# The Cooperation Acid Rains Effect on to Historical Monuments, a Case Study from Canakkale Province; West Anatolia

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**Abstract:** Canakkale Monuments Observing data presented that the acid rains effect to in which has main $CaC0_3$ structure Apollo Smithion, Parion and Alexandria Troas according to particular by DTA graphics. The main reason of standing up of historical monuments in the region is caused by resistant greywacke structure, existence of quartz as a thermodynamically decisive form of $SiO_2$ has increased the resistance to time and acid rain in the region. Getting originated from industry and transportation which give rise to $SO_x$ and $NO_x$ inputs into the atmosphere on to Canakkale's historical monuments. Water loss coming out or high Uv energy which depends on temperature rise. Preserving measures maximum wet sediments in the seasons of autumn and winter rains effect coming from Balkans to study area, as a result to the density reach to the maximum level.
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**Keywords:** Acid rain, historical monument, environment, Canakkale, Turkey

## 1. Introduction

The effect of acid rains first became visible in Scandinavia in 1960s; contamination by acid was observed in thousands of lakes especially in Southern Scandinavia and in hundreds of lakes in Northern America. Also, it is known that water biota was affected and fish populations became reduced or extinct. Water contaminated by acid passed to soil and underground water, and this caused the rapid rusting of drinking water pipes in Scandinavia (Brundtland et al., 1987). On the other hand, in the middle of 1980s, the fresh waters in Sweden too acidified to support hydrophilic life and almost all of 1800 lakes became dead dormant (Kormondy 1996). Fish were determined to become extinct in the 24% of the lakes here (Environmental Resources Limited, 1983). The main reason for the interaction in these lakes is that the lakes had a catchment basin and is the possibility that snow waters could include 100 times more acid.

The effects of acid rains have increased in different environments in recent years. The studies regarding the emission values in the air at the surface of sea in the northeastern Atlantic proved to be over the previously- foreseen figures. This emission amount with the figures of 1995 is 1.37 million tons of sulfur dioxide and 1.94 million tons of nitrogen oxide (Acid News, 1997). Acid deposition continues to threaten many sensitive ecosystems, and analysts say deeper emissions cuts are needed to prevent future pollution from undoing the gains of the past 20 years (Malakoff D. 2010).

## 2. The Formation and Effects of Acid Rain

The pH of the atmosphere ranges between 7 >pH>5.6 because of the carbonic acid brought about by carbon dioxide. Rain water is of slightly acidic character in an environment not contaminated by any purity and its pH value is 5.6. With the fall of inflammable gases such as SOx, $O_2$, NOx, compound acid can come into being. The acid rains happen when the so-called gases rain onto the earth. pH can take place depending on biological and meteorological factors. The pH taking place in this way falls below 5.6. One of the main reasons for acid rains to affect wide range of areas is the Industrial Revolution. Another reason is the fact that the construction applications of elevated chimneys became wide-spread so as to rescue the atmosphere of the city from the emissions of sulfur dioxide. The factories and thermal power plants processing nickel and copper ores including sulfur compounds produced local problems in many countries; high chimneys were added to these plants as a solution. These chimneys the heights of which reach up to 250-300 meters (Boşgelmez, A. et al. 1997) reduced the local damage to a certain level, but produced negative effects to more larger areas.

Several industrial activities, fossil fuels used for heating in the houses, exhaust gases from the motor vehicles, and thermal power plants are polluting the air and are emitting sulfur dioxide, nitrogen oxide, particle matters and hydrocarbon. These pollutants that can hang on the air as dry and wet precipitates can sometimes be carried to far places and can compose sulfurous acid ($H_2SO$), sulfuric acid ($H_2SO_4$), nitric acid (HNO) by reacting

with water particles or other components in the atmosphere. The pollutants hanging in the air touch on the plant and soil surfaces with condensation. As the water contacts of dry compositions accumulating at the surface of geographical places increase, the negative effects increase (Harvey, 1989). The returns of them are dry and wet acid deposition. In wet deposition all the products in the atmosphere are carried in rain or snow in a solved way. In dry deposition, there is no rain and snow during the carrying of particles and gases in the atmosphere onto the earth ground. Mainly the effect of acid precipitation depends on: acid concentration, the period of exposure to concentration, the temperature of the environment and the moisture of rock, soil, body and air and cell structure.

The species in aquatic environment cannot live for a long time through its effect on aquatic environments. Many kinds of fish cannot reproduce when the pH reaches the value of 5.5. The old die and the young have difficulty in living. Fish die when the pH is 5.5 (Adriano and Johnson, 1989). It is not possible for fish to be alive more than a few minutes within the pH range of 3.0- 3.5, only some plants and inter vertebrate can exist (Alabaster and Llyod, 1979). For example, there is no fish in 20 thousand lakes of 100 thousand lakes in USA. Calcium hydroxide is still sprayed to get rid of the acidity in many lakes (Yılmaz, 1985). For instance, the more the pH value of water decreases, the more the species of Sphagnum can increase. 350 varieties of Sphagnum kind, which is of economic importance, grow in the marshy habitats and bring about wide meadows. Every year, new plants produce on the top, the lower part dies and may create thick layers of moss (Villee, 1972; Tanker et al, 1993).

Acid rains reflect on human metabolism as well. Heavy metals at high concentrations can be taken from drinking waters carried by pipe lines made of lead or copper. For example, the intake of copper at a high concentration is reported to give rise to diarrhea in small children. In the chain of aquatic food, the intake of heavy metals such as mercury and cadmium can be under discussion (Environmental Resources Limited, 1983). The acute and chronic effects of sulfur dioxide are in question. In acute effects, there are some reactions that cause the widening of capillaries and leakage of liquid. The general physiological reaction that happens with sulfur dioxide resembles to allergic asthma. In chronic effects, sulfur dioxide becomes included in lung diseases such as chronic bronchitis and pulmonary fibrosis and makes the symptoms aggravated by causing a decline in the pulmonary function through irritation and by increasing the burden on the heart (Kupchella and Hyland, 1993).

Acid rains are directly harmful on trees and other living beings in the forest ecosystem as well as their causing them to be affected negatively with the harmful effects which they produce in the roots by deteriorating the natural features of the soil. For this reason, the trees the nourishing relations of which are deteriorated die in the event that the negative effects continue or become intensified (Charles, 1995). In a survey made at Kaz Dağları district in the Marmara Region, acid rains were determined to cause leaf burns especially in a kind of pine (*Pinus nigra*) (Bayçu, 1997). Leaves are plants digesting and the most important respiration organs. Plants produce sugar and amino acids shortly organic materials by combining water and $CO_2$ in their bodies with sun shine. Plants can live feed, grow and produce fruit if the carbohydrates produced as the result of $CO_2$ digestion is more than those consumed through respiration (Carlson and Haines, 1989; Chew et al., 1980). Thus this effect on leaves causes product deficiency, leading to financial losses. However, the resistance of plants is also important. For example, it is observed that olive plants in the field soils show higher tolerance to the damage, while those growing on the slopes or mountainous places show lower tolerance. Trees in fertile soils with deep profile which can be watered and fertilized are more resistant to acid (Onoğur and Çaylak, 1989).

Its effect on soils and graywackes/rocks (kayaçlar) is quite important. According to Kantarcı (1995) and Kasap (1995), the acid accumulation in the soil affects some abnormalities in the system of soil and plant because it impairs the chemical structure of the soil. The concentrations of earth-related elements in the dry summer season lasting long and marine salt elements due to their near lines were found high. In the study, even though $SO_4^{2-}$, $NO_3^-$ are high, H+ ion proved to be low because of neutralization. Marked differences were observed in the short (daily) and long (seasonal) period in the element and ion concentrations. Salt-related element such as Na and C1 increased due to stronger wind in winter. In the summer period, on the other hand, the soil's being dry and soil cultivation in the area together with the salt from Africa give rise to coming out of the concentrations of the soil-related ions such as $A1^{3+}$ and $Fe^{3+}$ (Al-Momani et. al., 1998). For example, in a study carried out in Ankara, cation ($H^+$, $Ca^{2+}$, $NH4^+$) and anion ($SO_4^{2-}$, $NO_3^-$, $Cl^-$) analyses of the samples taken in the lab were carried out and as a result of the analysis, it was determined that pH value was under 5.6 in 23% of the rainfalls. Ion changes of sulphate, nitrate and calcium are excessive in Ankara rainfalls (Tuncel and Ungör, 1996). The acid deposited in the soil may become harmful when they cannot become cushioned by basic ions. In fact, basic

compounds subscribe to soil in the consequence of the abrasion of the rocks around; that's why, pH value of the soil reduces when unit rate of acid exceeds the rate of abrasion. Aluminum ions become in free position when the soil's pH value falls below 4.2 and they are absorbed by the plants like nutrients and very serious damages arise. When pH value falls below 3, iron ions damage the trees by becoming free. Very old main greywacke/rocks negatively affect meadow and forest plantation, and also aquatic eco-systems by causing their acidification because these rocks contain nutrients set free due to acid (Kinniburgh and Edmunds, 1984; Hornung et. al., 1995). At the same time, it is observed that in the studies carried out, geographical rock structure and the characteristics belonging to that area affect the acidic density and thus the natural water sources are affected (Stevens et al., 1997).

## 3. The research field and historical objects subject to research

Çanakkale is one of the two cities which is in the northwest of Turkey and located between 25'' 35' and 27'' 45' meridians and 38'' 30' and 40'' 45' parallels, and is situated in Asia and Europe with its lands on Gallipoli Peninsula and Biga Peninsula and which has lands on two continents. This city has a location at the geographical place where the Turks carried out the first conquest. The city is surrounded by Balıkesir in the East and Southeast, the Aegean Sea in the West, the city of Edirne in the Northwest, and Tekirdağ and the Marmara Sea in the North, and has a geographical space of 9.737 $km^2$. The study was conducted in the city that constitutes 1.29% of Turkey's acreage, having coast of 671 km to the sea bearing the transition climate between the Mediterranean climate and the Black Sea climate. It is the city that has 11 counties, 34 municipalities and 568 villages and whose total population is 464.957 and having the annual population growth of 7.3%. The city's population density is 47 and it hosted many civilizations in the course of history.

There are a lot of historical objects belonging to Hellenistic, Byzantium, Seljuk, the Ottomans and modern Turkey in the city. Some objects determined to be protected as historical heritage in the city of Çanakkale are as follows.

## 4. Material and Method

A study was carried out in the form of the land survey that is in the supportive quality for "The Studies of the Protection of Natural, Historical and Cultural Values" formed within the scope of the Studies of the Preparation of National Environment Action Plan, literature review and in-place observation. The method of problem solving which has emphasis of the anticipation of difficulty, the definition of the problem, the determination of the observable examiners and their evaluation were used. Collection of the samples from the historical objects found throughout the city between the dates of 05.01.2003 and 19.01.2003 and the study of the land were carried out. The analytical supply presented in this report are intended to aid researchers in the assessment of the effects of acidic deposition on building materials after collected-samples phases:

**a)** The determination of thermal analysis, and
**b)** The infrared spectroscopy were made in MTA-Ankara laboratories,
**c)** Determination of moisture,
**d)** Solubilization of the samples,
**e)** The loss of weight, and
**f)** Determinations of pH effect were made in ÇOMU Chemistry Department Laboratory.
**g)** Determination of the effect of temperature was carried out in Kale Ceramic/Semedeli

1- Chemical and crystal components
% $SiO_2$, CaO, $Al_2O_3$, $Fe_2O_3$, MgO, ZnO, $K_2O$
2- Mineralogical components
(boytovnit, calcite, quartz, albite, dolomite, tremolite, muscovite, etc.)
3- The examination of the samples' ionization values in pH2 - pH9 variability (at 25 $^oC$).
4- in 30 -120 minute at 25 $^oC$ (weight loss)
5- in ph5 5 $^oC$, 10 $^oC$, 15 $^oC$, 20 $^oC$ , 25 $^oC$ for 1 hour (weight loss)

The samples were not symbolized. The samples grinded in the scattered form in a homogeneous way in the values under the 205 MESH measurement unit were compressed and were contaminated with Shimatzu XRF 1700 device in XRF fluorescence Spectrometer. In addition, thermal analysis acidic interaction was made.

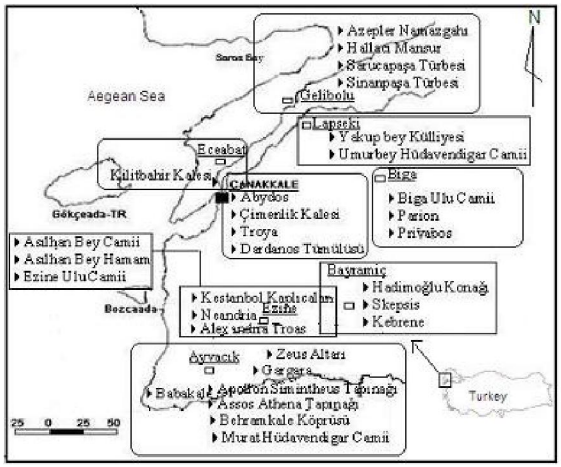


Figure 1. The Historical Sample Stations in Çanakkale Province

**5. Schedule and the other components**

Operation Program:

a) Compilation of source and literature
b) Determination of the historical objects to be protected in Çanakkale
c) Examination of the land
d) Managerial and institutional structures
e) Regulations
f) Financial and economic frames
g) The problems resulting from societal, cultural and political structure
h) The attempts to generalize the protection consciousness and protection education

**6. Findings and Interpretation**

In the construction of the historical objects in the city of Çanakkale, the materials in the area were used in general. The abundance of mine reserves that are the return of the present geological structure is related to its magmatic and the tectonic characteristics. As the result of the studies carried out in the land, it is emphasized that there may be a ore potential of 15-20 tons in terms of copper, lead-zinc. However, this potential was accumulated in a restricted area and it has spread to a vast area. In becoming ore, Paleozoic old magmatic are dense in acidic copper, lead, zinc, tungsten, molybdenum and iron and Tertiary old magmatic are dense in lead, zinc, antimony and quicksilver. In radio metric carbon dating carried out by C-14 method, it was determined that the metallic mine reserves have been operated since 3000 years. For example, it is estimated that the golden ore found in the Oligocene old silisilica tufas near the historical city of Truva was also being exploited 2455±70 ago. It was discovered that production was being made in the lead ore near Yenice Bekten village 2220±45 years ago (Ilgar R., 2004). It was mentioned that the constructors who live around Çanakkale attended to the building of 'Al-Aqsa Mosque' (Kural, 1988.) In brief the history of the region is rich in monument supplies and building and this also turned into application. A wealth of historical monuments is affected and unspoiled.

The effects of acid rains on the supplies used in building historical monuments are as follows.

Sulphat sulfur which can be in the state of Calcium, iron, copper and magnesium salts is in the state of loose crystal. The amount of sulphat coal in coal is quite little, but it can increase by surface deterioration when it contacts with air. Sulphat sulfur may not cause a problem in the purification of coal because it dissolves in water (Doğan et all, 1991). The kind of the Stone used is more the marble which is the most decisive form of mineral of CaC03 thermodynamically. Marble is a metamorphic greywacke. While marble is the big crystalline form of calcite, limestone is the small crystalline form of calcite and it has got a more porous structure. Because this difference affects the appearance and usage and also the marble is shinier, it has been used for minor historical buildings. In compliance with the results of the mineralogical studies made on the historical monuments taking place in the region, more limestone has been used as seen in the findings.

Figure 2. A Sample Exposed to Deterioration By Acid From The Research Field: The Column in Koçali Quarry

It is unavoidable that acid interaction is seen in the form of dry sediments except the direct effect of acid rains inside the available structure, because $H_2O$ may join to the atmosphere and oxidation may take place. The generating possibility of this situation is strengthened by the following metrological data.

That the rains in the city take place in winter, as seen in the following table increases $S0_2$ and $NO_2$ relevant rise to acid rain. The findings got relevant to interaction of historical monuments which has the structure of the abovementioned greywacke with the acid and their mass losses are at appendices.

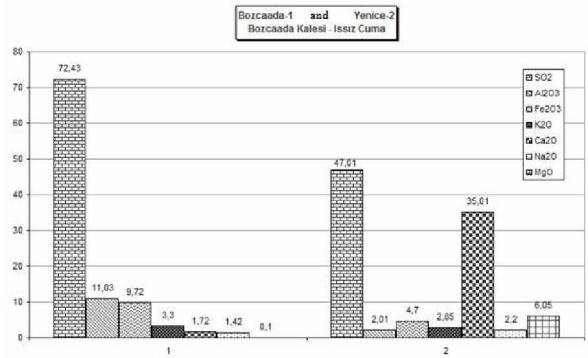


Figure 3. Mineralogical Analysis in The Historical Monuments of Bozcaada and Yenice Region

Great number of exothermic reactions have been seen in thermal analysis tests made on the samples taken from historical monuments. The

existence of the peaks in the reaction stands out. Mass loss and energy defect's occurrence has been noticed. There is water loss coming out or high Uv energy which depends on temperature rise. This condition is observed from DTA graphics. Consequently, It has been determined that acid rains have given rise to change relevant to degradation on the historical monuments in that region. This situation stands out more in Apollo Smithion, Parion and Alexandria Troas in particular.

The main reason of standing up of historical monuments in the region is caused by resistant greywacke structure.

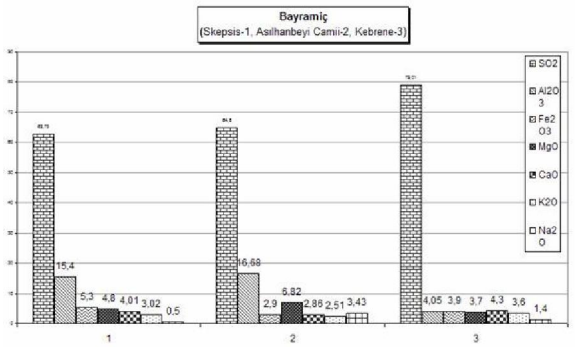


Figure 4. Mineralogical Analysis in the Historical Monuments of Bayramiç Region

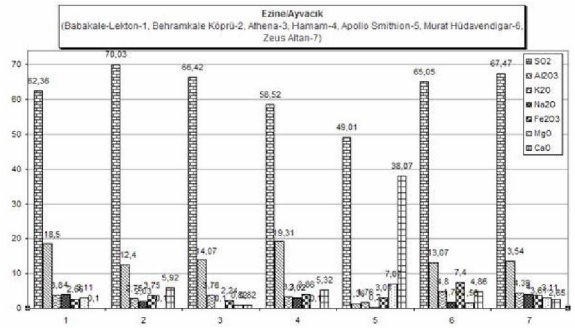


Figure 5. The Mineralogical Analysis in The Historical Monuments of Ezine and Ayvacık

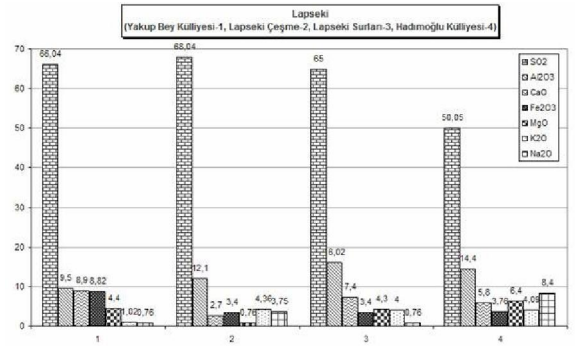


Figure 6. The Mineralogical Analysis in the Historical Monuments of Lapseki Region

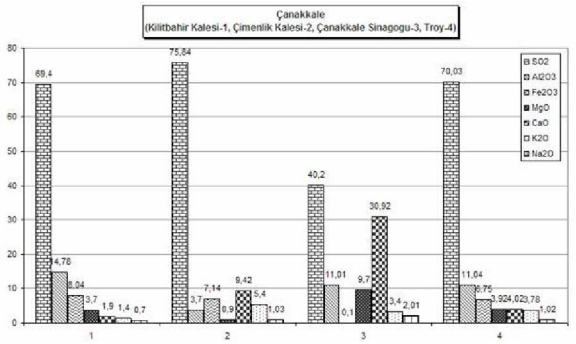


Figure 7. The Mineralogical Analysis in The Historical Monuments of Çanakkale and area's

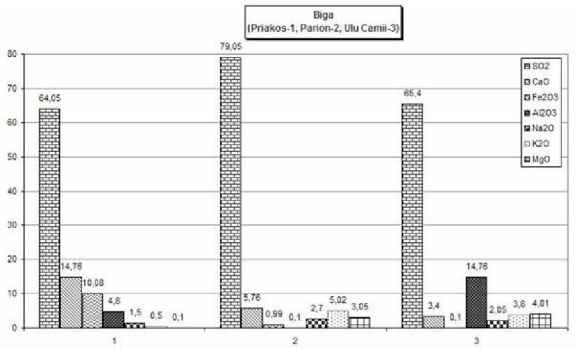


Figure 8. The Mineralogical Analysis in the Historical Monuments of Biga Region

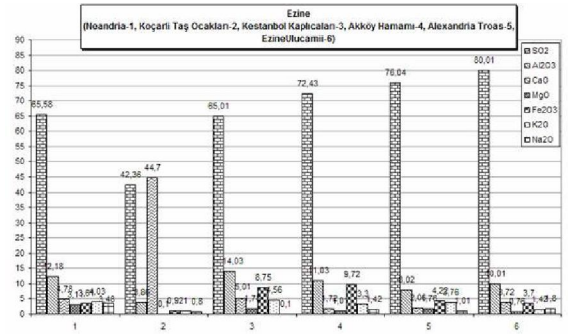


Figure 9. The Mineralogical Analysis in the Historical Monuments of Ezine

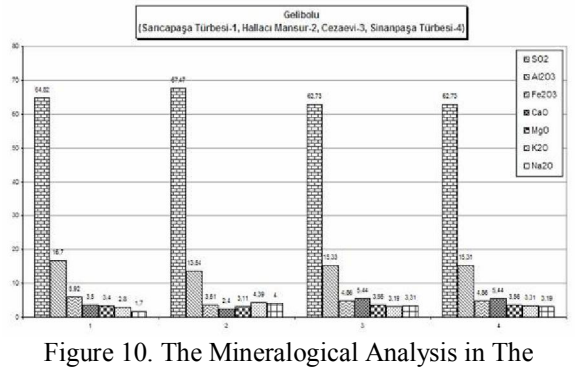


Figure 10. The Mineralogical Analysis in The Historical Monuments of Gelibolu

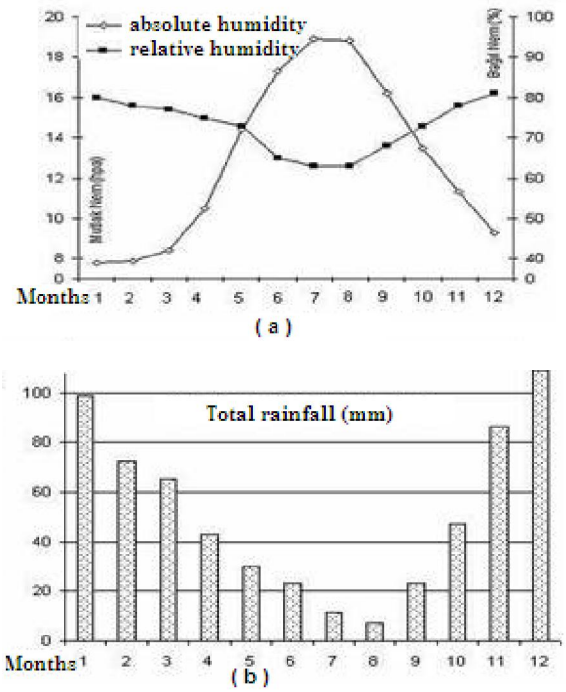


Figure (a-b) 11. The Moisture and Rain Condition Affecting Acid Rains in The Province (DMI, 1970-2002)

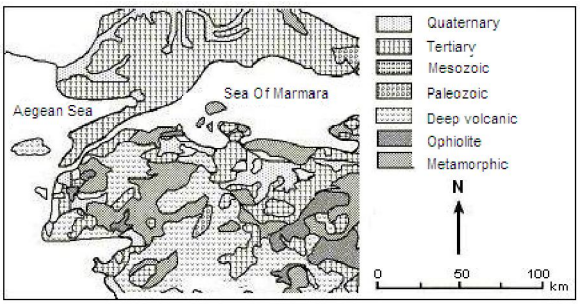


Figure 12. The Geological Structure of the Province of Çanakkale

There is resistance of the historical monuments to the acidification due to volcanic and metamorphic residing commonly in the structure of Biga peninsula. Sandstone takes place as a sedimentary greywacke. The dominance of greywacke with $CaC0_3$ is quite important. But sand particles include quartz herewith. Beside this, the existence of quartz as a thermodynamically decisive form of $SiO_2$ has increased the resistance to time and acid.

## 7. Recommendations

The density of greywacke with calcium carbonat of the historical monuments in the province of Çanakkale is great. The situation rises in the historical places of Çanakkale city center and nearby. This neutralizes with acid in the historical monuments. While the effect of acid is being absorbed mass and weight loss generates. It will be useful for dry savings to be prevented to hinder this situation. Inputs originated from industry and transportation which give rise to $SO_X$ and $NO_X$ inputs into the atmosphere where the historical pieces are must be prevented. Preserving measures must be taken for wet sediments. As a precaution, roofing and topping can be preferred in the seasons of autumn and winter the density reach to the maximum level. To that end, it is suggested for many international councils and nature preserving organizations to secure national historical monuments and for at least 10% or 12% of the total area taking up space in the ecosystem to be secured (McNeely J. A. and Miller K.R.1983, Noss R. F, 1996). If the success is achieved the territory which is called as the national park or the similar territory secured can be tripled (World Resources, 1996). It will be useful for this condition to be taken into consideration in the example of Çanakkale.

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**9. Appendix**

App.1. Rain Interaction Levels Belonging to Historical Monuments