the means of LC-MS solid phase extraction method, 15 pharmaceuticals were traced along the sampling points. Naproxen, Chlortetracycline, Doxytetracyclin hyclate, Pencilin and Oxacillin record the highest concentrations up to 21.189, 20.955, 20.89, 20.09 and 20.029 µg/l, respectively, while Oxytetracycline, Tetracyclin, and Ofloxacin were not detected, the study reveals that ferrate proved itself as a green coagulant alternative for the conventional treatment. Ferrate has accomplished the required treatment of surface water of Koshla WTP. Using ferrate in surface water treatment accomplish almost 100% removal for 14 pharmaceuticals, however, ferrate failed to remove erythromycin by significant efficiency.

Keywords: Emerging Micro pollutants; Pharmaceuticals; Water Quality.

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Dear Author(s),

We are delighted to inform you that your paper entitled: **"Occurrence, Sources, and Fate of Pharmaceuticals Products along Rosetta Nile River Branch"** Authorized by: ***A.M. Fareed, R. Wahaab, Tarek S. Jamil, Amr A. Hassan and Eglal R. Souaya*** has been accepted for publication in the ***Middle East Journal of Applied Sciences, ISSN 2077-4613*** based on the recommendation of two referees and will be published in Vol. 8, No 3, 2018.

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With Regards

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Occurrence, Sources, and Fate of Pharmaceuticals Products along Rosetta Nile River Branch

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ABSTRACT

In recent years, because of the advanced analytical instrumentation and new analytical techniques, scientists have been able to detect very low concentrations of many chemicals in natural and drinking waters. These low levels of emerging micropollutants in raw waters and drinking water may not cause the immediate lethal effect to humans but may promote disastrous impacts on human health in a long term. While the risk that low concentrations of emerging contaminants pose to humans and the environment requires further investigation, it is important to identify the concentrations of these compounds in water streams and drinking water thereby, an effective technique could be developed to treat these contaminants. An investigation of the emerging micropollutants was done along the Rosetta branch, the founded results demonstrated an adverse effect of 5 drains along the branch those drains reserve untreated wastewater from unserved villages located in the domain of the branch watershed. 18 sampling points were investigated by the means of LC-MS solid phase extraction method, 15 pharmaceuticals were traced along the sampling points. Naproxene, Chlorotetracyclin, Doxytetracyclin hyclate, Pencilin and Oxacillin record the highest concentrations up to 21.189, 20.955, 20.89, 20.09 and 20.029 µg/l, respectively, while Oxytetracylin, Tetracyclin, and Ofloxacine were not detected, the study reflects effect of the untreated waste along the Rosetta branch.

Keywords: Emerging Micro pollutants; Pharmaceuticals; Water Quality.

Introduction

In the last years, traces of pharmaceuticals, typically at levels of nanograms to low micrograms per liter range, have been noticed in the water cycle, including surface waters, wastewater, groundwater and, to a lesser extent, drinking-water. Advances in analytical technology have been a key factor driving their increased detection. Their presence in water, even at these very low concentrations, has raised concerns among water stakeholders, such as drinking-water regulators, governments, water suppliers and the public, regarding the potential risks to human health from exposure to traces of pharmaceuticals via drinking-water (Lishman *et al.,*2006).

Pharmaceuticals are synthetic or natural chemicals that can be found in prescription medicines, over-the-counter therapeutic drugs and veterinary drugs. Many surveys and studies have confirmed the presence of pharmaceuticals in municipal wastewater and effluents, and these have been identified as a major source of pharmaceuticals in drinking-water. Figure (1) demonstrate the delivery ways of pharmaceuticals to the drinking water.

Routine monitoring programmers to test drinking-water for pharmaceuticals have not been implemented so far in Egypt, as is the case for regulated chemical and microbial parameters. Generally, data on the occurrence of pharmaceuticals in drinking-water have resulted from surveys or targeted research projects and investigations. Available studies have reported that concentrations of pharmaceuticals in surface waters, groundwater and partially treated water are typically less than 0.1 µg/l (or 100 ng/l), and concentrations in treated water are generally below 0.05 µg/l (or 50 ng/l).

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Pharmaceutical and personal care products (PPCPs) and endocrine disrupting chemicals (EDCs) are classified as emerging micro-pollutants, which have been a significant issue of environmental and public health concern because they may be significant adverse environmental and human health effects although the occurrence of these pollutants in the environment is usually in a very low concentration range; from µg/l to ng/l. Pharmaceuticals such as antibiotics, ant inflammatory drugs, Β-blockers and X-ray contrast media are widely used, these pharmaceuticals and their metabolites cannot be fully utilized by human beings or animals and are inevitably emitted into the waters by execration (Lishman *et al.,* 2006; Nakada *et al.,* 2006; Comeau *et al.,* 2008; and Wang *et al.,* 2010) and/or through the discharge of industry effluents and hospitals waste waters (Ternes et al., 1998 and Lee *et al.,* 2007). Results of toxicology studies have revealed that some pharmaceuticals are suspected to have direct toxicity to certain aquatic organisms (Ferrari *et al.,* 2003; Jjemba *et al.,* 2006 and Grung *et al.* 2008) and they could accumulate slowly, and finally lead to irreversible change on wildlife and human beings (Daughton and Ternes, 1999). The adverse environmental and human health effects could take place under a very low concentration range; from several µg L^{-1} to ng L^{-1}.

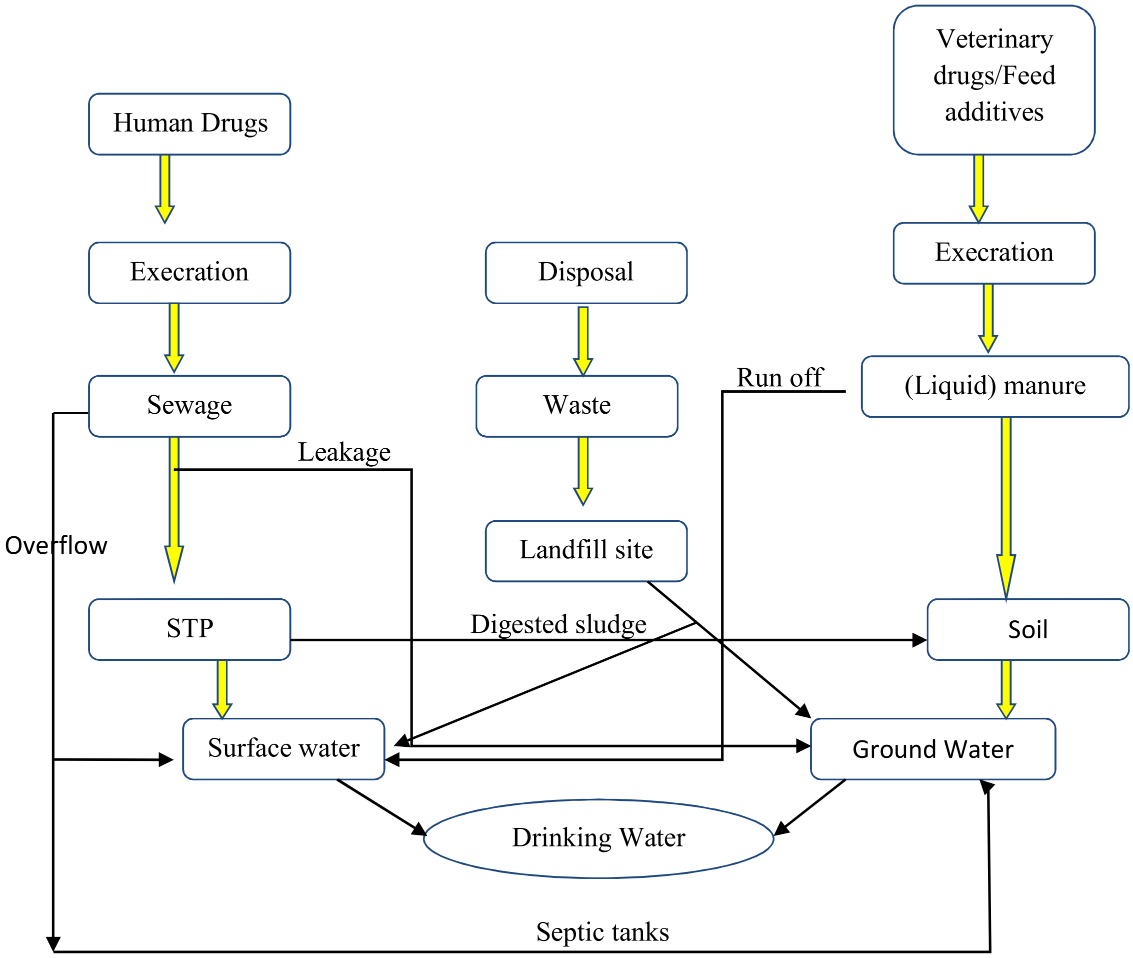


Fig. (1): Fate and transport of pharmaceuticals in the environment.

The presence of emerging micro pollutants and their potential toxicity are challenge to the global water industries as there is no unit process specifically designed to remove these pollutants; activated sludge and secondary sedimentation in most wastewater treatment works (WWTWs) seems to be inefficient to eliminate them (Ternes *et al.,* 1998; Paxeus *et al.,* 2004; Castiglioni *et al.,* 2006;

Nakada *et al.,* 2006 and Santos *et al*., 2007). Thus, a number of recent studies have been carried out to explore suitable technologies to treat pharmaceutical residuals from water and wastewater. Ozonation was found to be effective to remove pharmaceuticals in municipal WWTWs (Comerton *et al.,* 2008).

Nanofiltration (NF) and reverse osmosis (RO) membrane filtration have been applied at bench, pilot and full scale (Snyder *et al.,* 2008). Activated carbon adsorption (Westerhoff *et al.,* 2007) has also been proved as an efficient process to remove pharmaceuticals; addition of 5 mg/l of powder activated carbon with a 4-h contact time removed 50% to >98% of the volatile PPCPs and 10% to >95% of the polar PPCPs (El-Sherbini and El-Moatassem, 2005).

Effective treatment processes are needed to remove the emerging micro pollutants, ferrate could be a possible potential treatment method due to its unique properties it act as multifunction chemical (oxidant, coagulant, and disinfectant) in one single dose this study aims at illustrate the occurrence of emerging micro pollutants in the West Nile Delta region water resources (i.e. Rosetta branch) and the effectiveness of ferrate as alternative water treatment chemical.

Rosetta branch is the main drinking water supply for areas along West Nile Delta with about 3.5 million capita, however the quality of raw water within the branch is badly deteriorated due receiving wastes discharged by agricultural, industrial and domestic activities throughout 5 large drains (Rahawy, Sabal, Tahreer, Zawitelbahr and Tala) discharging water and transporting pollutants from domestic and settlement areas directly into the branch (Okuda *et al.,* 1990).

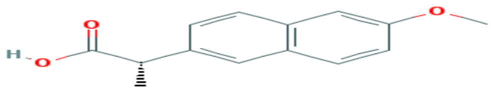
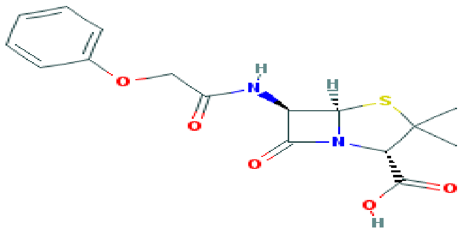
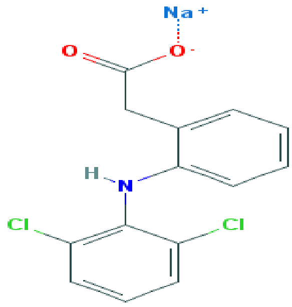
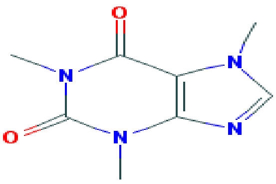
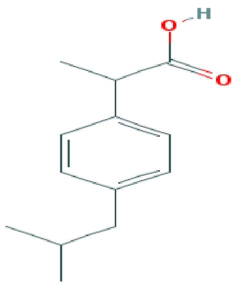
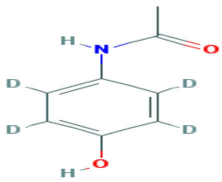
It was estimated that the amount of discharged wastewater from the five drains to be around 8.14 Mm^3/day, about 75% of this waste is untreated/partially treated.

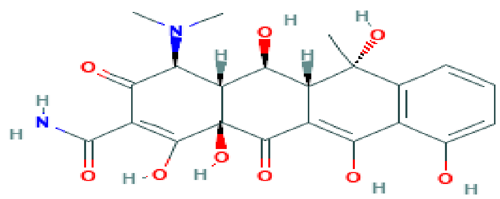
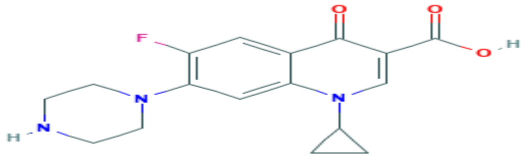
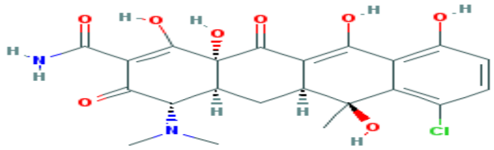
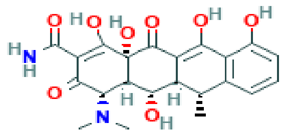
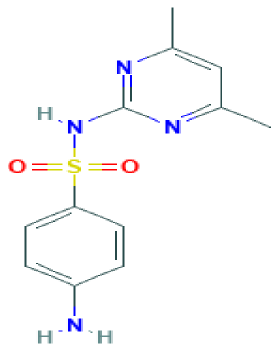
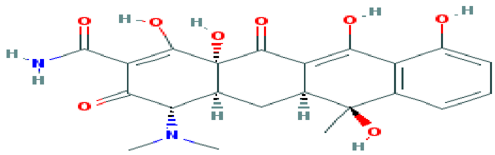
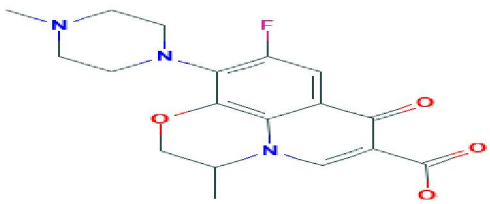
The aim of this study is tracing of emerging micro-pollutants pharmaceuticals (Naproxene, Chlorotetracyclin, Doxytetracyclin hyclate, Pencilin, Oxacillin, Oxytetracyclin, Tetracyclin, Ofloxacin, Paracetamol, Ibuprofen, Diclofenac Sodium, Caffine, Erythromycins, Sulfamethazine, and Ciprofloxacin) together with other physicochemical parameters along Rosetta branch.

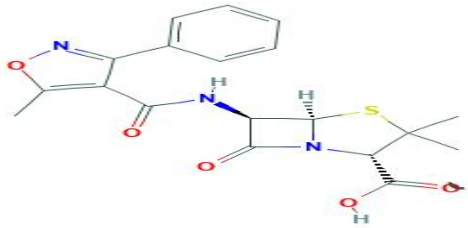
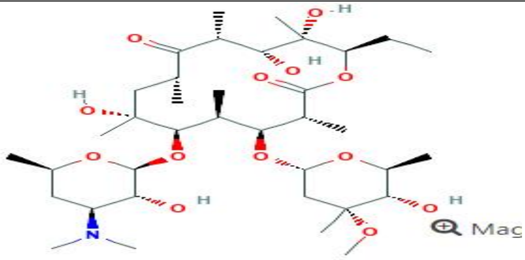
Material and Methods

An intensive monitoring along the Rosetta branch was done to investigate the occurrence of emerging micropollutants. 18 sampling points lying in Rosetta branch were analyzed by means of LC-MS/MS with solid phase extraction technique SPE, Oasis HLB cartridges) + liquid chromatography (LC)-mass spectrometry (MS) was employed, which was conducted in the reference lab for drinking water, Egypt. Figure (2) represents a map that shows the sampling points. The samples were taken from the middle of the waterway. On-site measurements were done immediately to avoid any unwanted change; further analysis was done according to SMWW 21th edition. 16 pharmaceutical's standards were purchased from Sigma-Aldrich including Naproxene, Chlorotetracyclin, Doxytetracyclin hyclate, Pencilin, Oxacillin, Oxytetracyclin, Tetracyclin, Ofloxacin, Paracetamol, Ibuprofen, Diclofenac Sodium, Caffine, Erythromycins, Sulfamethazine and Ciprofloxacin (≥98%, HPLC grade); other chemicals and reagents used were obtained from Fisher Scientific. All chemicals and reagents were used without further purification. The investigated pharmaceuticals structures are shown in table (1).

Table 1: The structure of investigated pharmaceuticals.

Drug	Structre
Naproxen	
Penciliin	
Diclofenac sodium	
Caffein	
Ibuprofen	
Paracetamol	

Oxytetracyclin	
Ciprofloxacine	
Chlorotetracyclin	
Doxytetracyclin hyclate	
Sulfamethazine	
Tetracyclin	
Ofloxacine	

Oxacillin	
Erythromycine	

Results and Discussion

The survey includes the investigation of 18 samples taken from the middle of the waterway covering about 260 km along the Rosetta branch. These sampling points include 5 samples from the drains. Sampling points are represented in figure (2).

Study region, data and methodology:

Physical and chemical analyses were carried out according to "Standard Methods for Examination of Water and Wastewater". Field parameters (temperature, pH, electric conductivity (EC), dissolved oxygen (DO) and total dissolved solids (TDS) were measured in-situ using a multi-probe system. ammonia, nitrite, and nitrate were carried out by a colorimetric method and the chloride done by argentometric method. figure (3) represent the data analysis of the 18 samples. Sample point s2 represents the discharge of El Rahawy drain, s6 represents the discharge of Sabal drain, s9 represents the discharge of Tahrir drain, s11 represents the discharge of Zaywet El Bahr drain and s13 represents the discharge of Tala drain. The first sampling point s1 represents the fresh water from Qanater barrage before mixing with the different drains.

Screening of pharmaceuticals concentrations were done a long the study area covering the 18 samples table (2), represent the concentration of the pharmaceuticals.

It is obvious from table (2) and Figure (4) that the concentration ammonia, COD, and pharmaceuticals are maximum at the points of the discharge of the 5 drains (s2, s6, s9, s11, and s13) which reflect the great adverse effect of the 5 drains in water quality at the Rosetta branch. El Rahway drain represents the most polluted drain this could be attributed to that many villages throw its untreated waste directly in the drain, the number of uncovered villages with wastewater systems that around El Rahway drain is about 65 villages with about 836715 capita drain. Self-purification in Rosetta branch allow the water quality to enhance after the point of the discharge, however, it's clearly that some of the pharmaceuticals are easily degradable as (Naproxen, Diclofenac Sodium, Paracetamol, Ciprofloxacin, Doxytetracyclin Hyclate, Oxacillin, and Erythromycin) while other pharmaceuticals show a higher stability as (Penicillin, Ibuprofen, Chlortetracycline, Caffin).

Naproxen recorded the highest concentration with (21.189 µg/l), while Sulfamethazine recorded the lowest concentration with (16.103 µg/l). Naproxen (brand names: Aleve, Naprosyn, and many others) is a nonsteroidal anti-inflammatory drug (NSAID) of the propionic acidclass (the same class as ibuprofen) that relieves pain, fever, swelling, and stiffness. It is a nonselective COX inhibitor, usually sold as the sodium salt. It is available in both an immediate release and extended release formulation. Naproxen is generally safe to use in breastfeeding mothers. Common adverse effects of naproxen include central nervous system effects (e.g. dizziness and headache), blood effects (e.g. bruising), allergic reactions (e.g. rash), and gastrointestinal complaints (e.g. heartburn and stomach ulcers). It has an intermediate risk of stomach ulcers compared to others drugs in the same class (NSAIDs). NSAIDs appear to increase the risk of serious cardiovascular events, though this risk appears to be less with naproxen compared to other NSAIDs. Serious drug interactions may occur in combinations with other drugs that affect the blood, or with drugs that also increase the risk of ulcers.

Sulfamethazine is only found in individuals that have used or taken this drug. It is a sulfanilamide anti-infective agent. It has a spectrum of antimicrobial action similar to other sulfonamides. Sulfonamides inhibit the enzymatic conversion of pteridine and p-aminobenzoic acid (PABA) to dihydropteroic acid by competing with PABA for binding to dihydrofolate synthetase, an intermediate of tetrahydrofolic acid (THF) synthesis.

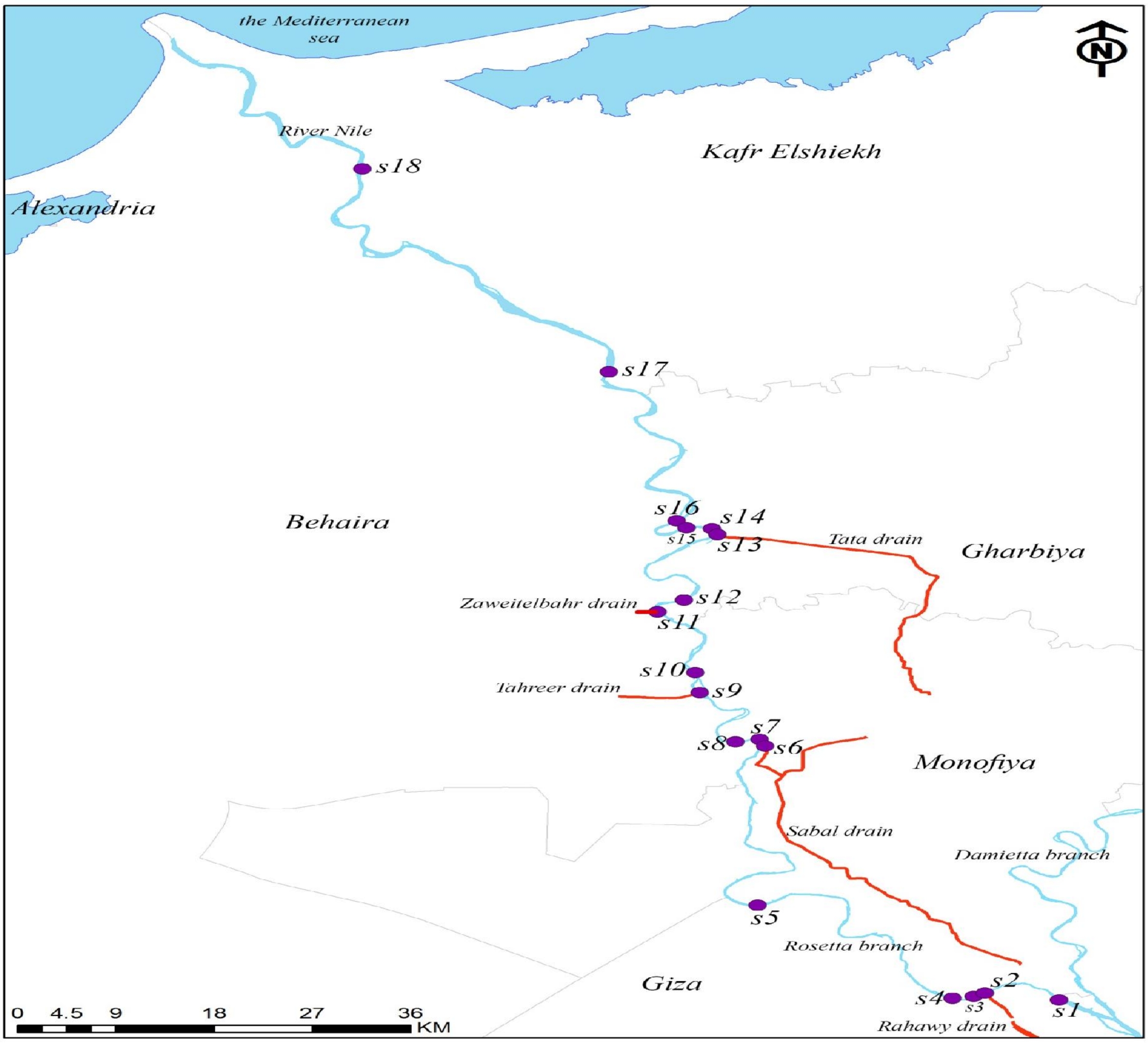


Fig. 2: Sampling points along Rosetta branch

Table 2: Concentration in µg/l for pharmaceuticals in 18 sampling points.

Sampling No.	s1	s2	s3	s4	s5	s6	s7	s8	s9	s10	s11	s12	s13	s14	s15	s16	s17	s18
Naproxen		21.189				9.024		0.919	1.681		1.015		0.591				0.922	0.917
Penciliin		20.029				9.982			2.007	0.657	0.969	0.68	0.514		0.702			
Diclofenac sodium		19.393				10.517			2.106		1.042		0.442					
Caffein	0.372	19.015	0.368	0.369		10.825	0.365	0.385	2.257	0.373	0.968	0.349	0.435	0.389	0.355	0.353	0.351	0.386
Ibuprofen	0.702	19.95	0.668	0.691		10.157	0.631	0.64	1.947	0.629	0.878	0.669	0.568	0.629	0.632	0.651	0.657	0.655
Paracetamol		18.023				11.455	0.595	0.509	3.011	0.512	0.575		0.436			0.509	0.536	0.55
Oxytetracyclin																		
Ciprofloxacine		19.774				10.57			1.804		0.652		0.7					
Chlorotetracyclin	0.705	20.955	0.708	0.693		9.151	0.708	0.709	1.873	0.748	0.941	0.71	0.58	0.708	0.707	0.707	0.707	0.709
Sulfamethazine		16.103				12.526			3.754		1.169							
Tetracyclin																		
Doxytetracyclin hyclate		20.89				10.208			0.389		1.286		0.727					0.621
Ofloxacine																		
Oxacillin		20.096				10.009			1.859		1.007		0.529					
Erythromycine		19.115				10.44			2.695		0.848		0.402					

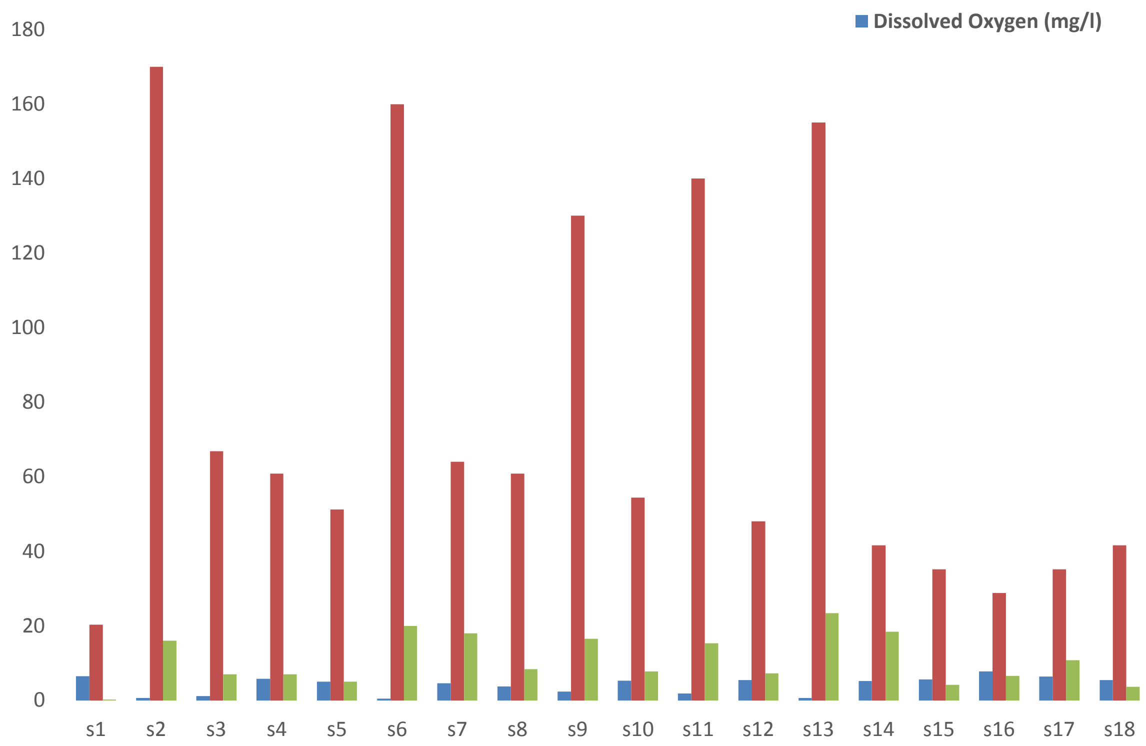


Fig. 3: COD, DO, and Ammonia concentration in mg/l for the 18 sampling points.

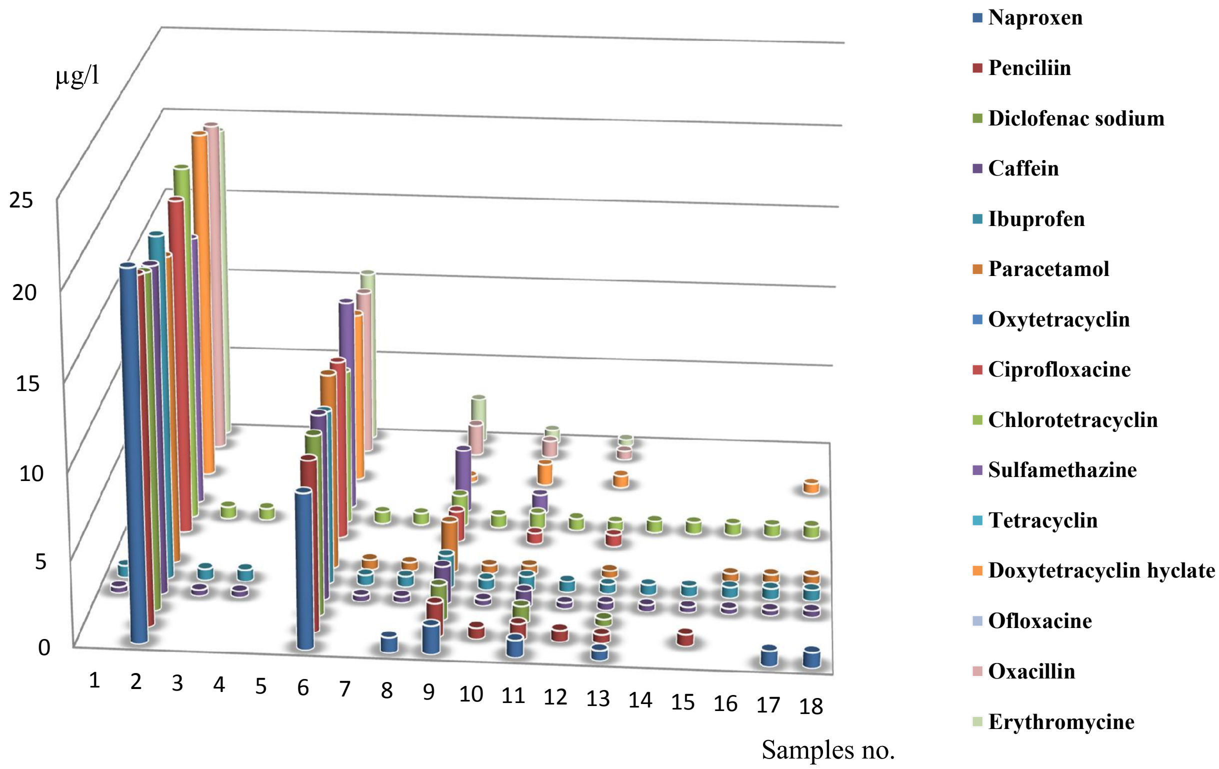


Fig. 4: Concentration in µg/l for pharmaceuticals in 18 sampling points.