



Calculation and interpretation of effluent discharge objectives of metal industry – case of Protuil manufacturing – Annaba (Northeast Algeria)

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Received 15 August 2016; Accepted 29 November 2017

ABSTRACT

The preservation and protection of wetlands are of paramount concern given their vulnerability, the rich heritage they can hold and the functions they perform. Economic development has led to negative impacts on the environment and the health of populations. Several methods have been developed to limit the concentrations and a load of effluents in the natural environment. Lakes, reservoirs and closed bays are particularly sensitive to contaminant inputs. Their hydrodynamics promote sedimentation and lead to slow mixing of the effluent in the medium. In this context, the present study was concerned with the environmental objectives of discharges (EOD) of the Protuil manufacturing (metal production) in a salted and protected area of the Fetzara Lake. This method permits the calculation of concentrations and loads of contaminants potentially discharged into an aquatic environment without the compromise of water quality. The calculation of EOD for heavy metals (Cr, Cu, Ni, Pb and Zn) has shown a significant overcoming of these toxic contaminants threatening the ecosystem integrity and/or the environment.

Keywords: Rejection Protuil; EDO calculation; Fetzara Lake; Heavy metals; Excess

1. Introduction

The impacts exerted on the environment are accentuated with the increase in industrial activities, urban developments and practical agricultural industrialization [1–3]. Wetlands are highly vulnerable and severely degraded. Threats remain serious and widespread: deterioration and harmful effects on the environment, depletion of natural resources and pollution of water, which is a major concern. The Protuil is the leader in the production of metal tiles, and hot-dip galvanizing is a real example. Fetzara Lake ecosystem (Ramsar site in 2002) is a salt water lake that is part of the Algerian Northeast wetland complex, known for its floristic and faunistic biodiversity. Industrial and agricultural activity and the growing

need for water resources have increased in the vicinity of the lake, threatening not only the ecological integrity of this site but also the well-being of human beings and of all animal and plant species that depend on it. This situation requires a permanent preservation of the aquatic ecosystem. Fetzara Lake evacuates its salted waters via the Meboudja Wadi, which connects with the Seybouse Wadi and the phreatic surface [4]. In order to protect this site, monitoring the quality of the lake's water remains crucial. The purpose of this study is to calculate the environmental objectives of discharges (EOD). They are values related to load and concentration values for a parameter associated with an effluent potentially discharged into a specific point of a water body without compromising water uses [5,6].

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2. General context of the study area

2.1. Geographic setting of the Fetzara Lake

The Fetzara Lake ecosystem is located 18 km southwest of the town of Annaba (Northeast Algeria). It is represented by a large asymmetric depression with an area of approximately 18,600 ha. It drains an area of 515 km². The flooded part of the lake is located in the center and covers an area estimated in winter to 13,000 ha. The presence of a drainage channel furrowing the lake from West to East ensures its drainage. The area is characterized by outcrops of metamorphic (Edough Mountain) and sedimentary formations that occupy the rest of the plain (Fig. 1).

Four soil classes are located at Fetzara Lake [7]. (1) The halomorphic soils are concentrated in the center and occupy 55% of the total area; (2) the poorly developed soils occupy the entire periphery of the lake with 28%; (3) the hydromorphic soils frequent in the western part of the lake with 13.7% and (4) the vertisol soils with 3.3% of the surface and occupy the western and southwestern parts of the lake. The statistics of the proportions of mineral particles (clay, silt and sand), on the triangle of the textures, reveals seven classes of texture, where the texture of the silty clay represents 50% of the study area [8].

Climatically, the study area receives an annual average of 680 mm/year of precipitation and an average annual temperature of around 17.50°C. The yearly evaporation is very important; it has an average of 1,375 mm/year [8].

2.2. Geographic location and economic activities of Protuil manufacturing

The metallurgical industries and mines known to be a source of environmental metallic contamination are implanted in coastal zones [9,10]. The Protuil unit is located to the south of the Berrahal industrial zone, to the north by

the national company Gesibat, to the east by the mills Beldi and the agglomeration of Kalitoussa in the South at 32 km west of the Annaba city (Northeast Algeria), on the national road 44 (Fig. 2). Protuil has a total area of 69,990 m², of which the undeveloped part represents 75%, and the remainder comprises the production, complementary and administrative offices; established after the parent company Prosidier (March 1998) dissolved. It is specialized in the manufacture of metal tiles and hot-dip galvanization until 2008. From this date to present, it has been limited to production and marketing of fabricated metal products; tubing, wire drawing, shearing, welded wire mesh, pylons and plates with a capacity of 600,000 units/year. The wastewater of this factory is discharged directly into the Fetzara Lake through an open-pit concrete channel.

2.3. Fetzara Lake discharge

Three rivers feed the Fetzara Lake: Zied Wadi, El Hout Wadi and El Mellah Wadi. These streams are characterized by a very irregular, torrential regime in winter and a dry system in summer (Fig. 3). At the outlet of the lake, the drainage canal transports the waters of the lake to Meboudja Wadi and Seybouse Wadi and then drained to the Mediterranean Sea.

The rivers that feed the Fetzara Lake dry up in dry seasons except for El Hout Wadi. The drainage of these waters is ensured by the main channel which crosses the center lake; but the evacuation of water remains insufficient, causing the phenomena of hydromorphia due to flooding effects, and also a large salinization [11].

The flows are unknown due to the absence of the gauging stations. The use of the exploration method of the field speed at the bridge station on Meboudja Wadi has allowed us to determine the low flow.

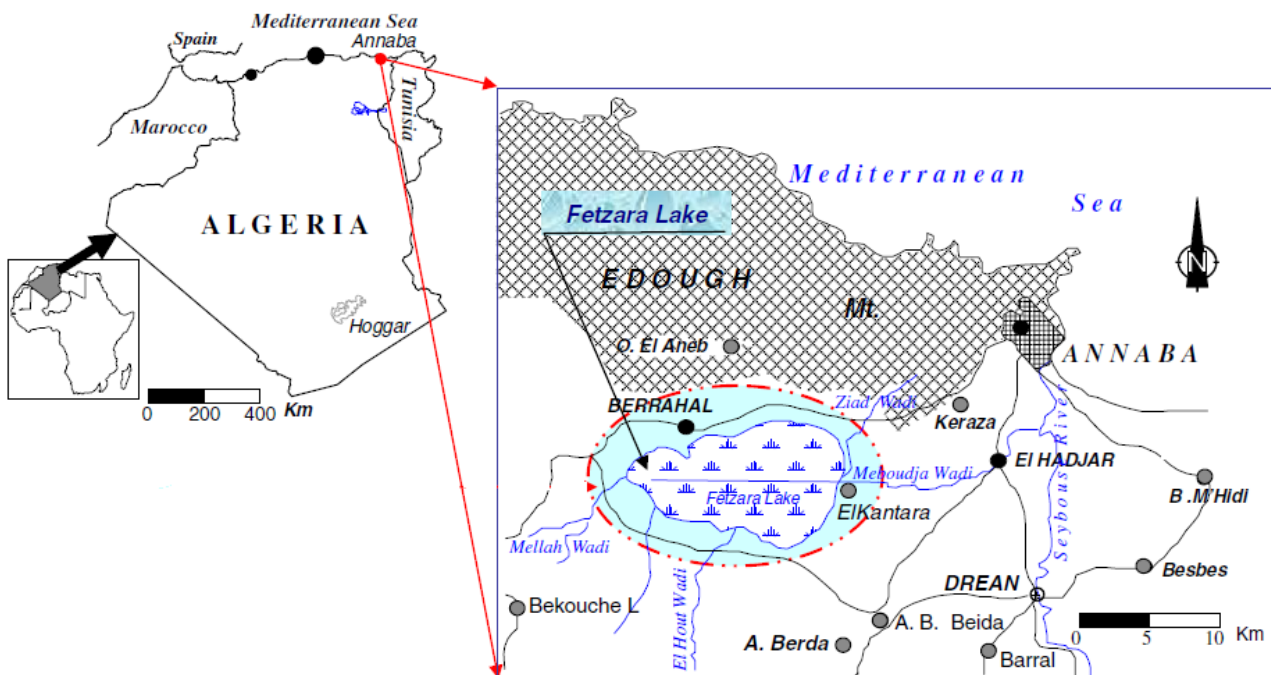


Fig. 1. Location of the Fetzara Lake.

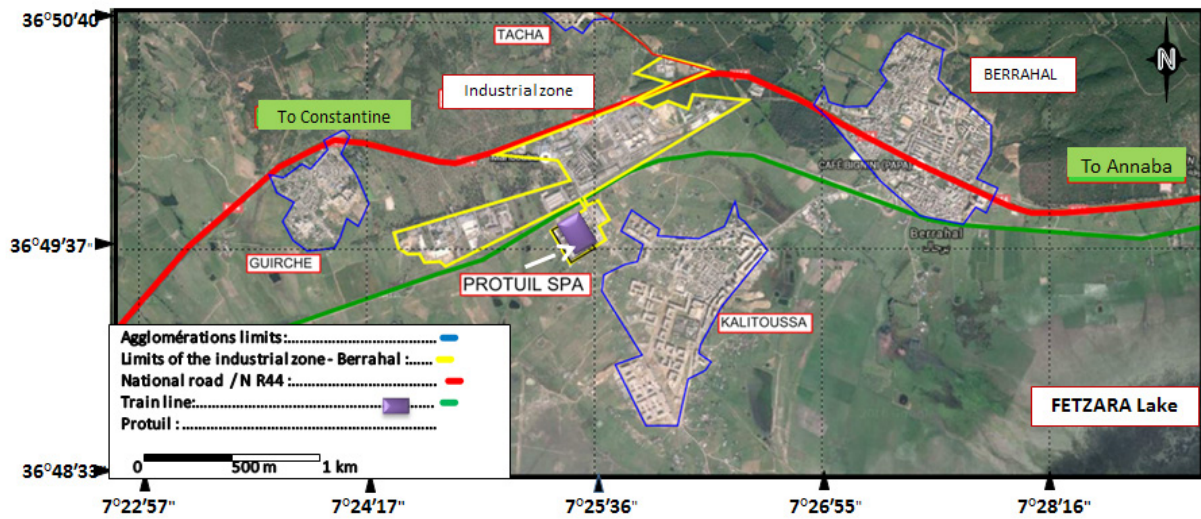


Fig. 2. Situation of Protuil factory.

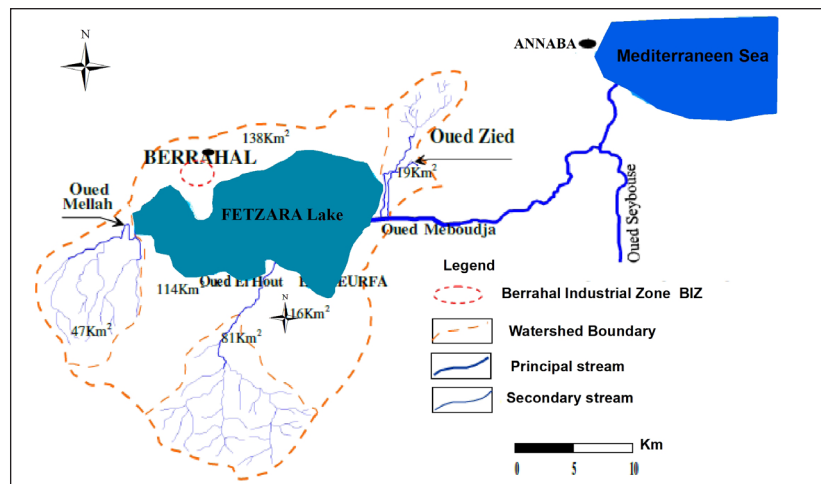


Fig. 3. The principal catchment of the Fetzara Lake [12].

3. Materials and methods

3.1. Materials

3.1.1. Site, method and frequency sampling

From the physico-chemical analyses and the median concentrations of contaminants' calculation in the upstream of the Fetzara Lake, five parameters have been selected: chromium, copper, lead, nickel and zinc. The follow-up process of the different contaminants was carried out along a period from January 2012 to March 2015 (Quarterly analyses). All samples were taken using a manual sampler with a foldable pole that has 1 m length, and about 25–50 cm depth of specimen. The samples were transported at a low temperature of 4°C till they reached the laboratory.

3.1.2. Physical–chemical parameters

The selected parameters were those that allowed assessing the various qualities of the released wastewater, the

potential impacts on the respective aquatic natural habitat and the whole ecological system. Many tests and analyses methods were adopted for these purposes. For instance, chromium (Cr(VI)) is measured by atomic adsorption spectrometer (Philips PU 8620 series spectrometer), copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) were measured by atomic adsorption spectrometer (PerkinElmer Analyst 3110).

3.2. Methodology

Several studies in the world have been focused on the effects of the industrial and urban wastes on the evolution of the surface water quality [13]. Among these studies, some have shown methods related to the subject [14,15]. Among these methods, we have chosen that of MDDEP method (Ministry of sustainable development, Environment and the Parks of Quebec 2007), inspired by the approach of the US Environmental Protection Agency [16].

Table 1
The values of the chronic and acute aquatic life criteria [18].

	Salt water			Conversion factor "Salt water" ^a	
	Chronic aquatic life criteria CALC (mg.L ⁻¹)	Effluent final acute values FAVE (mg.L ⁻¹)	Acute aquatic life criteria AALC (mg L ⁻¹)	CALC	AALC
Chromium VI	0.05	2.2	1.1	0.993	0.993
Copper	0.0037	0.012	0.0058	0.83	0.83
Lead	0.0085	0.44	0.22	0.951	0.951
Nickel	0.0083	0.15	0.075	0.997	0.998
Zinc	0.086	0.19	0.095	0.946	0.94

^aConversion factor of total extractable metal to dissolved metal.

The EDO factor is a value of fully loaded weight and concentration calculated for an associated parameter with an effluent that is discharged in a definite point of the stretch of water. It also evaluates whether the capacity of a waterbody to receive contaminants has already been exceeded [17].

In order to calculate the EDO factor, to protect the living organisms, we must know the criterion of water quality of the chronic aquatic life criteria, where two levels of protection are necessary to prevent effects on aquatic life: an acute effect level AALC (severe short-term effects) and a chronic effect level CALC (sublethal medium- and long-term effects). This is related to the flow of the effluent, the parameters of concentration in the flow rate and, usually, the critical low flow of the receiving environment [17].

The calculation of EDO is based on the method of applied loading defined by the portion of the stretch of water (Table 1). This method is made out in a manner in which for every contaminant, the additional amount of the effluent's load on the upstream discharge load respects the maximal tolerable load on the limit of the restricted mixing zone. That zone is allocated in the measurement where it does not damage the set of the water body. The dilution rate of the discharge in the receiver's environment frequently becomes a determinant factor in the assessment of EDO's preservation.

$$C_s Q_{ams} + C_e Q_e = C_c (Q_s + C_e) \quad (1)$$

$$C_e Q_e = C_c (Q_s + Q_e) - C_s Q_s \quad (2)$$

$$Fd = \frac{Q_e}{Q_s + Q_e} = \frac{Q_e}{(Q_r + fQ_e) + Q_e} \quad (3)$$

$$C_e = \frac{C_c}{Fd} - C_s \frac{Q_r - fQ_e}{Q_e} \quad (4)$$

$$Q_r = \frac{Q_e}{Fd} + fQ_e - Q_e \quad (5)$$

$$C_e = \frac{C_c}{Fd} - \frac{C_s}{Q_e} \left(\frac{Q_e}{Fd} + fQ_e - Q_e - fQ_e \right) \quad (6)$$

$$C_e = \frac{C_c}{Fd} - \frac{C_s}{Q_e} \left(\frac{Q_e}{Fd} - Q_e \right) \quad (7)$$

$$C_e = \frac{C_c}{Fd} - \frac{C_s Q_e}{Q_e Fd} + \frac{C_s Q_e}{Q_e} \quad (8)$$

$$C_e = \frac{C_c}{Fd} - \frac{C_s}{Fd} + C_s \quad (9)$$

$$C_e = \frac{C_c - C_s}{Fd} + C_s \quad (10)$$

C_e (mg L⁻¹): the environmental objective of discharge in concentration, C_s (mg L⁻¹): median upstream concentration in the Lake, C_c (mg L⁻¹): quality of water criterion. Q_r (L s⁻¹): the low flow in the lake; Q_e (L s⁻¹): effluent flow, f : fraction of effluent's flow, Fd : dilution factor.

From Eq. (10), we defined, the Protuil load allowed to the effluent C_d (kg d⁻¹):

$$C_d = C_e \times Q_e \quad (11)$$

3.3. The effluent's flow of the Protuil factory

The flow of the Protuil has been determined by Doppler rate meter height (H)/speed (S) (mainstream IV) in order to measure the pressure. It has been done using the probe of a piezoresistivity level and speed: by Doppler effect. We have used a speed sensor of Doppler effect. An ultrasound ray is transmitted by a submerged probe, following the axe of canalization. These waves are reflected by all the particles in suspension in water. They are analyzed to determine the average speed of water. ($S = f(H)$ and $Q = S \cdot A$. Q : flow, A : area). The analysis of data has been possible using Winfluid software and the flow has been measured with an average error estimated at $\pm 1\%$ (Table 2).

4. Results and discussion

4.1. Lake Fetzara flow

The critical low flow recorded at the bridge station of Meboudja Wadi for 10 years by the method of exploration

of the velocity fields is 18.4 L s^{-1} [12]. The Protuil factory did not draw its water from the receiver's medium ($f = 0$). For the toxic contaminants, 50% of the low flow of the effluent mixing has been retained.

4.2. Calculation of EDO for the heavy metals in the Protuil manufacturing

The EDO values were calculated by Eq. (10) of the mass balance. According to the available data, we have limited the method in order to look for the EOD. In fact, the contaminant concentrations in the water would allow the water consumption and the aquatic organisms without harmful effects on health. In addition, the highest concentrations of these contaminants which do not result in any dangerous effect on the chronic aquatic life (chronic effect) were demonstrated.

The studied EDO in the location of the wastewater of Protuil has to respect the water quality criteria in the limit of the mixing zone considered between the waters of the receiving environment (Fetzara Lake) and the effluent of Protuil. We take this to consider the flow of the effluent, the characteristics of the natural receiving environment, the concentration of the upstream stretch in contaminants and the dilution in critical conditions.

4.3. Discussion of the calculated EDO

Like other heavy metals, zinc, lead and chromium have some characteristics which make them have a potential hazard to the health of humans and the ecosystems and also to cause major environmental problem. Being persistent and mobile and their commercial/industrial use increase their possibility of accumulation in the water, soil [19].

The results of the EDO calculations for the use of CALC (chronic effect) (Table 3) have shown negative values for

copper, nickel and lead (-0.61 , -0.67 and -1.53 mg L^{-1} , respectively) which means that Fetzara Lake presents a high concentration of this element and then its rejection in this natural environment must be protected. In this case, we retain as EDO the quality criterion of this use (Table 2).

Concerning the use of AALC (acute effect), the excess was recorded at the level of three heavy metals namely copper, nickel and lead. In fact, the increase of these contaminant concentrations was -0.70 , -0.45 and -0.63 mg L^{-1} , respectively, compared with the imposed concentration of the criterion [17], and to the important level of pollution of the receiver's medium, the values showed were higher. In this study, the retained EDO has shown that the criteria of water quality were maintained (Table 2).

The chromium and zinc contaminants did not cause major excess for the two uses, and the calculation of discharge environmental objective has given 0.16 and 3.64 mg L^{-1} for the chromium and 0.15 and 0.18 mg L^{-1} for zinc (Table 3). Chromium III or IV have bioconcentration capacities in the living organisms. In a much important way than for zinc and nickel, the mobilization of Cr(IV), its accumulation, its higher absorption and toxicity are controlled by its speciation, in as much of its concentration in the environment and living organisms [20]. The zinc is principally used to galvanize pipes by protecting them against corrosion. Zinc is found mainly in a divalent form in the environment. It has got bioaccumulation properties (penetration of a present substance in a biotope, within an organism and accumulation in its tissue) and biomagnification (concentration increase of a substance present in a tissue) and measure so that it can circulate through a more significant net space of a tropical network [21].

The daily admitted load of discharge (kg d^{-1}) (Table 3) in the medium receiver varied on the basis of its use and the contaminant. In fact, it was the sequence of 0.014 kg d^{-1} for the chromium use of CALC and 0.31 kg d^{-1} AALC. On the other hand, it was 0.0026 kg d^{-1} CALC and 0.0004 kg d^{-1} AALC for copper. The Protuil load for nickel, lead and zinc CALC were 0.0007 , 0.0006 and 0.0129 kg d^{-1} . The Protuil load for nickel, lead and zinc using AALC were 0.0064 , 0.0180 and 0.0155 kg d^{-1} , respectively.

In addition, nickel shows some bioconcentration possibilities in space (absorption of substances by human beings and accumulation in an organism at a concentration higher than that in which they are found in the natural environment [21]). The hexavalent form is highly toxic for human beings. It is soluble, more mobile in the soil and more bioavailable than the Cr(III) [22].

Table 2

The average effluent flow of Protuil manufacturing measuring by mainstream IV

Flow	$Q_{\text{average/d}}$ ($\text{m}^3 \cdot \text{d}^{-1}$)	$Q_{\text{average/s}}$ ($\text{L} \cdot \text{s}^{-1}$)	$Q_{\text{(peak flow)}}$ ($\text{m}^3 \cdot \text{s}^{-1}$)
Flow of discharge: recorded in the last inlet of the canal's evacuation the Protuil effluent	305.2	3.6	19.15

Table 3

Concentration and load of chronic and acute aquatic life criteria

	Median upstream concentration in the lake C_s (mg L^{-1})	Standard deviation SD (mg L^{-1})	CALC (mg L^{-1})	AALC (mg L^{-1})	Protuil load (kg d^{-1})	
					dL (CALC)	dL (AALC)
Chromium(VI)	0.35	0.17	0.16	3.64	0.014	0.31
Copper	1.86	0.75	-0.61	-0.70	0.0026	0.0004
Nickel	0.12	0.20	-0.67	-0.45	0.0007	0.0064
Lead	1.12	0.86	-1.53	-0.63	0.0006	0.0180
Zinc	1.97	14.85	0.15	0.18	0.0129	0.0155

Chemical products, fertilizers, urban wastes and wastewater, all these polluting inputs deteriorate the environment, without taking into account that these contaminants can have a direct impact on human health and biologic resources [23–25].

The solubility of heavy metals in aquatic systems is controlled by a competition between insolubilization (precipitation and adsorption) and solubilization (dissolved complex) reactions. This rejection of the Protuil factory might cause contamination of the environment and a migration of these toxic pollutants towards the bottom of Lake Fetzara partially clogged with fine materials “silt and clay.” The silty clayey texture represents 50% of the Fetzara Lake. These fine materials are suitable for the installation of reducing conditions. The concentration of heavy metals is proportional to the fraction (silt + clay) of the lake bottom vases, leading to a migration of these pollutants to groundwater.

5. Conclusion

The calculation of EDO, use chronic and acute aquatic life for the Protuil manufacturing discharge is perceived as significant even at high level of important pollution of the Fetzara Lake. The decontamination of this natural medium remains crucial, and a systematic program of automatic supervision of all these toxic contaminants should be implemented in urgency.

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