ACID RAIN IN TURKEY

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Abstract: Acid rain is rain or any other form of precipitation that is unusually acidic. This form of air pollution is currently a subject of great controversy because of its worldwide environmental damages. For the last ten years, this phenomenon has brought destruction to thousands of lakes and streams in the United States, Canada, and parts of Europe. It has harmful effects on the environment and on structures. Acid rain is mostly caused by emissions due to human activity of sulfur and nitrogen compounds which react in the atmosphere to produce acids. These acids can be carried away far from its origin. This study is aimed to view acid rain and its effects in different sites of Turkey. The results in the literature have indicated that large amounts of acids are transported to these sites. But the data reflect that alkaline nature of the soil and alkaline particles in the atmosphere neutralize the acidity.

Keywords: Acid rain, rainwater, air pollution.

1. Introduction

"Acid rain" is a popular term referring to the deposition of wet (rain, snow, sleet, fog and cloudwater, dew) and dry (acidifying particles and gases) acidic components. A more accurate term is "acid deposition". Acid deposition acidifies the surface water, damages the forest and deteriorates ancient monuments by dry and wet pathways. These detrimental effects have caused the phenomenon of acid precipitation to receive special attention and become one of the most important global problems (Gülsoy *et al.*, 1999). More than thirty years ago, scientists noticed that in certain lakes in remote wilderness areas, fish populations were mysteriously declining. Some lakes that once teemed with fish were found to contain none at all. In their search for what caused the fish to die, scientists concluded that acid rain was the problem. Researchers continue to document that acid rain is harmful or fatal to fish (Walk and Godfrey, 1990). Other materials such as iron, steel, zinc and paint also can be damaged by acid rain. The human health effects of acid rain are also of concern. Although people aren't directly in danger from exposure to acid rain, the particles in air that lead to acid rain may be a risk to human health.

Pure water has a pH of 7.0. However, normal rain is slightly acidic because carbon dioxide (CO2) dissolves into it forming weak carbonic acid, giving the resulting mixture a pH of approximately 5.6 at typical atmospheric concentrations of CO_2.

$$H_2O\ (l) + CO_2\ (g) \rightarrow H_2CO_3\ (aq)$$

Carbonic acid then can ionize in water forming low concentrations of hydronium ions:

$$2H_2O\ (l) + H_2CO_3\ (aq) \rightleftharpoons CO_3^{-2}\ (aq) + 2H_3O^{+}(aq)$$

The extra acidity in rain comes from the reaction of primary air pollutants; primarily sulfur oxides and nitrogen oxides, with water in the air to form strong acids (like sulfuric and nitric acid). The main sources of these pollutants are vehicles and industrial and power-generating plants. Sulfur dioxide and nitrogen oxides go through several complex steps of chemical reactions before they become the acids found in acid rain. The steps are broken down into two phases, gas phase and aqueous phase.

$SO_2 (g)+O_2(g) \rightarrow SO_3(g)$

Afterwards, it becomes sulfuric acid when it joins with hydrogen atoms in the air.

$SO_3(g)+H_2O(l) \rightarrow H_2SO_4(aq)$

This reaction occurs quickly, therefore the formation of sulfur dioxide in the atmosphere is assumed to lead this type of oxidation to become sulfuric acid. Like sulfur dioxide, nitrogen oxides rise into the atmosphere mainly from automobile exhaust and are oxidized in clouds to form nitric or nitrous acid. In the atmosphere it reacts with water.

$NO_2(g) + H_2O(l) \rightarrow HNO_3(aq)+HNO_2(aq)$

Since the Industrial Revolution, emissions of sulfur dioxide and nitrogen oxides to the atmosphere have increased (Weathers and Likens, 2006). Acid rain was first found in Manchester, England. In 1852, Robert Angus Smith found the relationship between acid rain and atmospheric pollution (Seinfeld and Pandis, 1998). Though acid rain was discovered in 1852, it wasn't until the late 1960s that scientists began widely observing and studying the phenomenon (Likens *et al.*, 1972). Occasional pH readings of well below 2.4 have been reported in industrialized areas. Industrial acid rain is a substantial problem in China, Eastern Europe, Russia and areas down-wind from them. These areas all burn sulfur-containing coal to generate heat and electricity. The principal natural phenomena that contribute acid-producing gases to the atmosphere are emissions from volcanoes and those from biological processes that occur on the land, in wetlands, and in the oceans.

These gases evaporate into the atmosphere and then oxidized in clouds to form nitric or nitrous acid and sulfuric acid. When these acids fall back to the earth they do not cause damage to just the environment but also to human health. Governments have passed laws to reduce emissions of sulfur dioxide and nitrogen oxide, but it is no use unless people start to work together in stopping the release of these pollutants.

In this study, we reviewed some of the researches about acid rain in Turkey. The studies investigating effects and current situation of acid rain in Turkey are following.

2. Results and Discussion

The atmospheric concentrations and deposition fluxes of major ions to the Turkey Lakes Watershed between 1980 and 1986 were investigated (Sirois *et al.*, 2001). For the ambient air concentrations and dry- deposition estimates, they considered only SO_2, SO_4^{-2} and total NO_3^-. In the case of precipitation chemistry and wet deposition, they considered SO_4^{-2}, NO_3^-, H^+, NH_4^+ and cations defined as Ca^{+2}, Mg^{+2} and K^+. These ions in precipitation were measured over 24-h sampling intervals using a three-stage filter pack mounted at a height of 10 m above ground level. Precipitation was measured using a standard rain gauge and a Nipher-shielded snow gauge. This study showed that daily SO_4^{-2} concentrations in precipitation decreased markedly, while NO_3^-, NH_4^+ and H^+ concentrations remained roughly constant. It appeared that precipitation acidity did not decrease in spite of declining SO_4^{-2} concentrations due to a concurrent and counterbalancing decrease in the concentrations of Ca^{+2}, Mg^{+2} and K^+ in precipitation. The reasons for the decline in base cations are unknown, but this decline is probably related to decreasing emissions of soil-derived particles from agricultural, industrial and road sources. Compared to several selected watershed/forest sites in Canada, the United States and Europe, the estimated total deposition of S and N at the Turkey Lakes Watershed was relatively high during the measurement period.

Tuncel and Ungör (1996) were investigated rainwater chemistry in Ankara. Samples of rain water were collected in Ankara for the period between September 1989 and May 1990, by using wet-only sampler. Concentrations of major cations (H^+, Na^+ K^+ Ca^{+2} and NH_4^+) and major anions (Cl^-, NO_3^- and SO_4^{-2}) were determined for the first time in Turkey. The rain water was not acidic owing to high concentrations of alkaline soil particles in the atmosphere. However, the concentrations of acid forming ions, such as SO_4^{-2} and $N0_3^-$, were higher than the concentrations expected in a typical urban atmosphere. Most of the SO_4^{-2} in rainwater was in the form of $CaSO_4$. Rain-aerosol coupling were examined by simultaneous sampling of aerosols with rain. The ions most efficiently scavenged from the atmosphere were found to be SO_4^{-2} and Ca^{+2}.

Topçu *et al.* (2002) reported the chemical characteristics of rainfall and its seasonal variation at the EMEP station located in Çubuk, Ankara for the period between September 1994 and December 1996. For collection of the rainwater samples, wet-only precipitation sampler was used. The samples were collected on a daily basis by using an automatic four-channel system in Çubuk station. In the samples, Cl^-, NO_3^-, SO_4^{-2}, Ca^{+2}, Mg^{+2}, Na^+, K^+ and NH_4^+ concentrations were measured by relevant methods. In this study, generally, maximum concentrations appeared in winter or autumn and minumum concentrations in spring or summer seasons. The average pH of rainwater samples was around 6.3 due to the neutralization. Only about 4% of rain samples had a pH below 5.0 and about 15% of the total rainwater samples had a pH below 5.6. This reflects strong inputs of alkaline species to rainwater samples in this location. The average pH of the samples higher than 5.6 observed in rural area of Ankara is due to high loading of calcium ions in the form of $CaCO_3$ because of the alkaline nature of the soil that is typical in central Anatolia.

Chemical composition of the precipitation in İstanbul was investigated by Gülsoy *et al.* (1999). İstanbul is the most important city of Turkey with a municipal population of well over 10 million. Precipitation samples were obtained from three urban areas Bahçelievler, Florya and Göztepe for the period of January to October 1996. Samples were stored at 4°C until they were transported laboratories. NO_3^-, SO_4^{-2}, NH_4^+, Ca^{+2} and HCO_3^- ions were analyzed. The effect of the urban heating demand on the chemical composition of the precipitation was observed clearly. During the heating season (December to March), SO_4^{-2} and $N0_3^-$ concentrations in the precipitation were very high; SO_4^{-2} fluctuating between 0 and 150 mg/L and $N0_3^-$ between 0 and 70 mg/L. On the other hand, they dropped to very low levels during the April to October period when the urban heating demand decreases or ceases. High pH values associated with high SO_4^{-2} and high $N0_3^-$ concentrations reveal that the acidity of the precipitation is neutralized. Correlations between Ca^{+2} and SO_4^{-2}, and NH_4^+ and SO_4^{-2} imply that $CaSO_4$ and $(NH_4)_2SO_4$ aerosols may merge with the precipitation, and neutralize the acidity.

3. Conclusions

The atmosphere araound Turkey is one of the most heavily polluted areas in Europe. High sulfate and nirate concentrations are due to strong SO_2 and NO_x emissions. If sulfate and nitrate ions in the precipitation were completely in the form of H_2SO_4 and HNO_3, the average pH of the precipitation would be as low as 3. However, acidity of the precipitation caused by anthropogenic sources may be neutralized by calcium and ammonium cations. This is also seen in other studies conducted in Turkey (Al-Momani *et al.* 1995a, 1995b; Okay 1996). The pHs of the rainwater measured are too high for these rains to be considered as acid rain. This dilemma is attributed to neutralization of acids in rainwater when air masses reach to Turkey. Large amounts of acids are neutralized and do not damage the ecosystem. $CaCO_3$ and NH_3 appear important neutralizing agents. The results have indicated that acid rain can be effected only a very small area in Turkey. Obviously calcareous soils in this country form a natural protection system for acid deposition.

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