Influence of Air Pollution on Chemical Quality of Wet Atmospheric Deposition: a Case Study in Urmia, Iran

Yaghoub Hajizadeh[1], Sepideh Nemati[2], Ali Ahmad Aghapour[2], Ali Abdolahnejad[3], Amir Mohammadi*[3], Hussein Panahi[4], Saeed Mousavi Moghanjooghi [5], Ali Nikoonahad[3]

1) *Department of environmental health engineering, Faculty of health, Isfahan University of Medical Sciences, Isfahan, Iran*
2) *Department of Environmental Health Engineering, School of Health, Urmia University of Medical Sciences, Urmia, Iran*
3) *Research Committee, School of Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran*
4) *Urmia municipality, Urmia, Iran*
5) *Environmental Research Center of West Azerbaijan, Urmia, Iran*

**Author for Correspondence: mohammadiurm@gmail.com*

Received: 26 Jan. 2017, Revised: 5Mar.2017, Accepted: 18 May 2017

ABSTRACT

Increased combustion of fossil fuel owing to the energy requirement is a main cause of air pollution throughout the world. Atmospheric precipitation is considered as a major water resource for indoor, municipal, industrial and agricultural uses. This study was aimed to evaluate the effect of air pollution on chemical quality of rain and snow in Urmia, a city in northwest of Iran.

Sampling was performed during the wet seasons from October to March at six sampling stations in different locations of the city. Acidity, alkalinity, NO_3^-, SO_4^{2-}, Cl^- and pH contents of the collected samples were analyzed.

All samples showed a pH value of more than 6.8, and lower acidity than alkalinity, therefore, the precipitations were not acidic. Maximum concentrations of SO_4^{2-} and NO_3^- in the samples were 5 and 8.8mg/L, respectively. Chloride was varied from 1 to 11.5 mg/L with the highest measures observing in autumn.

According to the results, concentrations of the analyzed parameters in wet precipitations in Urmia were within the natural ranges except chloride ions, which was higher than its common level in the atmosphere. This phenomenon may be the result of desert dusts which transfers by wind from the west border to Iran.

Key words: Atmospheric precipitation; Chemical quality; air pollution; Urmia

INTRODUCTION

Rapid population growth and increased vehicles, factories and industries have resulted in air pollution problems throughout Iran, especially, in its large cities such as Urmia, a 10th most populous city, located in northwest of Iran [1, 2]. Acid precipitations including acid rain, acidic snow and dust are the most frequent and concerning pollutants from the city. The pH of acid precipitations is lower than 5.5 because of air pollution. Major precursors for acid rain formation are NO_2 and SO_2 which are released to the atmosphere mainly by fossil fuel and waste combustion, and industrial activities [3]. Global deposition of sulfur and nitrogen are generally high near emission sources and very low in areas largely free of anthropogenic influences [4]. Acidic deposition can also happen through natural sources such as volcanoes eruption. When these pollutants are released to the atmosphere, they disperse over large areas and react with water, oxygen, and other gases to form fine droplets of sulfuric acid, ammonium nitrate, and nitric acid. These in turn adhere to the rain, snow or particulate maters to form wet or solid depositions [5, 6]. In recent years, acidic depositions were frequently observed in northeastern of the United States, southeastern of Canada, and much of Europe including portions of Sweden, Norway, and Germany. In total, parts of South Asia, South Africa, Sri Lanka, and Southern India are in risk of being impacted by acid deposition in the future [3, 7-9]. Anthropogenic emissions of acid precipitation precursors were increased from 2010 in Northwestern of Iran including Urmia. The main sources of these pollutants attributed to vehicles, inversion and fuel combustion in residential areas. Also, vehicles to population ratio in Urmia were reported to be 0.3, which is 1.5 time higher than the Iran's average [10-12].

Acid deposition reduces the pH of clay soils leading to release of metals such as aluminum and magnesium. Further lowering of pH in some areas disrupts soil nutrients, kills microorganisms and can cause calcium deficiency. If the pH of a lake drops below 4.8 by acidic precipitations, its plants and animals are faced with risk of death [5, 13].Due to ability of destroying materials, acid rain has impact

on buildings, art, cars, railroad tracks, airplanes, steel bridges, and pipes network above and below ground. All types of acid precipitations are harmful for human health as well [3].

Most studies on acid deposition have only focused on its potential of pH reduction. However, to investigate its further effects on the environment and to achieve more accurate results, it is necessary to examine chemical characteristics of the acid deposition such as predominant anions, alkalinity and acidity [14]. There are alkaline compounds such as limestone ($CaCO_3$ or CaO) in airborne dust. Due to the neutralizing capacity of these compounds existed in the high level of atmospheric dust; reduction of the precipitation pH can be significantly compensated. Acid rain has adverse health effects to human and other living organisms [8]. It can lead to acidification of surface waters and soils. Acid precipitation can damage trees by increasing the solubility of toxic metals such as aluminum and by nutrient deficiency [15]. The main sources of dust in the air include windblown dust from deserts and seas, volcanic activity, industrial activity and construction [8]. The main goal of this study was to investigate the chemical quality of rain and snow in Urmia.

MATERIALS AND METHODS

Study Area

This cross sectional study was conducted from October 2014 to March 2015 by collecting and analyzing of rain and snow samples from different regions of Urmia and comparing them with the air quality data at the same time, which was obtained from Urmia department of the environment Urmia have 100 Km^2 area and placed in Northwest of Iran in longitude of 45 00′ to 45 07′ E and latitude of 37 29′ to 37 34′N. This city has arid-cold winters, mild springs, hot dry summers and warm autumn's climate. Due to centralization of precipitation in autumn and winter, the sampling was done in these seasons. Fig. 1 shows the location of the precipitations sampling points (S1 to S6) and the position of online air quality monitoring stations (A1 and A2).

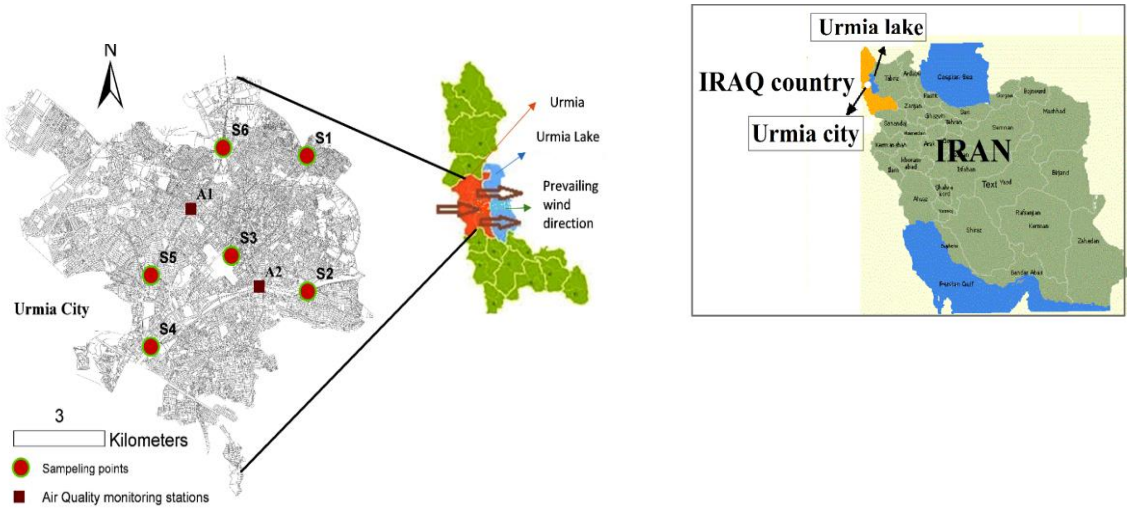

Fig. 1: Geographical location and map of the Urmia city, prevailing wind direction, precipitation sampling points (S1 - S6) and location of air quality monitoring stations)

Sampling Methods

Throughout the city 6 sampling points were selected in such a way that covered all area of the city. Samples were collected by glass jar. All of the jars were washed with cleaning acid (H_2SO_4, 10%), then by tap water and rinsed by deionized water. Sampling jars were placed in the open area and on a stand having 2 meters height from the ground. All samples were stored in temperature below $4^{\circ C}$ and analyzed within 24 hours.

Experiments

The pH of the samples was measured in the field at sampling time by a portable pH meter (WTW 3110). The concentration of SO_4^{2-}, NO_3^- , Cl^-, acidity and alkalinity were analyzed according to the standard methods for examination of water and wastewater 2005 (2320B, 2310 B and 4500Cl–B) in the water and wastewater laboratory of faculty of public health in Urmia. All the experiments were conducted in triplicate, at room temperature ($20 \pm 2^{\circ C}$), and the average of the results was reported.

Statistical Analyses

Arc GIS software version 10. 1 and inverse distance weighting (IDW) was applied for zoning and concentration distribution of the analyzed parameters. SPSS v.16.0 was used for the statistical analyses of the data. One-way ANOVA was used to determine

seasonal differences for SO_4^{2-}, NO_3^-, Cl^- and pH. A statistical significance level of $\alpha = 0.05$ was used throughout the study.

RESULTS

The results of precipitation quality showed that maximum SO_4^{2-}, NO_3^- concentrations in the rain or snow samples were 8.8 and 5mg/L, respectively (Table 1). The 24 hours averages of SO_2 and NO_x (NO and NO_2) concentrations in the ambient air analyzed before precipitation are given in Table 2. Those values in station A1 were higher than station A2. Based on table 1 and Figs. 2 and 3 the pH, alkalinity and acidity values of the sampled precipitations did not show a tendency to acidic condition. Anions variation patterns in different sampling points are presented in Figs. 4-6. Based on the results of ANOVA, there was no significant difference for SO_4^{2-}, NO_3^- and Cl^- values in autumn and winter ($\alpha < 0.05$), and significant difference for pH values in autumn and winter.

Table 1: Some physico-chemical characteristics of rain and snow water at the autumn and winter in Urmia

Season	Samples	SO_4^{2-} (ppm)	NO_3^- (ppm)	Cl^- (ppm)	pH	Alkalinity (mg/l $CaCO_3$)	Acidity (mg/l $CaCO_3$)
Rain water (Autumn)	S1	N.D*	N.D	1.0	7.6	10.0	8.0
	S2	3.0	0.6	11.5	6.7	6.0	8.0
	S3	3.0	5.0	2.0	7.2	14.0	6.0
	S4	N.D	N.D	2.5	7.2	14.0	10.0
	S5	3.0	0.4	9.5	7.1	10.0	8.0
	S6	5.0	1.4	2.5	6.8	6.0	4.0
Average		3.5	1.9	4.8	7.1	10.0	7.3
Snow water (Winter)	S1	1.0	0.7	4.5	7.3	12.0	4.0
	S2	N.D	N.D	2.5	8.1	16.0	5.0
	S3	1.0	8.7	3.5	7.9	14.0	6.0
	S4	N.D	N.D	2.5	7.7	10.0	4.0
	S5	2.0	0.3	3.5	7.2	18.0	12.0
	S6	0.9	8.8	3.0	8.0	18.0	10.0
Average		1.2	4.6	3.3	7.7	14.7	6.8

*Not detected

Table 2. Average 24 hour NOx and SO_2 concentrations in Urmia air quality monitoring stations before snowing

Station	A1		A2	
Season	Autumn	winter	Autumn	Winter
NO_x (ppb)	379	338	43	50
SO_2 (ppb)	31	14	54	18

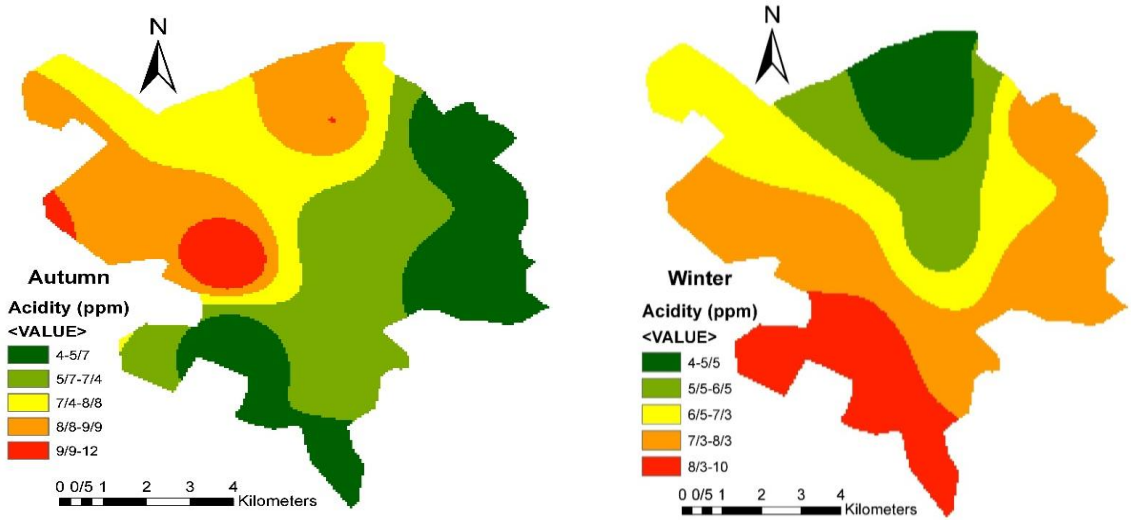

Fig. 2: Mapping of acidity levels (mg/L $CaCO_3$) in wet precipitation samples taken from study area in autumn and winter 2014-2015

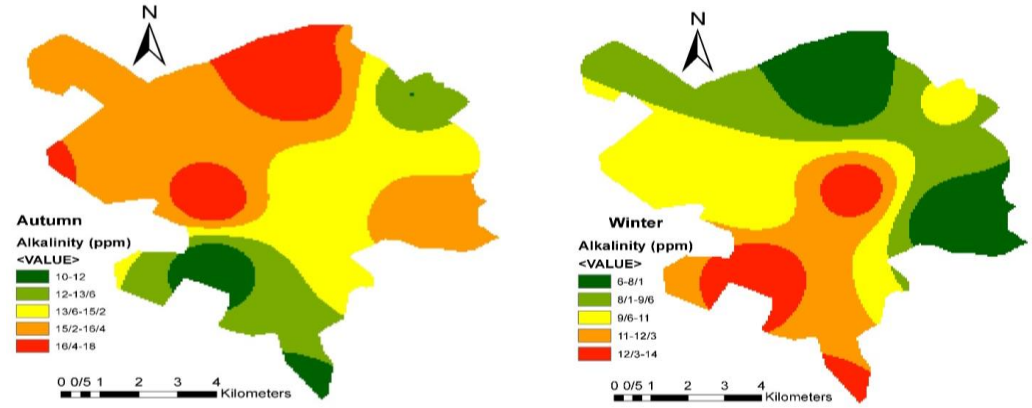

Fig. 3. Mapping of alkalinity levels (mg/L $CaCO_3$) in wet precipitation samples taken from study area in autumn and winter 2014-2015

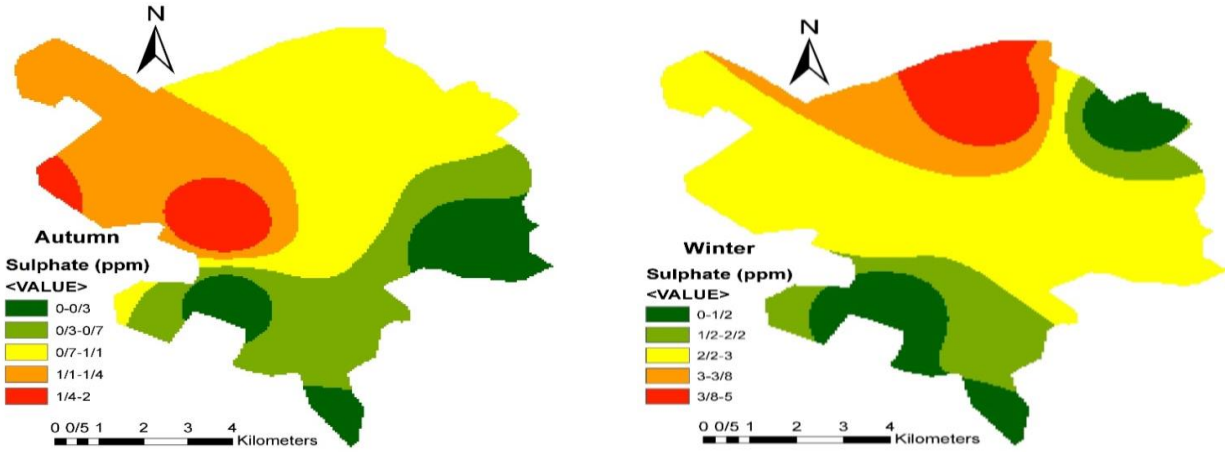

Fig. 4. Mapping of sulphate concentrations (mg/L) in wet precipitation samples taken from study area in autumn and winter 2014-2015

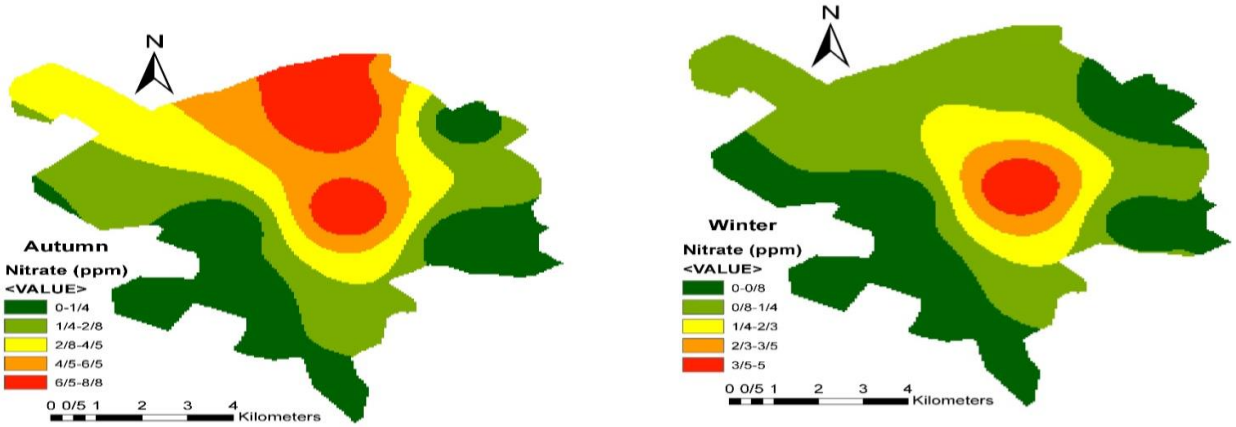

Fig. 5. Mapping of nitrate concentrations (mg/L) in wet precipitation samples taken from study area in autumn and winter 2014-2015

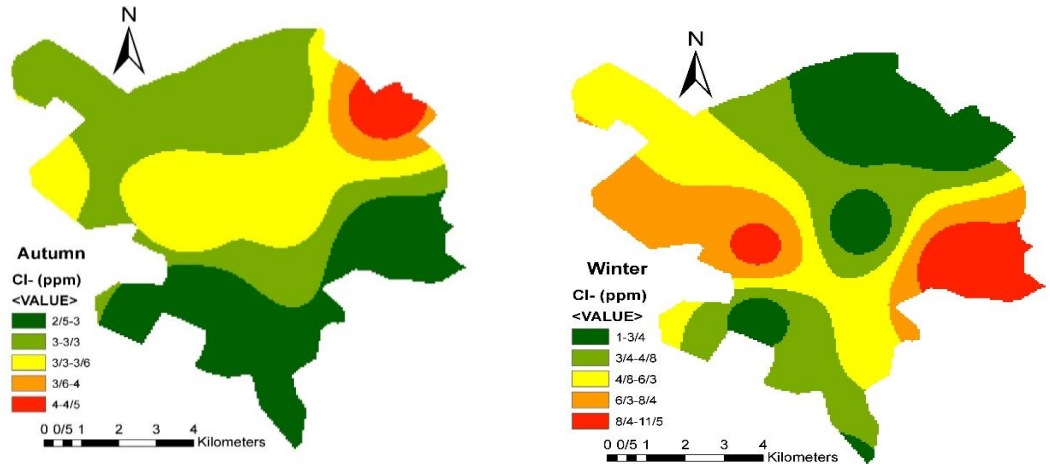

Fig. 6: Mapping of chloride concentrations (mg/L) in wet precipitation samples taken from study area in autumn and winter 2014-2015

DISCUSSION

According to the results, the pH of all collected samples from wet depositions in the city were not in acidic ranges, e. g. the lowest values of pH in the autumn and winter were 6.8 and 7.2, respectively. This could be attributed in one hand to the high neutralization capacity of the precipitants, and on the other hand the presence of lower concentration of gaseous precursors for acid formation in the atmosphere. Whereas, in Tehran, the capital city of Iran, the pH of rains was between 4.2 and 7.1 in 2013, in which a main cause of this has been reported to be emission from vehicles [16].

Alkalinity in the atmospheric precipitation can be formed from $CaCO_3$ which may have natural or anthropogenic origin. Such alkaline can neutralize much of the acidity from the SO_2 by forming neutral $CaSO_4$ in the atmosphere [8]. Alkalinity and acidity of water are depended on pH values. As presented in Table 1 and mapped in Fig. 2 and 3 the average acidity of rain water and snow water are less than that of alkalinity, so that, atmospheric precipitations in Urmia were not acidic. The majority of acidic deposition is produced from SO_2 and NO_x which are mainly emitted to the atmosphere via fossil fuel combustion. These pollutants in turn, take part in further oxidation reaction in the presence of atmospheric oxygen and are converted to H_2SO_4 and HNO_3 reducing the pH of precipitations [3, 5].

A maximum concentration of SO_4^{2-} ions in rain and snow water was 5mg/L (table 1). According to Fig. 4, the amount of SO_4^{2-} in autumn was more than that in winter. This may be in part due to more pollutants release from industrial activities and more frequency of heavy traffic occurrence in autumn than winter. Also the role of limited precipitation in autumn compared to winter could be taken into account, which causes more accumulation and increased residence time of the pollutants in the atmosphere. In comparison, the SO_4^{2-} concentrations of 6.4 to 35mg/L has been reported in Tehran [17].

The maximum concentration of NO_3^- in Urmia in the study period was 8.8 mg/L. According to the reports of the department of environment, north-west Azerbaijan, in the online air quality monitoring stations, NO_x concentration was more in winter than in autumn (Table 2). As Fig. 5 shows maximum amounts of NO_3^- in the rain and snow water were measured in winter. This could be attributed to the high NO_x emission in winter due to more natural gas burning for indoor heating in the city. In Tehran, the NO_3^- concentration of rain water has been reported to be between 3.5 and 14mg/L which is much higher than our study [17].

Chloride concentrations of the rain and snow water were in ranges of 1 - 11.5mg/L. The highest value was obtained in autumn amounting 11.5 mg/L, whereas, its maximum amount in winter reached to 4.5mg/L (Fig. 6). A major origin of Cl^- anion in the atmosphere is natural sources (e.g., sea sprays and windblown dust from the desert). According to reports of west Azerbaijan metrological office, prevailing wind direction in Urmia is from west to east (Fig. 1) [18-19]. Thus, salt sprays from Urmia Lake cannot considerably affect the city. However, dust transportation by desert storms from west borders of Iran to Urmia is a common threat. It contains a high amount of chloride which can transfer to the atmospheric depositions.

Analysis of variance did not show a significant difference for SO_4^{2-}, NO_3^- and Cl^- values in different seasons ($\alpha < 0.05$). This may be related to their same sources of emission in two seasons. For SO_4^{2-} and

NO_3^- anthropogenic activity and for Cl^- desert storms from west borders of Iran were reported to be the main sources of emission in Urmia.

CONCLUSION

This study showed that the chemical quality of precipitation in Urmia lies within the natural range. Rain and snow water was not acidic. However, there was a high concentration of chloride in all of the atmospheric precipitations, which may be the result of desert dusts transfers by windstorms from north-west border to Iran. Therefore, an immediate action should be taken on controlling dust storms blowing from the deserts, and also, further studies need to be carried out to address the risk of chloride containing rain on the environment.

ETHICAL ISSUES

There is no ethical issue to be outlined in this study, as the samples was just collected from the ambient air.

The authors declare that there is no conflict of interest for this study.

CONFLICT OF INTEREST

Authors declare that we have no conflict of interest.

AUTHORS' CONTRIBUTION

The study was directed by Amir Mohammadi (cosponsoring author). Sepideh Nemati and Saeed Mousavi Moghanjooghi performed all the experiments and drafted the manuscript. Yaghoub Hajizadeh (First author) and Ali Ahmad Aghapour edited the manuscript. Hussein Panahi and Ali Nikoonahad were participated in Spatial and statistical analysis and Ali Ahmad Aghapour was involved in discussion of the results. All authors have read and approved the final manuscript.

FUNDING/ SUPPORTS

Deputy of Research Department of Urmia University of Medical Sciences was supported this research project.

ACKNOWLEDGEMENT

This paper was inspired by the results of student research in Urmia School of Health. The authors are grateful to the Deputy of Research Department of Urmia University of Medical Sciences for providing this research project with the required financial and credit.

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