# Assessment of the Variations in the Composition of the Leachate Generated in Open Dumps in Three Provinces of the Caspian Sea Region, Iran

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## ABSTRACT

**Background**: The municipal solid wastes (MSWs) are disposed in open dumps, which have no leachate collection and removal system, in the Caspian region of Iran. Leachate readily reaches the nearby water resources such as streams, rivers, lakes, and sea. Therefore, understanding the quality and quantity of open dump leachate is vital to the proper treatment of leachate.

**Methods:** The leachate samples from 18 open dumps were monitored and analyzed in terms of 21 different variables, namely pH, EC, temperature, TS, TSS, TDS, VSS, COD, $BOD_5$, $PO_4^{3-}$-P, $SO_4^{2-}$, $NH_4^+$-N, TKN, and $NO_3^-$-N based on the priority to analyze parameters as prescribed by accepted procedures outlined in “Standard Methods for Examination of Water and Wastewater”. Moreover, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, total Fe, $Mn^{2+}$ and $Zn^{2+}$ elements were determined using a Shimadzu flame atomic absorption spectrophotometer, Model 67OG.

**Results:** The mean values of parameters in the sites’ leachate samples of the three provinces were compared. The results of comparing the mean values of the parameters in the leachate samples from these provinces demonstrate that Golestan province had a significantly higher concentration of the parameters than Mazandaran and Gilan provinces.

**Conclusion:** These results may be due to the warmer weather conditions in Golestan province in comparison with other provinces. Furthermore, relatively low pH (6.15-6.90), high COD concentration (2607-25307 mg/l), high $BOD_5$/COD ratio (0.56-0.87), and high heavy metal concentration indicated that the open dumps were representative of the acid phase and/or the end of the acid phase and the beginning of the methanogenic phase.


**Keywords:** Caspian Region, Iran, Open Dump Leachate, Solid Waste Management.

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## INTRODUCTION

Nowadays, solid waste management is among the world’s most significant problems, especially in developing countries while municipal open dumps receive a mixture of household, commercial, and industrial waste [1, 2]. In most cities of developing countries, open dumps and simple landfills are common destinations for waste disposal, resulting in soil and water resource contamination by leachate [3-5]. In recent years, one of the important issues in the management of municipal solid waste (MSW) open dump is the management of leachate [6- 9]. Major environmental problems associated with open dumps are infiltration and migration of leachates into the surrounding environment, and subsequent contamination of the land and water [5,10]. Therefore, it is essential and useful to understand the quantity and composition of leachates for their proper treatment and to determine the effects of raw leachate pollution’s on the environment [3, 11,12]. Leachate is a type of wastewater that drains or “leaches” from a landfill. Leachate characteristics can fluctuate widely due to variables such as waste composition, temperature, moisture content, climatic changes and so forth [3, 13]. Landfill leachate contains high concentrations of organic matter (both biodegradable and non-biodegradable carbon), inorganic macrocomponents (cations and anions), heavy metals, and xenobioticorganic compounds [3, 5, 11,12].

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In Iran's Caspian Sea region, which includes Golestan, Mazandaran, and Gilan provinces, MSW has been a major environmental problem. In the cities of this region, MSWs are dumped in simple, uncontrolled open dumps near sea or surface waters, rivers, streams, and lakes. Furthermore, these open dumps lack leachate collection systems and the generated leachate migrates beyond the open dump site. Accordingly, the main objectives of this study were: a) to investigate the physicochemical composition of leachate samples in all 18 open dumps in Iran's Caspian Sea region; b) compare the mean values of various parameters in leachate samples from the three provinces of the Caspian Sea region; and c) examine relationships among different parameters in leachate samples.

## MATERIALS AND METHODS

### *Waste Management in the Caspian Sea Region of Iran*

In the Caspian Sea region, 7.2 million residents generate approximately 2450 tons/day of MSW. The generation rates of MSW in Golestan, Mazandaran, and Gilan provinces were 0.84, 0.76, and 0.64 kg/capita/day, respectively. Generally, average percentages of putrescible materials, paper, plastics, metals, textile, wood, glass and other items, in the Caspian Sea region were 77.74%, 8.43%, 7.61%, 0.89%, 0.47%, 0.96%, 0.91%, and 1.77% of MSWs, respectively. Generated MSW is disposed in simple, uncontrolled open dumps, with no management of sanitary conditions or treatment of leachate. Most of the open dumps are located near the sea, ground waters, and/or surface waters. Open dump locations are displayed in Figure 1. Hence, it is vital to understand the characteristics of open dump leachate for its proper treatment.

### *Sampling and Analytical Methods of Studying Leachate*

MSW leachate samples were collected from all 18 open dump sites of cities in the Caspian region of Iran in 2012 (Table 1 and Figure 1). In the field, all samples were stored in dark polyethylene bottles and kept in an ice chest. The collected samples were immediately transferred to laboratory and kept in a refrigerator at a temperature below 4°C until analysis [14]. Leachate samples were filtered through a 0.45μm pore membrane filter pending measurement. The parameters analyzed in this study included pH, EC (conductivity), TS (total solid), TSS (total suspended solid), TDS (total dissolved solid), VSS (volatile suspended solids), COD (chemical oxygen demand), $BOD_5$ (5 day-biological oxygen demand), $PO_4^{3-}$-P (phosphate), $SO_4^{2-}$ (sulfate), $NH_4^+$-N (ammonia nitrogen), TKN (total kjeldahl nitrogen), $NO_3^-$-N (nitrate), and metals including $Mg^{2+}$ (magnesium), $Mn^{2+}$ (manganese), $Na^+$ (sodium), $Ca^{2+}$ (calcium), $K^+$ (potassium), total Fe (iron), and $Zn^{2+}$ (zinc). All concentrations were expressed in mg/l, except for pH and EC (in mS/cm). In laboratory, the parameters of TS, TSS, TDS, VSS, COD, $BOD_5$, $PO_4^{3-}$-P, $SO_4^{2-}$, $NH_4^+$-N, TKN, and $NO_3^-$-N were analyzed without delay, based on the priority to analyze parameters as prescribed by accepted procedures outlined in "Standard Methods for Examination of Water and Wastewater" (APHA 1998). For analysis of metals, 50 mL of each sample was digested with the addition of 10 ml concentrated nitric acid and boiled for 60 minutes at 120˚C [15].

After digestion, the concentrations of $Mg^{2+}$, $Mn^{2+}$, $Na^+$, $Ca^{2+}$, $K^{2+}$, total Fe, and $Zn^{2+}$ were determined using a Shimadzu flame atomic absorption spectrophotometer, Model 67OG. The limit of detection (LOD) of these metals is presented in Table 2. The purity of reagents and the presence of possible contaminants were determined with one blank for each set of 5-6 samples, using the same procedure utilized for the samples. Contaminants were determined to be less than 5% of each metal determined in the samples. The recoveries were calculated by the analysis of a known standard sample prepared from the metals in dematerialized, distilled water, and subjected to the same process as the sample. This step determined the recoveries for different metals in this method. Overall, recoveries obtained were greater than 90% in all heavy metals.

**Table 1.** Location of sites for leachate sampling and leachate solid waste management.

| Sampling site | Name of the county | Location | Leachate solid waste management |
|---|---|---|---|
| 1 | Astara | 38° 20′ 59.3″N, 48° 51′ 57.4″E | Uncontrolled and discharged into the surface water and groundwater |
| 2 | Talesh | 37° 50′ 35.1″N, 48° 58′ 08″E | Uncontrolled and discharged into the sea |
| 3 | Anzali | 37° 30′ 17.7″N, 49° 20′ 51.8″E | Uncontrolled and discharged into the surface water and groundwater |
| 4 | Rasht | 37° 04′ 10.2″N, 49° 37′ 56.1″E | Uncontrolled and discharged into the surface water and groundwater |
| 5 | Langaroud | 37° 10′ 48.5″N, 50° 09′ 33.3″E | Uncontrolled and discharged into the sea |
| 6 | Roudsar | 37°07′ 58.3″N, 50° 18′ 58.18″E | Uncontrolled and discharged into the surface water and groundwater |
| 7 | Ramsar | 36° 50′ 36.8″N, 50° 34′ 45.9″E | Uncontrolled and discharged into the surface water and groundwater |
| 8 | Tonekabon | 36° 41′54.7″N, 50° 49′ 01.7″E | Uncontrolled and discharged into the surface water and groundwater |
| 9 | Nowshahr | 36° 36′ 54″N, 51° 30′ 58.2″E | Uncontrolled and discharged into the surface water and groundwater |
| 10 | Noor | 36° 28′ 41.5″N, 52° 03′ 40.2″E | Uncontrolled and discharged into the surface water and groundwater |
| 11 | Frydoonkenar | 36° 40′ 53.3″N, 52° 29′ 06.6″E | Uncontrolled and discharged into the sea |
| 12 | Babolsar | 36° 42′ 05.2″N, 52° 36′ 56.1″E | Uncontrolled and discharged into the sea |
| 13 | Babol | 36° 18′ 18.4″N, 52° 41′ 49.6″E | Uncontrolled and discharged into the surface water and groundwater |
| 14 | Ghaemshahr | 36° 29′ 22.4″N, 52° 49′ 09″E | Uncontrolled and discharged into the surface water and groundwater |
| 15 | Neka | 36° 36′ 43.6″N, 53° 20′ 57.9″E | Uncontrolled and discharged into the surrounding environment |
| 16 | Behshahr | 36° 41′ 15.7″N, 53° 34′ 39.6″E | Uncontrolled and discharged into the surrounding environment |
| 17 | Galugah | 36° 43′ 11.8″N, 53° 50′ 25.5″E | Uncontrolled and discharged into the surrounding environment |
| 18 | Gorgan | 37° 09′ 36.2″N, 54° 26′ 24″E | Uncontrolled and discharged into the surrounding environment |

**Table 2.** Composition of municipal open dump leachate from 18 open dumpsites in the Caspian region of Iran.

| Parameter | Unit | Detection limit | Minimum | Maximum | Average | RSD% | Duncan's test |
|---|---|---|---|---|---|---|---|
| pH | | | 6.15 | 6.90 | 6.56 | 1.83 | _c |
| EC | mS/cm | 1 | 6.13 | 42 | 20 | 63 | 3>2; 3>1 |
| Temp | °C | | 28 | 34 | 32 | 6.25 | - |
| TS | mg/l | 1 | 5383 | 29444 | 14663 | 58 | 3>2; 3>1 |
| TSS | mg/l | 1 | 845 | 3489 | 1687 | 45 | 3>2; 3>1 |
| TDS | mg/l | 1 | 4109 | 27502 | 12976 | 63 | 3>2; 3>1 |
| VSS | mg/l | 1 | 308 | 1212 | 606 | 44 | 3>2; 3>1 |
| $BOD_5$ | mg $O_2$/l | 3 | 1817 | 19667 | 7739 | 78 | _c |
| COD | mg $O_2$/l | 10 | 2607 | 25307 | 10374 | 69 | _c |
| $BOD_5$/COD | | | 0.56 | 0.87 | 0.71 | 13 | - |
| $PO_4^{3-}$-N | mg/l | 0.002 | 9 | 127 | 38 | 67 | _c |
| $SO_4^{2-}$ | mg/l | 1 | 50 | 202 | 83 | 48 | _c |
| $NH_4^+$-N | mg/l | 0.01 | 230 | 3490 | 1586 | 58 | _c |
| TKN | mg/l | 0.15 | 455 | 6785 | 2108 | 69 | _c |
| $NO_3^-$-N | mg/l | 0.01 | 10 | 48 | 19 | 53 | _c |
| $Mg^{2+}$ | mg/l | 0.10 | 29 | 762 | 213 | 73 | 3>2; 3>1 |
| $Na^+$ | mg/l | 0.50 | 875 | 4380 | 2150 | 45 | 3>2; 3>1 |
| $K^+$ | mg/l | 0.40 | 525 | 4047 | 1765 | 53 | 3>2; 3>1 |
| $Ca^{2+}$ | mg/l | 0.02 | 23 | 400 | 143 | 88 | _c |
| Total Fe | mg/l | 0.05 | 5 | 202 | 46 | 116 | _c |
| $Mn^{2+}$ | mg/l | 0.05 | 0.16 | 9.34 | 2.35 | 107 | _c |
| $Zn^{2+}$ | mg/l | 0.02 | 0.15 | 2.79 | 1.18 | 76 | 3>1>2 |

1: Gilan province, 2: Mazandaran province, 3: Golestan province

## Statistical Analysis

The descriptive statistical parameters were performed using SPSS 17.0 and Excel 2007. Prior to analysis, data were inspected for normality and homogeneity of variance through Shapiro-Wilk's test and Levene's test, respectively. The mean values of different parameters in leachate samples of the three provinces were compared by one-way analysis of variance (ANOVA), separating the different means through Duncan's tests. Multivariate Pearson's correlation analysis was used to examine the relationships between different parameters. In all tests, the level of significance was set at $P<0.05$.

## RESULTS

In this study, leachate compositions were investigated at 18 municipal open dumps along southern coastline of the Caspian Sea. The results of physicochemical characteristics of the leachate samples are presented in Table 2. Table 2 shows that pH values from the leachate samples from the 18 open dumps ranged from 6.15 to 6.90 with no statistically significant difference among them. Also, as shown in Table 2, the average values for EC were relatively high, ranging from 6.13 and 42 mS/cm in the open dump sites. The concentrations of TS, TDS, TSS, and VSS varied between 5383 and 29444 mg/l with an average value of 14663 mg/l, 4109 and 27502 mg/l with an average value of 12976 mg/l, 845 and 3489 mg/l with an average value of 1687 mg/l, and 308 and 1212 mg/l with an average value of 606 mg/l, respectively (Table 2).

The $BOD_5$ and COD values of leachate samples from the open dumps ranged from 1817 to 19667 mg/l with an average value of 7739 mg/l, and from 2607 to 25307 mg/l with an average value of 10374 mg/l, respectively (Table 2). As it is shown in Table 2, phosphate and sulfate values fluctuated between 9 and 127 mg/l with an average value of 38 mg/l and between 20 and 202 mg/l with an average value of 83 mg/l, respectively. The concentrations of TKN, $NH_4^+$-N, and $NO_3^-$-N in this study varied between 455 and 6785 mg/l, with an average value of 2108 mg/l, 230 to 3490 mg/l with an average value of 1586 mg/l, and 10 to 48 mg/l, respectively (Table 2). Table 2 displays the concentrations of cations in the leachate samples from the open dumps ranging from 29 to 762 mg/l for $Mg^{2+}$, 875 to 4380 mg/l for $Na^+$, 525 to 4047 mg/l for $K^+$, and 23 to 400 mg/l for $Ca^{2+}$. Total Fe concentrations ranged from 5 to 202 mg/l with a high average value of 46 mg/l. Table 2 shows that $Mn^{2+}$ and $Zn^{2+}$ in the leachate samples varied between 0.16 and 9.34 mg/l and 0.15 and 2.79 mg/l, respectively.

The results of the comparison of different parameters in leachate samples from the three provinces are shown in Table 2. Table 3 shows the comparison of the results of this study with parameters previously identified as characteristic for the acid and methanogenic transformation phases of municipal open dumps. Moreover, the results of Multivariate Pearson's correlation analysis of the different parameters are shown in Table 4.

**Table 3.** Comparison of variable parameters in leachate samples.

| Parameter | Acid phase | | Methanogenic phase | | This study | |
|---|---|---|---|---|---|---|
| | Average | Range | Average | Range | Average | Range |
| pH | 6.10 | 4.5–7.5 | 8 | 7.5-9 | 6.56 | 6.15-6.90 |
| $BOD_5$ | 13000 | 4000-40000 | 180 | 20-550 | 7739 | 1817-19667 |
| COD | 22000 | 6000-60000 | 3000 | 500-4500 | 10374 | 2607-25307 |
| $BOD_5$/COD | 0.58 | | 0.06 | | 0.71 | |
| $SO_4^{2-}$ | 500 | 70-1750 | 80 | 10-420 | 83 | 50-202 |
| $Mg^{2+}$ | 470 | 50-1150 | 180 | 40-350 | 213 | 29-762 |
| $Ca^{2+}$ | 1200 | 10-2500 | 60 | 20-600 | 143 | 23-400 |
| Total Fe | 780 | 20-2100 | 15 | 3-280 | 46 | 5-202 |
| $Mn^{2+}$ | 25 | 0.3-65 | 0.7 | 0.03-45 | 2.35 | 0.16-9.34 |
| $Zn^{2+}$ | 5 | 0.1-120 | 0.6 | 0.03-4 | 1.18 | 0.15-2.79 |

**Table 4.** Pearson correlation coefficients of chemical contents.

| | pH | EC | TS | TSS | TDS | VSS | $BOD_5$ | COD | $PO_4^{3-}$-p | $SO_4^{2-}$ | $NO_3^-$-N | $NH_4^+$-N | TKN |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | 1 | -0.47 | -0.29 | -0.24 | -0.41 | -0.11 | -0.65* | -0.56* | 0.27 | 0.09 | 0.26 | 0.15 | 0.42 |
| EC | | 1 | 0.98** | 0.35 | 0.99** | 0.22 | 0.73** | 0.69** | 0.18 | 0.43 | -0.23 | 0.42 | 0.26 |
| TS | | | 1 | 0.46 | 0.99** | 0.29 | 0.72** | 0.7** | -0.12 | 0.49 | -0.2 | 0.4 | 0.2 |
| TSS | | | | 1 | 0.39 | 0.91** | 0.41 | 0.45 | 0.06 | 0.43 | 0.3 | 0.09 | 0.09 |
| TDS | | | | | 1 | 0.22 | 0.71** | 0.68** | -0.13 | 0.47 | -0.24 | 0.41 | 0.25 |
| VSS | | | | | | 1 | 0.34 | 0.39 | 0.02 | 0.46 | 0.31 | -0.01 | -0.01 |
| $BOD_5$ | | | | | | | 1 | 0.99** | -0.18 | 0.04 | -0.01 | 0.38 | 0.12 |
| COD | | | | | | | | 1 | -0.16 | 0.01 | 0.05 | 0.4 | 0.19 |
| $PO_4^{3-}$-P | | | | | | | | | 1 | 0.18 | 0.27 | -0.08 | -0.03 |
| $SO_4^{2-}$ | | | | | | | | | | 1 | -0.11 | -0.03 | -0.14 |
| $NO_3^-$-N | | | | | | | | | | | 1 | -0.29 | 0.14 |
| $NH_4^+$-N | | | | | | | | | | | | 1 | 0.66** |
| TKN | | | | | | | | | | | | | 1 |

## DISCUSSION

Landfill leachate commonly contains heavy metals, organic matter, and inorganic ions, such as ammonium, phosphate, and sulfate [16, 17]. Physicochemical composition of leachate depends primarily on the waste composition and water content in total waste [3, 16]. Extensive research on the quality of leachates produced from landfills has been reported in the literature [3, 18-21].

Results in Table 2 show that the variation in pH value is mainly attributed to the type of biological decomposition of the wastes and dilution effects [13]. The results of EC (Table 2) show that the high values of EC are attributable to high levels of anions and cations in the samples. Generally, EC is used as an indicator of the presence of dissolved inorganic compounds or total concentration of ions [3, 6, 22]. As Tables 2 illustrates, the high values of TS, TDS, TSS, and VSS indicate that all open dump leachates in this study could be undergoing biodegradation, thereby increasing the solids [23].

The results from Duncan's test, also detailed in Table 2, demonstrate similar trends for TS, TDS, TSS, and VSS. This means that TS, TDS, TSS, and VSS values of leachate samples from Golestan province were statistically higher than those from Mazandaran and Gilan provinces. However, there were no statistically significant differences among TS, TDS, TSS, and VSS values between Mazandaran and Gilan provinces. These results may be due to weather conditions and the climate specific to Golestan province compared to Mazandaran and Gilan provinces [3, 24].

As it is shown in Table 2, even though the means of $BOD_5$ and COD values of leachate samples in different cities of the Caspian Sea region have fluctuated widely, BOD and COD values in the three provinces had not reached a statistically significant level (Table 2). This finding indicated the presence of high organic matters in the waste [5, 25]. Meanwhile, the ratio for $BOD_5$/COD in leachate samples was between 0.56 and 0.87 with an average value of 0.71. The $BOD_5$/COD ratio is commonly known as the degree of biodegradability of organics in leachate. This indicates that the majority of the organic compounds present are biodegradable [5, 26, 27].

These high phosphate values in different open dumps' leachate may be due to the organic load of the refuse that contains phosphorus; this organic material (mainly phospholipids and phosphoproteins) during its biodegradation releases phosphorus and, eventually, increases phosphate concentrations [10]. The high value of sulfate can be due to the presence of domestic waste in open dumpsites [5]. Moreover, the highest TKN content was found to be in ammoniacal form. Ammonia nitrogen can have a negative environmental impact, and it is known as one of the major toxicants to living organisms [6,10, 26]. Given the nitrogenous compounds, ammonia nitrogen was present in high concentrations. This can result from the deamination of amino acids during the destruction of organic compounds [6, 27, 28]. As shown in Table 2, similar findings were observed in Duncan's test for $BOD_5$, COD, phosphate, sulfate, TKN, $NH_4^+$-N, and $NO_3^-$-N. This indicated that the mentioned factors in the three provinces of Caspian region had not reached a statistically significant level. This can be due to the presence of high values and the similarities among putrescible wastes in all open dumps of Golestan, Mazandaran, and Gilan provinces.

The high values of cations in all leachate samples indicated that the possible sources of cations include domestic waste and industrial waste, such as cosmetics, cement, and textile, were being dumped in the open dump [3-13]. As it is shown in Table 2, mean concentrations of $Mg^2$, $Na^+$, and $K^+$ in Golestan province were higher than those of Gilan and Mazandaran provinces, while Gilan and Mazandaran provinces had not reached a statistically significant level. These results show higher concentrations of cations possibly due to higher evaporation effect under warmer weather of Golestan province than Gilan and Mazandaran provinces.

The results of high concentrations of total Fe indicated that the open dumps received waste iron, steel materials, and tin-based garbage (Table 2). Iron is a metal common to MSW leachate. Its presence in high concentrations gives the leachate a dark brown color [3, 6, 29]. Results shown in Table 2 demonstrate that the presence of $Mn^{2+}$ in the leachate samples can be caused by the presence of industrial waste in the open dump. High $Mn^{2+}$ concentrations suggest a strong reducing environment [5]. $Zn^{2+}$ concentrations ranged from 0.15 to 2.79 mg/l with an average value of 1.18 mg/l (Table 2). This implies that the open dump receives waste from batteries and fluorescent lamps, raising concerns for plant and aquatic life [3, 6, 30]. As shown in Table 2, mean total Fe and $Mn^{2+}$ values of leachate in the three provinces were not significantly different, and the sequence of Zn was Golestan > Gilan > Mazandaran.

Table 3 compares the results of this study with parameters previously identified as characteristic for the acid and methanogenic transformation phases of municipal open dumps. This indicates that the leachate samples collected from open dumps represent the acid phase and/or the end of the acid phase and the beginning of the methanogenic phase [17, 26-28]. Generally, high COD (2607-25307 mg/L), high $BOD_5$ (1817-19667 mg/L), and high $BOD_5$/COD ratios (0.71) are characteristic of all leachate samples from young open dumps, indicating a lack of proper management of municipal solid waste [27, 28].

Correlational analysis is a preliminary descriptive technique to evaluate the strength of the relations between variables [11]. Thus, Multivariate Pearson Analysis was subsequently performed to determine the possible relationships between the parameters analyzed in this study. Results shown in Table 4 indicate that pH was negatively correlated with BOD5 and COD while EC was positively correlated with TS, TDS, BOD5, and COD. Moreover, TS was positively correlated with TDS, BOD5, and COD, TSS was positively correlated with VSS. In addition, TDS was positively correlated with BOD5 and COD and BOD5 was positively correlated with COD. There were also positive correlations between $NH4^+$-N and TKN. Therefore, these relationships may provide useful means to determine the parameters for easier analysis and prediction of other important pollution parameters for Pearson analysis and to design or control a leachate treatment plant more easily.

## CONCLUSION

This study is the first investigation of physicochemical composition in leachate samples of all open dumps in Iran's Caspian Sea region. The research findings revealed high concentrations of physicochemical compositions in leachate samples from 18 municipal open dump sites of the cities there. Comparison of mean values of parameters in these leachate samples shows that Golestan province had a statistically significant higher concentration of more varied parameters than Mazandaran or Gilan provinces. In addition, the relatively low pH and high values of COD, $BOD_5$, $BOD_5$/COD ratio, and heavy metals concentrations characterize all leachate samples from young open dumps, presumably due to a lack of proper management of municipal solid waste in Iran's Caspian Sea region.


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