The assessment of Acid concentration and Wet deposition in Spring and Autumn Rainfalls in Mashhad

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Abstract

Acid rain has been a big problem for urban area during recent decades. Acid rain comes from high concentration of air pollutant, including man made or artificial and natural, in the atmosphere. Mashhad, as the biggest religious town in Iran, has also been imposed with this problem. In this investigation the samples of rains during autumn 2002 and spring 2003 are analyzed. The results showed that concentration of different ions (SO_4^{-2}, NO_2^- , NO_3^- and NH_4^-) is higher than normal. Using the concentration of ions and average precipitation in Mashhad, the amount of wet deposition acid was calculated. Based on this calculation, the rate of acid that comes to the ground due to the rainfall was more than 24 Kg ha^{-1}. Unfortunately we haven't got any critical load map for our terrain of interest to estimate the hazard. Comparing the wet deposition amount in Mashhad and North Wales in the UK shows that the wet deposition of acids in Mashhad are nearly the same as Wales that is a very pollutant area in UK. If we assume that the amount of dry deposition is something like wet deposition we can get an idea about the amount acid that comes to the ground during each year. According to the results of this research, paying more attention to Mashhad environmental issues is recommended.

Keywords: Acid rain, Acid concentration, wet deposition

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Introduction

Nowadays talking about the air pollution is a general discussion among different groups of people in the society that most of them directly concern with the air pollution and its effect on their life. From scientific point of view, air pollution may be defined as any atmospheric condition in which substances are present at concentrations high enough above their normal ambient levels to produce a measurable effect on, man, animals, vegetation, or materials (Reist, 1984). By “substances” we mean any natural or man-made chemical elements or compounds capable of being airborne. These substances may exist in the atmosphere as gas, liquid drops, solid particles or ion clusters (Dore et al 1999).

The concentration of pollutants emitted directly into the atmosphere (primary pollutants) and substances formed from them (secondary pollutants), and hence the pattern of acid deposition over a region, are related to the chemical processes that occur simultaneously with transport and dispersion through the atmosphere (Blas et al 1998). The principal primary pollutants of concern are sulphur dioxide and nitrogen oxides, which are converted, through oxidation during atmospheric transport, to sulphate and nitrate which are associated with acidity in rain. We are also concerned about ammonium and chloride, which have an important role in the acidity of rainfall and consequently wet deposition (Dore et al 1999).

Concentration of pollutants that enter into the atmosphere directly (primary pollutants) and materials that form from them (secondary pollutants) is a function of atmosphere conditions and processes that occurs during transition of atmospheric dynamic systems (Blas et al 1998). Most important atmospheric pollutant that we are concern about them in this study are SO_2, NO, NO_2 and NH_3 which in atmospheric processes flow changes to ammonium, nitrate and sulphate ions and cause to form acidic rain(Rogers 1996). The sources of these pollutants and their reactions in atmosphere are as follows (Review Group on Acid Rain, 1997):

- Sulphur dioxide (SO_2) in the global atmosphere comes from direct emission of SO2 from man-made sources, volcanoes and biomass burning and also from secondary products of natural emission of dimethyl sulphide (DMS), H_2S, CS_2 and COS. Sulphur dioxide after deliverance in atmosphere, either due to gravity or due to combination with atmospheric humidity in the form of acid rain return to the earth surface.
- The principle nitrogen oxide air pollutants nitric oxide (NO) and nitrogen dioxide (NO2) are collectively termed NOx. The major sources of global NOx are man-made such as combustion of oil, coal, gas and aircraft, bacterial action in soils, lightning,

bio-mass burning (forest fires), NH3 oxidation, stratospheric fluxes arising from reaction of O1 (D) with N2O, galactic rays and solar proton events.

- The main source of ammonia NH_3 emission in the western countries is the waste from farm animals. A small part of ammonia emissions also come from nitrogen fertilizers.

<u>Acid rain, dry and wet deposition</u>

Cloud formation requires particles in the atmosphere as condensation nuclei (These cloud condensation nuclei can be clusters of ions or combustion particles that are either natural or anthropogenic in origin (Review Group on Acid rain, Forth Report 1997). These ions become dissolved in the cloud droplets and during the time that precipitation occurs they are deposited onto the ground surface. These kinds of clouds which contain sulphur dioxide and nitrogen oxides can become acidic, and the rain produced by such acidic clouds called 'acid rain'. As mentioned before, acidic pollutant can be deposited from the atmosphere to the earth's surface in wet and dry forms (Carruthers & Chularton, 1984). The common term to describe this process is acid deposition. Robert Angus Smith was the first person used the term 'acid rain' in 1852 in the Memoirs of the Literary and Philosophical Society to describe the state of precipitation falling near Manchester during the industrial revolution (Dore, 1990). Acid rain and deposition of acid is not a new problem but it now operates on an international scale and many countries are concerned about it.

The acidity of substances dissolved in water is commonly measured in term of pH. According to this measurement scale solution with pH less than 7.0 are described as being acidic, while a pH greater than 7.0 is considered alkaline. The pH of unpolluted rain is estimated to be somewhere between 5.0 and 5.6. It is slightly acidic because CO_2, dissolves in cloud drops to form carboxylic acid. Harmful effects are thought to be produced by rainfall with a pH value of less than 4.6. After the rain has fallen to the ground it can become less acidic, as it passes through soil, if the soil contains alkaline compounds that neutralize the acid, (Macilveen, 1995).

If there are ion concentration in rain and annual rainfall, we can calculate the amount of wet deposition as follows:

$D_M(\text{g M m}^2)=[\text{ M}](\text{mgl}^{-1})\times\text{ainfall(mm)}\times 10^{-3}$

Where D_M is amount of wet deposition of special ion and [M] is the ion concentration. For example if concentration of sulphuric acid in all over the year 8 mg/l and annual precipitation is 400 mm, amount of wet deposition of sulphuric acid will be:

DSO4 (gMm-2) = [8.00] (mg/l) × 400 (mm) × 10-3 = 3.2 gm-2 = 32.0 kg ha-1

During dry deposition aerosol particles of the acidifying pollutants are deposited straight on to the surfaces of vegetation, soil and other objects under gravitational force or impaction. If the surfaces are moist then acids are formed in the same way as in clouds, or if the material contains oxidizers, NO_2 and SO_2 can be oxidized to form acids. Dry deposition plays a large role in damaging buildings and materials in urban areas.

This research has been done to estimate the concentration of acidifier pollutants of autumn and spring rains of Mashhad because it is one of the most contaminated cities of the country and pollutant sources in this city are usually artificial. Other purpose of this study is calculating of the amount of acidic deposition of acid rains that can be good index for life surrounding programmers. At the end, results of this study was compared with the result of same study done in north Wales that is one of the most pollutant points of Europe.

Materials and Methods

Five points were selected in different places of Mashhad and special cumulative rain collector in these points erected. We were careful about these points that called sites 1 till 5 selected that may spread in city surface and not near to points with special conditions means that attempt stations erected in zones that describe usual conditions of city.

The sites were visited at the same time at the end of each run and the water samples from each site were collected during three month periods in 2003 (Autumn in Iran) 2004 (Spring in Iran). The visitors have recorded the collection date, collection time and the volume of the rainwater at each site in every run and took two samples from them.

From collected samples those with special characters were selected for next investigates. These characters are: (a) Duration of rainfall is not lower than 6 hours and more than 24 hours. (b) At least 24 hours before rainfall, there is no another rainfall. (c) Before or during the raining period, there is not storm and unnatural dust. (d) Precipitation is only in rain form and there aren't other sorts of precipitation such as snow or hail.

Rainfalls lower than 6 hours period don’t have significant volume and collecting samples don’t have chemical analysis ability. Although, samples with the raining time of more than 24 hours were recorded as few numbers but they were detected because much less concentration can not describe usual conditions of air. Therefore, from various rainfalls in each season, 5 rain events and totally 10 rain events with suitable condition were selected.

For all rain events, the collectors were washed with de-ionised water shortly after collection, so dry deposition to the collectors was not important. The volume of rain in each event was large enough for liquid left on the funnel and not collected to be insignificant. All samples were stored in special plastic dishes in a cold room before being taken to the laboratory. In the laboratory all rain and cloud samples from the collectors were analysed for pH and the concentration of different chemical material such as sulphate, ammonium, chloride, magnesium, calcium, potassium and sodium. Tables 1 and 2 show the average concentration of different ions during the spring and autumn respectively.

Table 1: Average concentration of different ions (mg/ l) in spring

Site No	NO_2-N	NO_2	NO_3-N	NO_3	NH_4-N	NH_4	SO_4-S	SO_4	pH
1	0.15	0.49	0.2	0.88	0.29	0.37	3.45	9.135	4.8
2	0.16	0.53	0.21	0.94	0.168	0.21	2.535	7.605	4.8
3	0.14	0.46	0.13	0.58	0.185	0.24	2.585	7.755	4.04
4	0.17	0.54	0.22	0.97	0.30	0.39	4.674	14.02	5.32
5	0.15	0.48	0.193	0.85	0.19	0.25	1.67	5.1	5.14
Average	0.15	0.50	0.198	0.46	0.228	0.29	2.9	8.7	4.82

Table2: Average concentration of different ions (mg/ l) in autumn

Site No	NO_2-N	NO_2	NO_3-N	NO_3	NH_4-N	NH_4	SO_4-S	SO_4	PH
1	0.075	0.25	0.126	0.558	0.172	0.22	2.07	6.21	5.6
2	0.182	0.60	0.246	1.08	0.16	0.21	3.5	9.15	4.8
3	0.25	0.82	0.114	0.504	0.143	0.18	3.03	9.09	4.8
4	0.36	0.12	0.480	0.212	0.10	0.13	1.0	3.0	5.2
5	0.18	0.58	0.382	1.69	0.137	0.176	5.25	15.81	4.95
Average	0.14	0.47	0.182	0.80	0.142	0.18	2.88	8.65	5.1

Results and Discussion

Average concentrations of different ions and rain pH in each station and average of them in Mashhad in autumn and spring seasons are shown in tables 1and 2. Results showed that acidic ions concentrations in ten cases of Mashhad city were high and pH of these rains from 5.6 means threshold pH in usual rains is lower too. In other words, the rains of Mashhad city with these characters are little acidic. Difference in pH amount in various rains is related to pollutants content in atmosphere. When time of two rains near each other, usually first rain is more dirty and second rain is a few more clean. In these conditions, first rain causes atmosphere washing and removing pollutants in large limit.

In comparing different profiles from one raining, it was observed that in the beginning (early part) of rain, pH of rain water drops is lower than pH at the end of rainfall. In other words, rains were more acidic in beginning.

Average amount of annual rainfall in recent years is about 237 ml in year (Khorasan

Water Management Organization, 2003). With attention to average rainfall and available ions concentrations in rain samples, amount of different ions wet deposition were calculated.

Table 3 shows average amount of wet acidic deposition of different ions. As average, in a rainfall, 20.5 kg sulphuric acid (H2SO4) in each hectare of Mashhad city comes down annually. Acid deposition from precipitation, averagely 24.23 kg acid on each hectare from area of Mashhad comes down. Considering precipitation falls in form of snow, since wet washing coefficient of snow is more than rain, it will bring more acid to the earth surface, so we can understand the volume of destructive acids which will deposit on Mashhad field. Furthermore, we should note to this point that a large amount of acid in dry form comes down on earth too. Since there is not true estimation of acid deposition in different zones of Iran, we compared the amount of wet deposition of acid in Mashhad with Snowdonia zone in Britain Wales.

Table3: Average wet deposition of different ions

	NO_2	NH_4	NO_3	SO4
Autumn Concentration	0.499	0.293	0.486	8.707
Spring Concentration	0.472	0.183	0.810	8.65
Average Concentration	0.486	0.238	0.828	8.676
Deposition (Kg/ha)	1.15	0.56	1.96	20.56

This area is located in south west of England in which intensity of acidic rains is much higher than other part of UK. So the amount of acid deposition only due to rainfall is much more than that from critical threshold (Mousavi-Bayegi 2001). It is due to existence of many animal farms that are the main source of different ions.

Figures 1 and 2 show different annual ion concentration and average acidic deposition amount in Mashhad and Wales area, respectively. Results show that ionic pollution of Mashhad rainfalls is almost similar to Wales region ionic pollution.

Even in case of H_2SO_4 Mashhad is more contaminated than Wales. Since pollution of Wales region is more than critical limit, therefore ionic pollution in Mashhad city is too high compared to standard limit. Unfortunately, no threshold limit has been described for acid acceptance per surface unit till now and it isn't possible to say about acid deposition destructive effects on water, soil, plants and buildings level of its dangerousness.

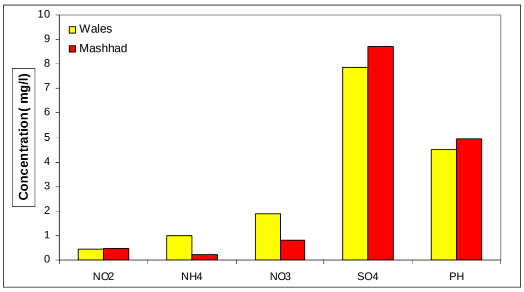

Fig 1: Comparison of ion concentrations and PH between Mashhad and Wales

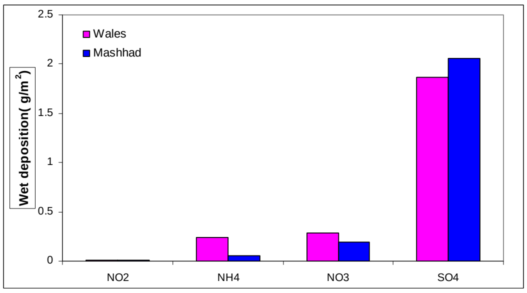

Fig 2: Comparison of acid deposition between Mashhad and Wales

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