

# Assessment of surface water quality on an oil extraction area in Albania

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Abstract Oil extraction activities in Albania are considered as highly polluting for surface waters, but more for the amount of direct spills in riverine waters. The aim of this study was to assess the

surface water quality for a period of 5 years (2014-2018) in four seasons based on different physicochemical parameters in the Seman River, in Zharreza reservoir and drainage canal, located in the district of Fier, Albania. Seventeen chemical parameters were monitored such as pH, DO, EC, TSS, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Total-N, Total-P, BOD<sub>5</sub>, COD, Cr(VI), Cu<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Total Oil Grass and Temperature. The values of pH, EC,  $Cl^{-}$ ,  $NO_{3}^{-}$ , Total-N, were in all cases within the limits set by EU, WHO and IFC standards, while DOs were below the limit values of 5.0 mg L<sup>-1</sup> in all stations. TSS exceeded the limit value 1000 mg L<sup>-1</sup> (according to EU standard) at the two Seman stations. Total-P, BOD<sub>5</sub> and COD also exceed the limits of EU and WHO but below the limit values of IFC for surface water of oil extraction fields. Total Oil Grass concentrations were  $> 0.5 \text{ mg L}^{-1}$ (EU standard) and  $> 10 \text{ mg L}^{-1}$  according to IFC in all cases except for the three values measured in the Zharreza reservoir. The concentrations of Cr (VI), Pb<sup>2+</sup> and Cd<sup>2+</sup> were higher than three references, and especially  $Cd^{2+}$  and  $Pb^{2+}$  were up to 20 times more than the standard. Also the concentrations of  $Cu^{2+}$  and  $Ni^{2+}$ were higher, according to IFC both upstream and downstream of Seman River as well as in the drainage channel.

**Keywords:** Seman River, chemical water parameters, EU standards, WHO standards, IFC standards.

### 1. Introduction

Environmental hazard of pollutants depends on the source, nature of the pollutant, transfer route, exposed compartment and biological targets (Kahru & Põllumaa, 2006). A number of studies show that natural factors and human activities with significant effects on the environmental concerns of aquatic and terrestrial ecosystems are often identified as: (i) bare soil erosion, (ii) runoff and infiltration from landfills, waste treatment

sites, operational mines and oil extraction fields, (iii) industrial wastewater effluents (iv) a gricultural activities and (v) overflow from combined and sanitary sewers (Carpenter et al., 1998; Richard et al, 2006; Howarth et al., 2000; Smith, 2003; Galloway and Cowling, 2002). In general, environmental risk assessment is performed by chemical measurement of some major hazardous pollutants (heavy metals, polyaromatic hydrocarbons, petroleum products) or integrated parameters (biological requirements of oxygen (BOD), chemical oxygen demand (COD), total nitrogen, total phosphorus). They are determined by polluted water or soil to compare with the level of permitted values, set by local and international legislation. Among the substances that rank at the top of the pyramid of pollutants in terms of hazard and toxicity to aquatic fauna and humans are those from oil exploitation. The contamination from oil production activities includes several sources: drilling mud, oil leaks from wells and heavy oil (sludge) which requires deep treatment or use as second-hand fuel source (Wernersson, 2004). The environmental effects are caused mainly from polycyclic aromatic hydrocarbons (PAH), whose ecotoxicity has been observed in some plant and animal species, including cancer in humans (Pelletier et al., 1997, Sebastian et al., 2001 and Wernersson, 2003). Test performed with aromatic hydrocarbons (PAHs) indicate that often oil pollution is a major problem in relation to inland waters (Malik et al, 2004), and coastal areas and lagoons (Stelmaszewski 2009, Wu et.al. 2011). The mining and oil extraction activities in Albania are considered as highly polluting for surface waters not due to the toxic character of substances released into the water, but more so for the amount of direct spills in surface waters due to their poor management (Sulce et al, 2018, Como et al., 2013, Cullhaj et al., 2005). The oil extraction industry is concentrated in central and southern Albania, it has started about 100 years ago and today occupies an area of approximately  $5,400 \text{ km}^2$  (NSEoA, 2018-2030). This article presents the dynamics of pollutants in the surface waters of the Seman River, a reservoir and a main drainage channel of the field, which due to the terrain are considered hosts of surface drainage waters of the main oil extraction field in Albania.

#### 2. Materials and Methods

#### 2.1. Monitoring area

The monitored area is part of the middle watershed of the Seman River, it includes the Marines oil field of about 700 ha and with some 120 active wells. The studied water bodies included a segment in the middle course of the Seman River Marinëz (Sampling Stations-SS1 and SS2), a drainage channel into which all the surface water of the area is drained (Vija e Ngjalës-SS4) and a water irrigation reservoir (Rezervuari i Zharrezes-SS3), with a volume of 6 million m<sup>3</sup> which also collects the precipitation water as well as surface runoff water of a part of the oil extraction area (Figure 1). The mentioned water bodies provide water for irrigation for an area of about 10,000 ha of a gricultural land and more than 80,000 inhabitants are supplied with drinking water from groundwater sources in the area.



Figure 1. Sampling stations at Marinëz Oil Field Extraction in Albania

### 2.2. Stations and sampling period

Four monitoring stations were determined in the Marinëz oil filed extraction area: two in the Seman River at a distance of about 10 km from each other where the first is located before the river is affected by oil field extraction and the second after passing the oil field (thus affected by the oil extraction activities); the third in the Zharreza reservoir (within the oil extraction area) and the fourth in the main drainage canal. The water sampling were conducted in four seasons (spring, summer, autumn and winter) for a period of five years from 2014 to 2018.

## 2.3. Marinëz monitored parameters and analytical methods

Four water samples (pursuant the preselected sampling stations) were taken in four seasons, namely summer, autumn, winter and spring in 2014, 2015, 2016, 2017 and 2018. Samples were taken with plastic bottles of 1 L volume, at a depth of about 20 cm below the water surface and then stocked in freezer boxes at temperatures of about 4°C during the transport to laboratory. The parameters such as temperature, pH, dissolved oxygen, EC, salinity and turbidity were measured *in situ* (HANA multiprobe instrument). Analysis of the mineral forms of nitrogen and phosphorus (PO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>) were conducted based on the spectrometry method.

Determination of orthophosphate was according to a mmonium molybdate spectrometric method - ISO 6878: 2004. Determination of mineral nitrogen forms dissolved in water, was conducted based on the water quality determination of ammonium spectrometric method ISO 7150: 1984 (for amoniacal forms). Determination of nitrate with 2,6 -dimethyl phenol spectrometric method ISO 7890-1:1986. For DO and BOD is used the Winkler Method (EPA, USA), and for heavy metals (Cu, Ni, Pb, Cd) the method applied is spectrophotometry (Cu – Neokuproine, Ditizone-Pb). Chlorine is used spectrophotometry (APHA 4500- CL-E: 1992) and for totaloil grass is used EPA method 1664:2010 (extraction in hexane, slilcagel and gravimetric). Despite efforts for approximation of the environmental legislation with the EU, Albania does not have limit values for surface water parameters; therefore three standards approved as Directives or guidelines by the EU, WHO and IFC are taken as a reference for the water quality.

#### 3. Results and discussion

The results of the four sampling stations in the four seasons are expressed as the average value and standard deviation, as the minimum and maximum. Both minimum and maximum pH values, 6.1 and 8.61 respectively, were measured during the summer season in the first sampling point (SS1), while the temperature values ranged from 9.4 in winter at SS4 to 23.6 °C in summer at SS3 station. For the Disolved oxygen DO values ranged from 4.7 mg  $L^{-1}$  to 9.7 mg  $L^{-1}$ , while the minimum and maximum values of BOD5 and COD were found in the same season and at the same sampling point: the minimum values were 8 and 23 in autumn at SS1; the maximum values were 81 and 134 in winter SS2, respectively for BOD<sub>5</sub> and COD. The minimum value for the electrical conductivity was 109 mmhos cm<sup>-1</sup> in winter at SS4 and the maximum value was 895 mmhos cm<sup>-1</sup> in autumn at SS2, SS3, and SS4. The minimum and maximum values for TSS were 126 mg L<sup>-1</sup> in winter at SS3 to  $3120 \text{ mg L}^{-1}$  in autumn at SS2; for the dissolved Total–N values ranged from  $0.64 \text{ mg L}^{-1}$  to  $3.7 \text{ mg L}^{-1}$ ; for the dissolved Total-P the values raged from 0.12 mg L<sup>-1</sup> in winter at SS3 to 1.44 mg L<sup>-1</sup> in summer at SS4; and for Cl values ranged from  $9.2 \text{ mg L}^{-1}$  in summer at SS3 to 110.0 mg L<sup>-1</sup> in autumn at SS4. Total oil grass values ranged from 5.22 mg  $L^{-1}$  to 207.1 mg  $L^{-1}$  in spring at SS3 to summer at SS4 stations, respectively. The values of monitored heavy metals expressed in  $\mu g L^{-1}$  ranged between 0.09 - 1.87 for Cd<sup>2+</sup>; 0.06 - 0.11 for Cr (VI); 0.07 - 1.90 for  $Ni^{2+}$ ; 0.15 - 8.14 for  $Pb^{2+}$ ; and 0.05 - 0.80 for  $Cu^{2+}$ .













Figure 2. Box plot comparing the concentration distributions of monitored parameters at all sampling stations and seasons during the period 2014-2018, where DO-Dissolved Oxygen;  $BOD_5$  – Biological Oxygen Demand; COD – Chemical Oxygen Demand; EC – Electrical Conductivity; TSS – Total Suspended Solids and Cl - Chloride.













**Figure 3.** Box plot comparing the distributions in concentrations of parameters monitored at the sampling stations and seasons for the period 2014-2018, where: Total-N – all forms of nitrogen dissolved; Total-P – all forms of phosphorus dissolved; Ni<sup>2+</sup> – bication Nickel; Pb<sup>2+</sup> – bication Lead; Cd<sup>2+</sup> – bication Cadmium.

#### 4. Conclusions

The environmental quality of the surface waters flowing in the surroundings of the oil field in the central part of Albania (Marinëz) is influenced by oil extraction activities. The measured parameters clearly shows that the chemical qualities of water bodies are different depending on the degree of influence of urban wastewater and industrial spills in the Seman River, and accidental oil spills in the main drainage channel of the a gricultural field as well as the transport of pollutants in the Zharrez reservoir. The concentrations measured in the Seman River, especially downstream at the SS2 station, were high for TSS, DO, EC, Total-P, BOD<sub>5</sub>, COD, and very high for Total Oil & Grass and heavy metals (Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup> and Cr(VI) exceeding all three standards taken for comparison (EU, WHO and IFC) for surface water at oil extraction industry locations. There are two main factors influencing the water quality of Semani River, namely urban wastewaters (especially sewage) discharged into rivers without any treatment and the oil extraction industry in Zharrës-Marinëz. There is no exact contribution of pollution pursuant the origin of the pollutant from these two sources, but it appears that urban wastewater is more determinant than the impact from the oil field. The indicators categorize the quality of the river based on (EU directive 2000/60/EC) as ClassIII "satisfactory" for upstream and downstream, with the consistent conditions with the achievement specified for biological elements. The same parameters were found with deteriorating values in SS4 but with the exception of heavy metals, were close to the IFC standard for oil extraction fields. In the Zharrez reservoir the values were within the limit values of the EU, WHO and IFC with the exception of the values for Total-P, Cd<sup>2+</sup>, Pb<sup>2+</sup> and TOG especially in the winter season. Determination of hydrocarbon compounds in surface waters needs to be closely monitored in the future and further studies should engage in assessing the connection of their toxicity with aquatic biota.

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