DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

CHAOTIC ANALYSIS OF ACID RAINS IN TURKEY

by
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İZMİR

CHAOTIC ANALYSIS OF ACID RAINS IN TURKEY

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M.Sc THESIS EXAMINATION RESULT FORM

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CHAOTIC ANALYSIS OF ACID RAINS IN TURKEY

ABSTRACT

Chaos theory is one of the new paradigms of the science since the last century. After determining chaos in the weather systems by Edward Lorenz, the popularity of the theory was increased. Chaos is observed in many natural systems and studies continue to defect chaos to other natural systems. Acid rain is one of the environmental problems that have negative effects on nature and people, and acid rain values are continuously monitored. The aim of this study is to analyze the chaotic behavior of acid rains in Turkey by using the chaotic defecting approaches. The pH level of the rain water, concentration of sulfate and nitrate data are obtained from the Meteorological Service of the Republic of Turkey. Lyapunov exponents, reconstruction of the phase space, and power spectrum analysis are employed to determine and predict the chaotic behaviors of acid rains.

Keywords: Acid rains, chaos, chaotic analysis, Lyapunov exponents

TÜRKİYE'DEKİ ASİT YAĞMURLARININ KAOTİK ANALİZİ

ÖZ

Kaos teorisi geçtiğimiz yüzyıldan beri bilimin yeni paradigması olarak görülmektedir. Edward Lorenz'in hava sistemlerindeki kaosu tespit etmesinden sonra teorinin popülaritesi artmıştır. Kaos çok sayıda doğal sistemde gözlemlenmektedir ve başka doğal sistemlerdeki araştırmalar da devam etmektedir. Asit yağmurları doğa ve insanlar üzerinde olumsuz etkileri bulunan çevresel sorunlardan biridir ve değerleri sürekli olarak izlenmektedir. Bu çalışmada kaotik analiz yöntemleri kullanılarak Türkiye'deki asit yağmurlarının kaotik davranışın tespit edilmesi amaçlanmıştır. Yağmur suyu pH seviyesi ve sülfat/nitrat konsantrasyonları verileri Meteoroloji Genel Müdürlüğünden alınmıştır. Lyapunov üstelleri, faz uzayının yeniden oluşturulması, güç spektrumları ile yapılan analizler asit yağmurlarının kaotik yapısını belirlemek ve tahmin etmek için kullanılmıştır.

Anahtar Kelimeler: Asit yağmurları, kaos, kaotik analiz, Lyapunov üstelleri

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CHAPTER ONE
INTRODUCTION

Chaos is a phenomenon which naturally occurs in nature. Due to their chaotic structure, the mainspring of the natural systems is unpredictable. Understanding this chaotic structure means understanding the nature. The system, which includes nature, society and human, contains the chaos in terms of its structure. Everything about life is designed as being sensitive to the initial conditions.

Chaos theory has come to exist from the unpredictability of nature and assumes that every dynamic structure in nature can be chaotic. Various parameters and structure of the system have an important role in the occurrence of chaos.

Newton is a pioneer to development of the classical Physics and Mathematics with his scientific revolution. Newton's new physics explains the dynamics of the objects with simple equations. Newton tells that nature is running regularly with a single law, and it is always possible to predict what will happen in the next step as long as the all variables are known. Newton's laws states that there is a reason behind every action.

Although the deterministic structure of nature has been making into law by Newton, it is clear that nature is unpredictable in real. Determinism is possible only in the conditions which all variables that affect the system can be measured with certain precision. However, it is not possible to foresee the natural systems since it is impossible to achieve this sensitivity. The need for new research in science occurs with remaining incapable of the determinism in explaining the natural phenomena after the revolutionary progress in science and transition from mechanical physics to quantum physics. As a result, chaos theory is seen as the new paradigm of science. It is clear that classical science is no longer sufficient and for this reason new scientific approaches are required. Chaos theory has the potential to combine various science disciplines.

Contrary to what is believed, nature has no regular structure. The weather is the one of the simplest examples of this. Variables such as air temperature, precipitation rate and humidity are constantly affected by the variables in the dynamic system to which they belong. This causes an irregular change in weather conditions and makes long-term predictability impossible. Natural events are unpredictable even they are not random. Therefore, chaos refers to the order of disorder in nature.

The mandatory condition for a system to indicate chaotic structure is that it has a nonlinear pattern. Linearity is a situation in which the increase and decrease in the system causes a regular change in the system. If this change is irregular, it means that there is non-linearity. Chaos is also important in showing that the systems which were initially seen as irregular or random, act in accordance with a different order. Chaos exists to detect the order within the complexity and disorder.

Chaos is not seen only on mathematically measurable systems. Lorenz's butterfly effect reveals itself in historical and social events. Small changes in the butterfly's wing flap have caused great results in history and will continue to be. Wars, economic crises, scientific discoveries that have made history have always begun with a small fire depending on the butterfly effect and have caused the results that affect the fate of the whole world. In this respect, chaos is a phenomenon that cannot be separated from the life that exists in both nature, society and the individual. Therefore, seeking for the chaos is a universal obligation.

The research of chaotic systems is also important in order to reveal the hidden order within the complex systems and provide predictability as modelling the systems.

Nowadays, it is quite easy to understand whether the system shows chaotic structure with the calculations made on the computer by recording the time series belonging to the system. In many areas such as environment, engineering, physics, chemistry, health, finance and psychology, chaotic analysis is performed by taking time series of systems. In order to understand a system is showing chaotic structure, the phase space of the systems must be reconstructed. From this point of view, it can be understood whether the system shows chaotic structure when the largest positive Lyapunov exponents are calculated. In addition, information about the chaotic structure can be obtained from the system's power spectrum graphics.

Acid rain is one of the natural systems where chaos can be examined. Although several studies have been carried out to model acid rain, there is no study conducted on the chaotic structure of acid rain. As in many other natural systems, showing chaotic structure of acid rains will provide evidence that nature is controlled by chaos.

In this thesis chaotic analysis of the acid rains is performed on the time series of nitrate, sulfate concentration and pH degree in the wet rainwater samples obtained from Amasra, Antalya, Balıkesir and Çatalca rain collection stations in Turkey. Relevant phase spaces were reconstructed, and Largest Lyapunov Exponents were calculated on MATLAB. In addition, power spectrum graphs of the series were interpreted by drawing on MATLAB.

A brief outline of this thesis is as follows. Chapter 2 gives an overview of acid rain and related literature. In Chapter 3, the background information about chaotic analysis methods and mathematical definitions used in this study are explained. It is also given examples from diverse applications of chaos theory with related literature. Chapter 4 is devoted to reveal chaotic behavior of acid rain data by applying the chaotic analysis methods described in Chapter 3. Finally, in Chapter 5, concluding remarks and potential extensions are presented.

CHAPTER TWO
ACID RAINS

The atmosphere is one of the most important elements for achieving ecological balance. As well as it surrounds the earth, it also serves as a vital protection shield for the living organisms. It is very important to maintain the balance between atmosphere and earth in order to provide sustainability of the natural balance. The researchers aim to understand the form of this balance and the necessary conditions for the continuation. Pollution in the atmosphere cause the deterioration on the balance. One of these pollution elements called as acid rains. In this section, an overview of acid rain and related literature will be given.

2.1 Overview of Acid Rains

The term of acid rain was first used by Scottish pharmacist Robert Angus Smith in the middle of the 19th century for defining the acid ratio increment of the rain which pours in Manchester. Smith realized the relation between acid rains and air pollution which increases because of industrialization and fossil fuel usage (Smith, 1852). Even though acid rains are explored in 1852, it has not investigated as full-scale approach. After the observation of ecocide on the plants which is located near large industrial areas and increment of acid ratio in the lakes and rivers, acid rains are started to be investigated by scientists. First of these research was conducted in areas located in North America (Likens & Bormann, 1974) and Sweden (Oden, 1976). The effects of the Sulphur dioxide and nitrogen oxides emissions to a large extent in the environmental areas were the main reason of the restart of these researches. After these studies, it is shown that there is a link between the emissions caused by acid rains and environmental effects such as toxicity on agriculture and animals, and acidification of surface waters (Burns, Aherne, Gay, & Lehmann, 2016). In the face of environmental risk of the acid rains, international agreements were made between governments for preventing the negative effects of this pollution (Quarrie, 1992).

The acidity of any deposition is measured on a pH degree ranging from 0 to 14 in which 7 is considered as neutral. In normal situation, rainwater has acidic feature and its pH varies from 5.5 to 5.6 as can be shown in Figure 2.1. It results from carbonic acid which occurs interaction between rainwater (H_2O) and carbon dioxide (CO_2) in the atmosphere. Acid rains are defined as rains whose pH is under the scale of 5.6. Sulfate and nitrate concentration also show the acidic characteristic of the rainwater.

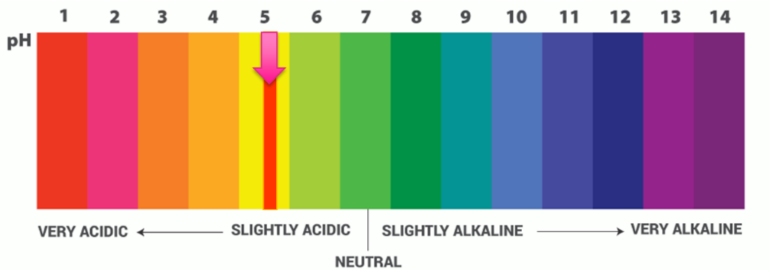

Figure 2.1 pH scale of rain water

Acid rains are occurred as a result of dissolving sulphur dioxide (SO_2) and nitrogen dioxide (NO_2) gasses in the water drops inside the clouds. Therefore, the acidity of water body increases in clouds and acid rain forms. Once these gases react with water, oxygen and some acidic chemicals, sulfuric acid (H_2SO_4) and nitric acid (HNO_3) are formed. Sulphur dioxide and nitrogen dioxide can be moved extra-territorium by prevailing wind after spreading from pollutant sources. Figure 2.2 shows the occurrence pathway of the acid rains in the atmosphere.

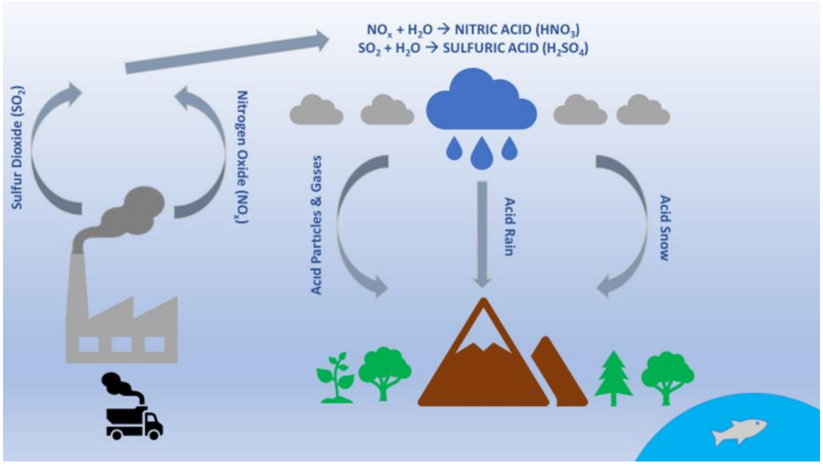

Figure 2.2 Pathway of the acid rains

Most of the nitric acid occurs from NO_2 gases in the atmosphere. However agronomic practice also effects acid rains because of the ammoniac. Fertilizers which are used for improving the quality of agricultural goods are rich in phosphor (P) and nitrogen (N). Most of the fertilizers in the fertilizer industry are obtained by Haber-Bosch technique. In this technique, non-reactive nitrogen (N_2) in the air turns to reactive ammoniac (NH_3). Ammoniac transforms to nitric acid (HNO_3) as directly evaporating in clouds or in consequence of some chemical reactions.

The common reasons of occurring the acid rains are volcanos, anaerobic depositions in the earth and sea, ammoniac caused by uncontrolled agricultural practices such as over-fertilization, SO_2 and NO gases which occurs from using fossil fuels in the power stations, cars , trucks and buses. New research show that acid rains especially which occur near residential areas are caused by nitrogen oxide gases (Schaefer, 1979).

Acid rains are the one of the results of the acid deposition and acid convection. The two types of acid depositions can be classified as wet and dry.

Wet deposition is occurred by penetration of acidic materials to the water mass in the clouds. Acidic waters, under pH 5.6, are carried by rainfall, snowfall, sleet and hail squall from the atmosphere to the earth. This water effect the living creatures negatively. Severity of effects depends on the degree of acidity, features of the effected organisms, chemical content and buffering capacity.

Dry deposition is accumulation of the acidic aerosols, particles, fly ashes and gases on the atmosphere. After that this dry accumulation can be transferred to the earth through atmosphere. Even these materials or gases have not acidic content, they can be converted to acids after contracting water in the form of rain, fog, etc. Dry deposition can both increase the acidic behavior of the rain waters and make surface waters acidic. This surface water can give rise to make other water sources acidic (Schaefer, 1979).

It is known that SO_2 and NO gases can travel for several hundred kilometers in the atmosphere per day and they can cross country boundaries. This long-distance transport effects the environment of the pollution sourced country’s neighbors indirectly and causes environmental and regulatory problems between them (Schaefer, 1979).

2.2 Literature Review

In this section, a review of literature concerning acid rains will be given. Swedish scientists was first to determine the acidity on the lakes in 1950s (Cowling, 1982). In 1960s some scientists confirmed the decrease on the fish population on a number of lakes and show the acid rains as reason of this (Walk & Godfrey, 1990). Acid rains have been underlined as nonlocal at United Nations Environment Conference in 1972. Significant amount of research has been conducted between 1980s and 1990s in different locations across the world. Sisterson and Shannon (1990) examined the rain samples in Chicago and investigated the effect of the emissions to chemistry of local precipitation. In the study of Plaisance, Coddeville, Guillermo & Roussel (1996) rain samples have been collected from 13 rural locations in France and it was found out that sea has been affected by rain chemistry. Another study was performed by Williams, Fisher, & Melack (1997) on the Calado Lake in Amazon forests with using wet rain samples and showed that acid rains are comprised of the organic acids.

Furthermore, various studies have been conducted in different regions of Europe. United Kingdom, Scandinavian and Central Europe countries were pioneer to acid rain studies (Gatz, 1991). European Acidification and Ammonium Maps which consider long distance convection and used EMEP model was prepared (Buijsman & Erisman, 1986). EMEP (The Cooperative Program for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe) is a program which is funded by European Union. Wet rain data distribution prepared with the data of rain concentration were received by EMEP database and related services of the countries. Sulfate, nitrate, ammonium, hydrogen, sodium, magnesium, potassium and calcium concentrations were mapped with provided high range of 824 data in the study of Leeuwen (1996). Anion, cation, pH and conductivity data measured from the rain samples in 10 different stations at the south of France shows those major ion concentrations are high in city centers. pH degree is lower in the city centers compared with rural area. The cause is determined as $CaCO_3$ source of soil structure near the city center (Sanusi, Wortham, Millet, & Mirabel, 1996). In the study of Raper & Lee (1996), maps of the chemical components of the rains in rural area of

United Kingdom were prepared to understand how chemical components are changing.

Limited number of research has been carried out in Turkey. Rains in the industrial area of Izmir were chemically analyzed by Al-Momani and Ataman et al. (1995). Also, studies about the aerosol change were carried out and results showed that meteorological parameters are effective on macro scale (Şen, 1988). In another study, the wet and dry major ion components in Antalya were investigated by Al-Momani and Tuncer et al. (1995).

Tuncel and Ungor (1996) presented a study about rainwater chemistry in Ankara. In this study, wet rainwater samples were collected between September 1989 and May 1990 in Ankara. Major anions and cations were measured for the first time in Turkey. The results showed that concentrations of acid forming ions have higher concentrations in urban areas. Another research was conducted by Toros et al. (2000) on Belgrad Forest in Istanbul. Variation of pH, conductivity and $SO4^{-2}$ concentration of precipitation were analyzed between November 1997 and June 1998. The results showed that the concentration of $SO4^{-2}$, pH and conductivity are measured much higher than the measurements made in the other countries of the world and the acid precipitations are on west-northwest direction. Bayçu (1997) presented that acid rains caused leave burns epically on some kind of pines in the Mount Ida. One of the EMEP stations is located in Cubuk, Ankara. Rainwater samples were collected in this station between September 1994 and December 1996. In the study of Topçu, İncecik and Atimtay (2002) pH degree, major ions and conductivity parameters were analyzed using this data. According to the results, only about 19% of the rain samples had acidic character because of the high loading of calcium ions in the form of CaCO3 because of the alkaline nature of the soil.

2.3 Effects of Acid Rains

Acid rains are accepted as environmental problem on the global aspect. They have different effects on wide variety of fields and environmental factors which are described below.

2.3.1 Effects on Features of the Soil

Acid rains have effect on chemical and biological structure of the soil. Chemical compositions in the acidic rain water decrease the pH level of the soil. Therefore, some useful elements such as Ca^{++}, K^{+}, Mg^{++} and Na^{+} move away from the ground and causes food imbalance on the soil structure. All of these affect the agricultural productivity as a negative way. Acid rains also affect the soil microorganisms while changing soil environment (Aydın & Sezen, 1990).

Another effect of the acid rains is demineralization of some minerals which can be used as nutrition in the ground. In consequence of demineralization, high acidic waters remove useful minerals and nutrition from the soil and move them to lakes, rivers and streams with runoff. At the same time, acid rains make harmful materials (such as heavy metals) free in the soil (Probst, El Gh'Mari, Aubert, Fritz, & Mc Nutt, 2000). This mobilization of the heavy metals in the soil can causes serious problems on the ecosystem and threat food safety (Cui et al., 2004).

2.3.2 Effects on Plants

Acid rains can lead to inhibition on the growth of the trees. Acid rains can cause stress on the forests coupled with other environmental problems.

Acidic rain water enters the stoma of the leaves and turn the structure of the cytoplasm which provides the water balance of the plant. For the green vegetables such as spinach, SO_2 covers the leaf surface as plastic coverture and stops photosynthesis activity. As a result, the plant loses water and dies in a short time. Additionally, when the plant loses leaves and becomes weaker, top body of the tree cannot perform windbreak activity and tree can be toppled because of strong winds (Takahama, Veljovic-Lavanovic, & Heber, 1992).

Leaves and trunks which touch on high acidic water are frayed firstly. Taking useful materials from soil is getting more difficult and taking some toxic materials is getting easier because of acid rains.

Acid rains have toxic impacts on the plant environment as it increases the heavy metal concentration. It is known that toxic effects of acid rains have been caused damage of rainforests in recent years (Öztan, 1985; Sezen, 1991; Yücel, 1995).

2.3.3 Effects on Microorganisms Lives in Soil

Soil microorganisms are intense at the root region of the plant which is called rhizosphere. Microorganisms have important role at converting nutrition to useful forms as having active role in these nutrition's food chain. Besides that, soil organisms contribute to soil organic materials which save soil from erosion and provide aggregation with the secretion materials.

Microbiologic aggregation increases the pores of the soil and stops flowing of the water on the soil surface. Also make the movement of the water in the soil easier as increasing infiltration. This causes a good structure on soil for cultivation with agricultural equipment and machinery (Kant & Kızıloğlu, 2003).

These activities of the soil microorganisms cause to be fertilization on the agricultural productivity. Acidic rains which pour on soil surface destroy the pH balance of the soil and effect soil microorganisms in negative way (Kızıloğlu, 1995).

2.3.4 Effects on Health of Human and Animals

Acid rains have important effects on the health of human and animals. SO_2 emissions can cause respiratory tract infections and heart diseases. NO_x emissions also cause destroying effects on human lungs.

Another important effect of the acid rains is acidic moisture produced by industrial activities. Acid moisture can react with toxic substances such as Hg, Cd, and Al that have landed in soil or lake beds. These substances, which are insoluble under normal conditions, can cause toxic effects by reaching the plant, animal and human by food chain or drinking water as a result of reaction with acidic moisture.

Acidic particles are comprised from scatter of the SO_2 and NO_x emissions to atmosphere. After that nitric and sulphuric acid cling on particles such as dust, soot and smoke. Direct breathing of these particles can cause destroying of upper respiratory. If these particles mix with blood chemically from wet and hot pulmonary alveolus, pneumonia can be occurred (Müezzinoğlu, 1987).

Acid rains can mix into the ground and surface drinking water, react with heavy soil metals and these can cause diseases such as struma, ulcer, chronic bronchitis, asthma and emphysema (Kızıloğlu & Bilen, 2000).

Acid rains also affect the animal health negatively in terms of respiration and food chain as well. Frogs and fish eggs are affected from acid rains the most. Chronic animal poisonings occur as a result of toxic effects of acid rains or absorbing of the pollutants to forage plants. Animal deaths increase in the areas which has that kind of meadows (Karpuzcu, 1991; Müezzinoğlu, 1987; Şişli, 1999).

Deforestation because of acid rains, also affects the natural habitat of the animals negatively. Reduction on the living space of the wild animals can cause spreading of the diseases, behavior changes on animals and reproduction problems. Changes on their habitat result waste of hunting ability and also increasing of the damages of the predator on some species (Traş & Elmas, 1998).

2.3.5 Effects on Water Ecosystem

Acid rains cause mortality of aquatic organisms, mixing of heavy metals to lakes and rivers and also reducing biological diversity. Both increasing acidity and level of heavy metal concentration have directly poison effect on the organisms and also make chronic stress. These cause problems on the health and adaptability of the organisms.

One of the harmful effects of the acid rains is observable on the lakes. These areas are particularly under the risk since lack of substances such as calcium carbonate and magnesium carbonate, which help to buffer acidity carried by acid rains (Singh & Agrawal, 2008). Only few species can be alive in the sudden pH changes, therefore fish population in the acid rain affected lakes can completely vanish (Wright & Henriksen, 1983). Acidification also reduces the biological diversity.

2.3.6 *Effects on Man Made Materials such as Buildings, Sculptures*

The last research show that metal objects, stones, paints, ceramics, textile materials, papers, glasses and leathers are directly affected by Sulphur oxides and other acidic gases. Arising from these acidic emissions; corrasion on metal objects, surface erosion and discoloration on stones, color change and fading on textile dyes, embrittlement on paper made objects, weakening and powdered surface of leather materials, damaged surface on ceramics, breakage of glasses can be occurred (Abulude, Ogunmola, Alabi, & Abdulrasheed, 2018).

It is shown that manmade materials such as sculptures, buildings, car surfaces, cultural heritage parts, paintings, tombstones are affected by acidic rain waters. The effects can be examined from measurable loss of details, rounding of the edges, and surface erosion (Schaefer, 1979). Most of the important historical structures and monuments in our country are under the risk of damage by acid rains. Paintings on the car surface also can be damaged by acid rains.

CHAPTER THREE
CHAOS

3.1 History of Chaos

In the ancient Greek civilizations chaos was used as the opposite of the cosmos which means the “absolute global order”. At 8th century, Hesidos said that “there were chaos before everything else” in his book titled Theogony (Akay, 2000).

Henri Poincaré is called as the pioneer of the chaos theory. In 1880, he analyzed the three-object problem and observed that existence of non-periodic orbits. He noticed that these orbits do not tend to infinitive nor converge to constant point. In 1898, Jacques Hadamard explained the chaotic movement of the free particles on the constant negative inclined surface. He detected that all of the unstable orbits diverge from each other with positive Lyapunov exponent.

Although the first studies of the chaos theory were carried out in the first half of the 21st century, chaos theory was formulated in the second half of the 21st century. Since linear system, logistic mapping and more of the similar theories are insufficient to explain many of empirical findings, the need for a new theory came out in the science. Dynamical behaviors such as noise and measuring error, which were excluded before, are accepted as basic components of the chaos theory. Edward Lorenz (1963), who has a significant position in the field of chaos theory, was the first person to explain the chaotic behavior with the mathematical modelling on weather systems.

In 1963, the concept of fractal was revealed by Mandelbrot. Fractals play an important role in understanding the mechanism of chaos. Mandelbrot has shown that Lorenz’s and Feigenbaum’s attractors have fractal dimensions (Mandelbrot, 1963).

After Lorenz's research, May (1976) studied on the deterministic systems as demonstrating the first examples of chaos in iterated mapping and identified chaotic movements by logistic differential equations.

Chaos theory was introduced to the literature by the study of Li and Yorke (1975). They proved that if at least three periods of doubling occur in a one-dimensional system, this system is chaotic.

Feigenbaum (1978) examined the nature of the transition from order to chaos by introducing the accurate and universal definitions. In this way, he stated that many different systems can be chaotic. His suggestion was based on the logistic equation and showed the transition to chaos graphically.

Physicist David Ruelle (1980) was the first to reveal the concept of strange attractor. He said that a strange attractor was the descriptor of a chaotic system in the phase space, and four different types of attractors had emerged. These are fix points, limit cycles, limit torches and strange attractor. In the next study, Eckmann and Ruelle (1985) proposed ergodic theory of chaos and strange attractors.

3.2 Dynamic Systems

Dynamic systems can be defined as systems in which their state changes over time. They contain the rules of initial conditions and variance of the system. The following factors must be known in order to estimate the system's behavior in any time: time equations, value of the system parameters and initial conditions. If these three factors are known, it can be said that the system is deterministic.

Time equations are the differential equation systems which predicate the variables controlling the whole system, their variation over time and their interrelations mathematically. Differential equation is the equation which converts the derivative of the dependent variable to independent variable.

Dynamic system is an important definition in chaotic analysis. The existing structures in nature are seen as dynamic systems and it is known that observing the behaviors of these structures is very important for the science. The chaotic time series analysis is one of the most commonly used methods for examining the behavior of nonlinear dynamic systems and gaining information about dynamic variables.

3.3 Chaotic Behavior

Chaos is the unpredictable behaviors of the system under deterministic conditions (Yılmaz & Güler, 2006). Occurrence of chaos depends on determined parameters but also related with structure of the system. Chaos usually occurs in unstable, complex and nonlinear systems.

According to chaos theory, everything which is changing during time period can exhibits chaotic behavior, for example population growth, economic changes, ice mass in the poles etc. Furthermore, medical applications of chaos theory are shown in wide spectrum like cardiology, physiology, neural system, cerebral activities, etc.

A system must provide following rules to be defined as chaotic system:

1- The system must be non-linear.
2- Different orbits of the system must not cross each other.
3- Orbits of the system must be limited.
4- Near orbits must be converge each other (sensitivity to initial conditions).
5- The system must have at least three dimensions.

The most important feature of the chaotic systems is their sensitivity to initial conditions. If the initial conditions and equations of the system are known, it is possible to determine the future situation of the system. In order to determine the future situations and evaluation of the chaotic system, the initial conditions should be known with infinitive sensibility. A smallest change in the initial conditions can affect the future situation of the system and can preclude the predictability of the system (Yılmaz & Güler, 2006).

Edward Lorenz was the famous meteorologist who reveals the sensitivity to initial conditions in chaotic systems. Once he was running the program of his atmospheric equations on his computer, he rounded the initial values from 6-digit decimals to 3-digits on his program. When he checked the results, he realized that output of the program is completely different from the first one. In this way, he determined the sensitivity to initial conditions (Gleick, 1987; Lorenz, 1993). He calls his finding as butterfly effect; as the famous metaphor said that “The fluttering of a butterfly’s wing in Rio de Janeiro, amplified by atmospheric currents, could cause a tornado in Texas two weeks later.”

In linear systems, changes of the parameters affect the output of the system but do not cause changing in system’s behavior. However, in non-linear systems small changes of the parameters can cause large and sudden changes in the output. In this respect, all chaotic systems have non-linear structure, but all non-linear systems do not have to be chaotic (Hilborn, 2000).

3.4 Chaotic Analysis

In order to get information about the dynamic features of a system, one-dimensional time series which belongs to the system can be generated in a variety of ways. In this way, a lot of information about the system can be obtained from the one-dimensional time series of the system. Characteristics of the system can be determined from the state variables of an irregular system and periodical measurements (Baker & Gollub, 1990; Rasband, 1990).

Signals, which are recorded as one-dimensional time series provides information about behavior of dynamic system. Response of the system in compliance with time is representing with orbits on the phase space as reconstructed by independent variables that define the dynamics of the system (Baker & Gollub, 1990; May, 1976).

The main purpose of chaotic analysis is obtaining information about the system’s dynamic. The qualitative features of chaotic attractor alone do not give exact information about the general behavior of the system in chaotic time series analysis. Therefore, quantitative analysis is also required for defining the systems. Quantitative identifiers provide us to distinguish noise behavior from chaotic behavior, as well as defining how many variables are required to model the dynamics of the system. Various studies show that the mathematical relationships between quantitative identifiers can be useful to understand the universal features of chaotic systems (Hilborn, 2000).

It is reported that chaotic time series have non-linear structure as mentioned above. Accordingly, nonlinear models must be preferred to represent a chaotic system. We can divide the naturally occurring facts (for dynamic systems which vary with one or more directions) into either continuous or discrete time in terms of measurement technique. Measurements taken at discrete time intervals can be obtained from a sub-sample of continuous time measurements. Therefore, discrete-time-changing dynamics can be solved by difference equations or repetition methods. The repetition method is a mathematical method that is obtained by repeating an operation. Solution of derivative equations are used in continuous time changes, if time is measured continuously and dynamic system is modeled by differential equations. However, no differential equation exists in time series derived from a variable that changes over time. In this case, the measured signal is dominated by the irregularity / noise originated from the environmental conditions. Chaotic time series analysis methods must be applied after eliminating this noise.

Takens's (1981) theorem suggests that the behavior of the system can be modeled as using a time sequence produced by only one variable, even if a system is multidimensional. The chaotic attractor which shows the geometric and topological structure of the phase space of such a system can be generated by sampling the time sequence of a single variable with a certain time delay. In chaotic systems, it is necessary to know the exact changes of the system over time and the initial values of the system parameters with infinite precision (Williams, 1997; Yang & Lai, 2005).

When examining signals from a dynamic system;

- The dynamics of the system should be fully understood.
- If there are signals obtained from the system beforehand, the relations between the two signals can be examined.
- If we only have signals covering a certain time interval, they can be analyzed accordingly.

When examining time series which are considered to contain deterministic chaos;

a. If the examined dynamic system was formed under unknown conditions in the past and the starting conditions of the dynamic system are defined, the behavior of the system will be monitored in an unchanging orbit.

b. The real phase space and trajectories cannot be observed where the motion equations of the dynamic system are unknown.

c. The only information obtained from the dynamic system is the time series measurement.

Additionally, dynamic systems can also be seen as a sequence generator of the time series to which they belong. In this case, the equations representing deterministic systems refer to the transition from one position of the system state to the other (Sprott, 2003).

The flow chart of the processing steps for the analysis of nonlinear time sequences is presented in Figure 3.1. The signal must be reconstructed in phase space when nonlinear analysis methods are being applied. Information about the non-linearity of the system can be taken from a point which is obtained by analyzing the equations of the dynamic system in phase space, the size attractor such as closed curve, or the results of Lyapunov exponents.

The analysis of chaotic time series is used to determine how the variables of a dynamic system change according to which parameters. The outcome of the analysis is important, as it helps us to determine how the system behaves in the next step (Reiss, 2001).

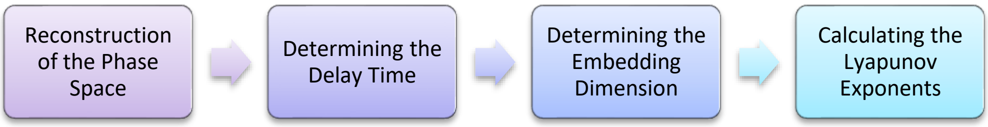

Figure 3.1 Steps of chaotic process

3.4.1 Reconstruction of the Phase Space

It is important to examine one-dimensional time series when performing chaotic analysis. The purpose of examining one-dimensional time series is to reconstruct the phase space of the system. Phase space is a collection of points corresponding to changes of system variables over time and shows the combination of all possible states of the dynamic system. There is one point in the phase space for each possible situation of the system. The concept of phase space was introduced by Henry

Poincare firstly. Each point in the phase space represents the state of the system in a different period, while each orbit represents the state of the different starting points. Trajectories that occur at different starting points are called the *phase portrait*. In a phase space, each system variable is shown as an axis in a multidimensional space. When the points formed in the phase space for different situations of the system are combined with a line, the path which is followed by the system occurs. This path is called as *orbit*. If the phase space is formed correctly, it is ensured that the trajectories that will take place in this reconstructed embedded space have the same characteristic as the orbits in the multidimensional real space.

The first stage of the chaotic analysis is reconstruction of the scalar signal in the phase space. A dynamic system can be represented by the orbits generated by the points in the reference coordinates using the independent variables in the axes. The time series generated from a variable in defined periods contains important information about the coordinates of the other orbits. Each dynamic variable of the system can be represented by trajectories which are called phase space. For a given dynamic system, the phase space is generated using the *x(t)* data recorded by the single argument. The scalar equation is shown in Equation 3.1.

$$x(t_0 + n\tau_s) = x_{(n)} \qquad (3.1)$$

In this equation, t_0 is the initial time and τ_s is the sampling time of the measurement device. Delay time embedding method is used for reconstruction the scalar data in the phase space.

Delay time embedding method is the only systematic method which is used for converting from scalar data of the dynamic system to multidimensional phase space. It is the most commonly used method for the reconstruction of phase space. This method indicates that if only one variant can be observed in the system over time, it is possible to calculate other dynamics of the system by using delay time copies of the original system (Takens, 1981).

If a time series is a component of the d dimensional (d is an integer number) attractor, topological features of the attractors are equipollence with topological features which are formed by vectors of m ($m \geq 2d + 1$) dimensional phase space.

The attractor of the signal is created by using delay time copies of the signal in m dimensional phase space at the following equation.

$$\vec{y_i} = (x(i\Delta t), (x(i\Delta t + T), (x(i\Delta t + 2T), \dots , (x(i\Delta t + (m-1)T)) \quad (3.2)$$

In this equation, T is delay time and m is embedding dimension. This d dimensional pattern in the phase space is called as "attractor". Different selections of the parameters T and m create different attractors (Akay, 2000).

According to the theorem of Takens (1981), selecting embedding dimension as ($m \geq 2d + 1$) provides information flow as preventing intersection of trajectories.

3.4.2 Determining of the Delay Time

Any time interval (τ) which is selected for reconstruction of the phase space may not be corresponded to take intended information from data. If too small interval (τ) is selected, $x(n + j\tau)$ and $x(n + (j + 1)\tau)$ coordinates cannot be distinguished in consequence of their closeness. In this case, the attractor to be drawn in the reconstructed phase space will be trapped on the diagonal of phase space. If a large time interval (τ) is selected, coordinates $x(n + j\tau)$ and $x(n + (j + 1)\tau)$ will be completely independent. Therefore, one projection on the attractor comprises on entirely independent and different directions. In this manner, the structure of the attractor will deteriorate, or the attractor will disappear. As it can be understood that selection of delay time is highly important (Brown, Bryant, & Abarbanel, 1991). Delay time can also be determined with different calculating methods. Average Mutual Information and Auto-Correlation Function methods are examples of these methods. Both of them offer solutions close to each other for the delay time.

3.4.2.1 Average Mutual Information

Average Mutual information (AMI) is average of all possible measurements of information which belongs to any two variables. In this method, time series and its embedded version is used. If these two series are independent of each other, mutual information becomes zero. The aim is to determine criteria for the statistically dependence level of the points of $x(n)$ and $x(n + \tau)$, which are neighbors in the time series. The first minimum mutual information point is selected as the delay time.

It has extensive usage for defining embedding dimension in chaotic analysis. The most important advantage of mutual information method is detecting the nonlinear relationship between the two variables. The measurement value, $x(n)$, becomes $x(n+\tau)$ after τ delay time. The average mutual information between the measured values of n and $(n+\tau)$ can be calculated using the following equation;

$$I(\tau) = \sum_{n=1}^{N}\big(x(n), x(n+\tau)\big) log_2[\frac{P\big(x(n),x(n+\tau)\big)}{P\big(x(n)\big)P\big(x(n+\tau)\big)}]\ I(\tau) \geq 0 \qquad (3.3)$$

In Equation 3.3 $P\big(x(n)\big)$ is the probability of the measurements $x(n)$ in all time series.

If τ is too small, $x(n)$ and $x(n+\tau)$ measurements do not show so many things about themselves. If τ is too large $I(\tau)$ converges to zero and it means there is no connection between $x(n)$ and $x(n+\tau)$. If the delay time is selected as $I(\tau)$'s smallest value, measurements are partly independent but not statically. If a linear analysis will be made, the first zero value of the autocorrelation function gives the appropriate delay time. On the other hand, the first minimum value of the mutual information function is taken as the delay time, while a non-linear analysis is to be performed (Frazer & Swinney, 1986; Sprott, 2003).

3.4.2.2 Auto-Correlation Function

Auto-correlation function is the one of the delay time (τ) selecting method which is used in the literature commonly. Auto-correlation function measures linear dependence between the time series $x(m)$ and $x(m+\tau)$. Correlation function measures how $x(j)$ differs from the mean value. According to Buzug and Pfister's (1992) study, applying auto correlation function to high dimensional systems can cause wrong results because of the correlations between other coordinates.

The autocorrelation function of x_t and x_{t+1} can be calculated as follows;

$$C_1 = \frac{\sum_{t=1}^{N-1}(x_t - \overline{x})(x_{t+1} - \overline{x})}{\sum_{t=1}^{N}(x_t - \overline{x})^2} \qquad (3.4)$$

where N is the number of observations and $\overline{x}$ is the mean value of x_t.

The correlation between two different series of observations in the k interval can be calculated as follows;

$$C_k = \frac{\sum_{t=1}^{N-1}(x_t - \overline{x})(x_{t+k} - \overline{x})}{\sum_{t=1}^{N}(x_t - \overline{x})^2} \tag{3.5}$$

where k is the delayed correlation coefficient. In practice, the auto correlation coefficient is generally calculated by using the auto-covariance coefficient as in the following.

$$C_k = \frac{1}{N-k}\sum_{t=1}^{N-k}(x_t - \overline{x})(x_{t+k} - \overline{x}) \tag{3.6}$$

The correlation function can be calculated by considering above equations;

$$C(k) = \frac{C_k}{C_0}, k = 1,2, \dots, m, m \leq N/2 \tag{3.7}$$

For a periodic signal, $C(k)$ oscillates between the mean values. For irregular and chaotic signals, $C(k)$ approaches zero while k increases. Thus, $C(k)$ can be used to determine the chaos.

3.4.3 Determining of the Embedding Dimension

The aim of the reconstruction of the signal in the phase space is to provide a sufficient large Euclidean space R_m and observe the attractor of the system without any uncertainty. Thus, two very close points in m dimension become visible in the space which has larger m value. Space R_m shows the embedding dimension of the attractor (Abarbanel, Brown, Sidorowich, & Tsimring, 1993).

The embedded dimension helps us to figure out how much dimensional phase space we need to create in order to make attractor, which is drawn from one-dimensional time series correctly visible. Taken (1981) stated that there are time-delayed variables that create sufficient embedded dimensions that provide smoothing and that all other variables are in pairs. Then, the number of time lags will be at least $2d_f + 1$ (d_f as selection criteria).

The number of embedded dimensions (m) also determines the number of Lyapunov exponents to be calculated for a system. In other words, a system with m dimension has m Lyapunov exponents. Therefore, the correct selection of embedding dimension is very important for the chaotic analysis of the system.

3.4.3.1 False Nearest Neighbor Method

Embedding dimension (m) can be calculated with False Nearest Neighbor Method (Kennel, Brown, & Abarbanel, 1992). If the attractor is embedding to space which has smaller dimension, non-related points can be visible as neighbor. In this situation, neighbors of each point in the attractor are found, and then the embedding dimension is increased one number. After the embedding dimension has increased, the points in the attractor which are not nearest neighbor anymore are now found. This procedure continues until the ratio of non-neighboring points to all points falls below the limit. The point that holds the ratio below the limit is defined as the embedding dimension.

The Euclidean distance between nearest neighbor vectors x_n and x_n^n for the m dimensional phase space can be calculated as follows;

$$R_m(n)^2 = \sum_{k=0}^{m-1}[x(n+k\tau) - x^{nm}(n+k\tau)]^2 \tag{3.8}$$

For the $(m+1)$ dimensional phase space, the distance can be calculated using the following equation;

$$R_{m+1}(n)^2 = R_m(n)^2 + [x(n+m\tau) - x^{nn}(n+m\tau)]^2 \tag{3.9}$$

If any of the following conditions are true, the vectors can be defined as false nearest neighbors due to a significant distance increment relative to the dimension increase.

$$\left[\frac{R_{m+1}(n)^2 - R_m(n)^2}{R_m(n)^2}\right]^{1/2} = \frac{|x(n+m\tau) - x^{nn}(n+m\tau)|}{R_m(n)} > R_{tol} \tag{3.10}$$

$$\frac{R_{m+1}(n)}{R_A} > A_{tol} \tag{3.11}$$

In this equation A_{tol} and R_{tol} are the limit values and R_A is the standard deviation of time equation. Kennel (1992) suggested that R_{tol} must be selected more than 10.

R_A can be calculated as follows;

$$R_A{}^2 = \frac{1}{N}\sum_{n=1}^{N}[x(n) - \overline{x}]^2 \tag{3.12}$$

The embedding dimension should also be greater than $2D + 1$; where D is the correlation size to calculate it correctly. If the embedding dimension is too large, the length of the data can be reduced and can also cause noise.

3.4.4 Lyapunov Exponents

Chaos has the sensitivity of initial conditions in deterministic systems. The divergence or convergence of the two different initial points, which are initially close enough to each other, is possible over the time period. This divergence of convergence shows an exponential behavior. This exponent is defined as Lyapunov Exponent. Lyapunov exponent (λ) is a measure of the sensitivity of the initial conditions and is defined as the average mean value of the local divergence of the neighbor curves in phase space (Eckmann, Kamphorst, Ruelle, & Ciliberto, 1986). If maximum λ is negative, the different initial points tend to give identical outcome and the system is not chaotic. If maximum λ is positive, the different initial points give different outcome and the system is chaotic.

Assume that a non-linear system is defined as follows;

$$\dot{x} = f(x, t) \tag{3.13}$$

Where $x \in R^n, n \geq 3$ the orbit of the system is defined below;

$$X(t) = (x_1(t), x_2(t), \dots, x_n(t)) \tag{3.14}$$

Assume that X_0 and $X'_0 = X_0 + \delta X_0$ are the closest points which are passing different initial points in a n-dimensional phase space as shown in Figure 3.2.

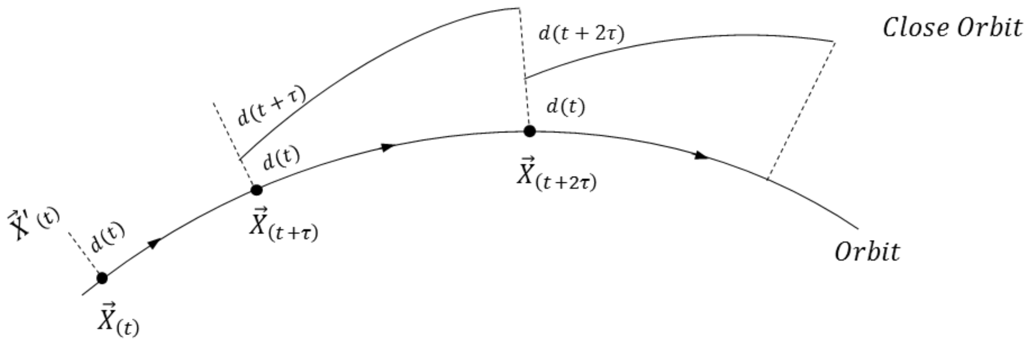

Figure 3.2 Distance between orbits

Orbits will be $X(t)$ and $X(t) + \delta X(t)$ in accordance with oclid norm;

$$d(X_0, t) = \|\delta X(X_0, t)\| \equiv \sqrt{\delta x_1^2 + \delta x_2^2 + \cdots + \delta x_n^2} \tag{3.15}$$

In this equation, $d(X_0, t)$ states the time dependent distance between X and $X'(t)$. Time dependence of δX can be considered as linearizing of the system and can be defined as in the following.

$$\delta \dot{X} = M(X(t))\delta X \tag{3.16}$$

In this equation, $M = \vartheta F / \vartheta X \ |x = x_0$ is the Jacobian matrix of the system. For this situation, the average divergence speed of the nearest two orbits can be defined as the Lyapunov exponent.

$$\lambda^{Lp}(X_0, \delta X) = \lim_{t \to \infty} \frac{1}{t} \log \frac{d(X_0, t)}{d(X_0, 0)} \tag{3.17}$$

On the other hand, n number of orthonormal e_i vectors exist where $i = 1,2, \dots, n$. As a result of these equations, the relationship can be written as shown below;

$$\delta \dot{e_\iota} = M(X_0)\, e_i \,,\, M = \; diag(\lambda_1^{Lp}, \lambda_2^{Lp}, \dots, \lambda_n^{Lp}) \tag{3.18}$$

From this equation, it can be shown that there are n numbers of Lyapunov exponents.

$$\lambda_i^{Lp}(X_0) = \lambda_i^{Lp}(X_0, e_i), \; i = 1, 2, \dots, n \tag{3.19}$$

Lyapunov exponents can be ranked from the largest to the smallest as shown below;

$$\lambda_1^{Lp} \geq \lambda_2^{Lp} \geq \cdots \geq \lambda_n^{Lp} \tag{3.20}$$

From Equations 3.19 and 3.20, the equation of Lyapunov function can be written as follows;

$$d_i(X_0, t) \approx d_i(X_0, t)\, e^{t\lambda_i{}^{Lp}},\ i = 1, 2, \ldots, n \tag{3.21}$$

In order to define whether the behavior of the movement is chaotic or periodic, the largest non-zero Lyapunov exponent $\lambda_m{}^{Lp}$ is considered (Lakshmanan & Rajasekar, 2012).

Possible Lyapunov Exponents are defined as follows.

$(i)\ \lambda_m{}^{Lp} < 0$ *Periodic Attractor – Balance Points*

When time t increases, $d(X_0, t)$ decreases through $d(0)$ and when $\rightarrow \infty$, $|d(t)| \rightarrow 0$. In this situation, when $t \rightarrow \infty$ stable equilibrium or stable periodic solution exists, there is no perturbation for divergence or irregular change.

$(ii)\ \lambda_m{}^{Lp} > 0$ *Chaotic Attractor*

When time t increases, $|d(t)|$ also exponentially increases. This increment refers sensibility to initial conditions and perturbation. Positive Lyapunov exponent is the basic component of the chaos.

The characteristics of the chaotic behavior of the dynamic system are given below (Lakshmanan & Rajasekar, 2012);

1. If one stable constant point's unit element decreases through every direction, all of its Lyapunov exponents are negative.
2. If one limit cycle attractor's unit element does not increase or decrease through orbit's direction, one Lyapunov exponent is always zero and one Lyapunov exponent is always negative.

3. As mentioned in the second item above, Lyapunov exponent is zero for a periodic orbit which has only one ω frequency. For a half-periodic orbit which has ω_1 *and* ω_2 frequency, two Lyapunov exponents are negative and other exponents are zero.

4. For chaotic behavior, at least one Lyapunov exponent must be larger than zero. It means this orbit divergence to neighbor orbits. If there are more than one positive Lyapunov exponents, this movement is called as hyper-chaos.

5. Exponential growth of incremental distance between close orbits is indicated as maximal Lyapunov exponent. The change rate of N-directional unit element is given by the sum of Lyapunov exponents;

$$\sum_{i=1}^{N} \lambda_i^{Lp} = Log|\mathrm{v} \,.F| \tag{3.22}$$

3.4.5 Power Spectrum Analysis

Data obtained from a dynamic system might have little noise while analyzing the system's dynamics. Power spectrum analysis is another method for non-linear time series analysis. Chaotic signals are very difficult to distinguish from noise because of their broad spectrum as noise. Therefore, wide power spectrum indicates the presence of chaos (Kamışlıoğlu & Külahçı, 2016). Calculating the time series and Fourier transform of a dynamic variable is the way to determine chaotic or periodic behavior of the system (Lakshmanan & Rajasekar, 2012). Dynamic systems can be represented by *F(t)* time series of continuous or discrete variables. *F (t)* function is formed by superposition of periodic components. The determination of the proportional size of these components is called as spectral analysis (Corana, Bortolan, & Casaleggio, 2004). *F(t)* can be shown as two different ways according to its structure.

If function of *F(t)* is periodic, spectrum frequencies are stated as the linear combination of the movements, which are the exact multiples of the frequencies. This combination forms the Fourier series.

If function of *F(t)* is not periodic, it is expressed by a combination of continuous frequency movements. This spectrum gives Fourier transform.

Fourier transform of the $F(t)$ is given in the following equation;

$$F(t) = \sum_{k=-\infty}^{\infty} C_{k} e^{ikt} \tag{3.23}$$

In this equation C_k can be calculated by the following equation.

$$C_k = \frac{1}{2\pi} \int_0^{2\pi} F(t) e^{-ikt} dt \tag{3.24}$$

Periodical or aperiodic behavior of the function can be determined from C_k.

The most important criterion to demonstrate the chaotic behavior of the system is that the power spectrum of the system has a wide band structure. This power spectrum consists of peaks whose width and height are random for a wide band.

CHAPTER FOUR
APPLICATION: CHAOTIC ANALYSIS OF ACID RAINS IN TURKEY

Although the relationship between nonlinear variation of meteorological variables and chaotic analysis methods has been studied by many researchers, the nonlinear structure of acid rains has not yet been addressed in scientific research to the best of our knowledge. In this study, the pH degree, sulphate and nitrate concentrations of rainwater from four different rainwater collection stations located in Turkey were analyzed mathematically and chaotic behavior of acid rains has been interpreted by the non-linear time series analysis methods.

Acid rains show their effect in Turkey like many parts of the world. The acid rain, which is usually caused by the transport from distant areas, shows its effect at Thrace and Black Sea region in Turkey mostly because of the air pollution source from the Northwest Europa and Siberia. The existing studies in the scientific literature related to rain water in Turkey are limited (Beyazıt & Ergun 1996; Boybay, Kaya, & Aslan, 1990; Demirak, Balcı, Karaoğlu, & Tosmur, 2006; Eğri, Güneş, & Pehlivan, 1997; Erbaşlar & Taşdemir 2006; Kaya & Tuncel 1997; Özdemir, Borucu, Demir, Yigit, & Ak, 2010; Saylan, Toros, & Şen, 2009; Topçu & Incecik 2002; Tuncel & Ungör 1996).

Wet deposition mechanisms have more important role in the transport of many pollutants from the atmosphere to the earth than dry deposition mechanisms. From this point of view, it is possible to obtain important information about the degree of air pollution in the local atmosphere with chemical analysis of pollutant parameters in the wet depositions (Beryland, 1982).

In this study, the required data were obtained from the data base of the Meteorological Service of the Republic of Turkey.

There are four rain collection stations which provide periodical rain water samples. The samples evaluated in this study were taken between the periods of 2004-2016. Amasra (41° 45' 09 N, 32° 22' 58 E), Antalya (36° 58' 53 N, 30° 23' 15 E), Balıkesir (39° 44’ 25 N, 27° 37’ 10 E), Çatalca (41° 20’ 28 N, 28° 21’ 24 E) stations can collect both wet and dry rain samples. Figure 4.1 shows the locations of the rain collection stations.

Figure 4.1 Locations of rain collection stations

In order to better detect cross-border pollution, rain collection stations were selected in the areas far from the city center to eliminate the effects of environmental and urban pollution. In addition, forest areas were preferred due to the fact that acid rains damage the forests firstly.

Amasra rain collection station is critical because of ability to monitor the pollution and acid rains which transport from the weather systems in the west and north direction. Balıkesir station is important to detect the arrival path of pollutants which are transported by general circulation in the Marmara region. Antalya station has also importance, as it presents the transport of pollutants in the Mediterranean region. Another important station is Çatalca station since its representativeness of the pollutants comes from the weather systems in southwest, west and northwest (İlhan, Öz, Dündar, Kenet, & Balta, 2006).

Automatic rain collection stations are located in Çatalca Radar Transmitter Station, Balıkesir Radar Transmitter Station, Amasra Observatory Park, Antalya-Bük Forest Sub-District Directorate. Automatic rain collecting sampler has significance in determining the source and path of air pollution. It is important to determine the amount and quality of pollutants carried by atmospheric convection.

Furthermore, the automatic rain collecting system, called the Andersen type rainfall sampler allows collection of wet and dry depositions separately. The automatic deposition samplers have two buckets for collecting wet and dry depositions separately, a moving lid to cover only one of these buckets, and a precipitation sensor that sends signals in order to provide the covering of dry deposition bucket during raining. Figure 4.2 shows the automatic rain collecting system which is used by the rain collecting stations in this study.

Figure 4.2 Automatic rain collecting system (İlhan et al., 2006)

In rain collection stations, transparent polyethylene nylon bags placed in buckets and wet samples are changed daily (falling rainfall in last 24 hours). Polyethylene bags in dry deposition bucket are changed weekly. Samples are sent to the Meteorological Service after labelling.

Wet samples are weighed in precision scales and transferred to sample bottles with sampling numbers. Dry samples are washed with ultra-distilled water and transferred to sample bottles. Bottled samples are kept under UV lights for 30 minutes to inhibit microbiological activities inside the sample water. Acidic level of samples is measured by 2001 model Selecta pH meter which is shown in Figure 4.3. After measuring the acidic level, the samples are transferred to the refrigerator for ion analysis. Ion analysis is performed by an electrical conductivity meter named Selecta CD 2002 model.

Figure 4.3 Selecta pH meter (Meteorological Service of Republic of Turkey archive, n.d.)

4.1 Analysis of Acid Rain Data

Nitrate, sulfate and pH data is analyzed on SPSS 16.0. Table 4.1 shows the summary of the related data. Time series analysis of Nitrate concentration for all stations is presented in Table 4.2. Tables 4.3 and 4.4 illustrate the time series analysis of sulfate concentration and pH degree respectively. It is shown that the acid rains in some stations exhibit a periodic trend in spite of nonlinear behavior of certain acid rain characteristics. Amasra and Çatalca stations have the largest number of data because they have more rainy days than other stations. Amasra station also has the most acidic rain water by comparison with the other stations. It results from the air pollution which is transported from the Northwest Europa and Siberia to Black Sea Region.

Table 4.1 Summary of Sulfate, Nitrate and pH Data

Station	**Start Year**	**End Year**	**# of Data**
Amasra	2004	2016	2364
Antalya	2005	2016	1718
Balıkesir	2004	2016	1636
Çatalca	2005	2016	2496
Total			**8214**

Table 4.2 Mean, Highest, Lowest Degree and Standard Deviation of Nitrate Concentration (ppm)

Station	Mean	Highest	Lowest	Standard Deviation
Amasra	7.23	169.04	0	12.52
Antalya	4.49	278.04	0	13.26
Balıkesir	8.69	289.75	0	18.03
Çatalca	8.92	286.04	0	16.81

Table 4.3 Mean, Highest, Lowest Degree and Standard Deviation of Sulfate Concentration (ppm)

Station	Mean	Highest	Lowest	Standard Deviation
Amasra	11.62	154.39	0	16.46
Antalya	5.49	230.62	0	16.02
Balıkesir	10.91	241.23	0	18.69
Çatalca	13.41	282.28	0	25.04

Table 4.4 Mean, Highest, Lowest Degree and Standard Deviation of pH degree

Station	Mean	Highest	Lowest	Standard Deviation
Amasra	5.53	8	4	1.04
Antalya	6.32	8	4	0.78
Balıkesir	6.07	8	3	0.90
Çatalca	5.90	8	3	0.91

4.2 Time Series Analysis

Before a qualitative and quantitative analysis, one-dimensional time series should be analyzed to understand the nature of the system's dynamic. Natural events mostly have nonlinear behavior. In order to determine this nonlinearity, analyzing dynamic state variables help us to observe information about the time series of dynamic systems. In this thesis, time series analysis is performed with the data from the rain collection stations in Amasra, Antalya, Balıkesir and Çatalca between the years 2004 and 2016.

MATLAB software program is used for chaotic analysis and SPSS 16.0 software program is used for the basic statistical analysis of the data. Time series graphic of Nitrate concentration for Amasra station is shown in Figure 4.4. The other time series graphics for each station are presented in Appendix A1. For Amasra station, time series of nitrate, sulfate concentration and pH degree are shown in Figures A1.1 through A1.3, respectively. Figures A1.4 through A1.6 in Appendix A1 show the time series of nitrate, sulfate concentration and pH degree for Antalya station. For Balıkesir station, time series of nitrate, sulfate concentration and pH degree are demonstrated in Figures A1.7, A1.8 and A1.9, respectively. Finally, Figures A1.10 through A1.12 presented in Appendix A1 depict the time series of nitrate, sulfate concentration and pH degree for Çatalca station.

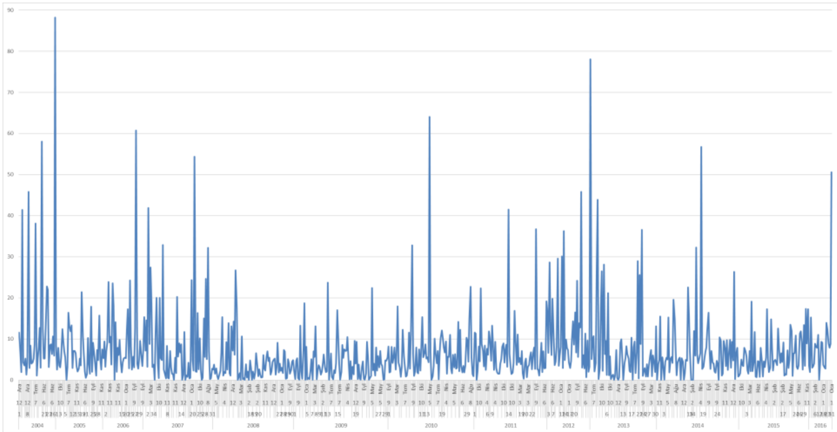

Figure 4.4 Time series graphic of Nitrate concentration (ppm) for Amasra station

As the time series graphs indicate, the parameters do not include any periodicity. It is a way to start investigating chaotic behavior in these systems. In the next section, chaotic detecting methods will be applied to these time series.

4.3 Chaotic Time Series Analysis

4.3.1 Lyapunov Exponents

The presence of the largest positive Lyapunov exponent is the most important indicator of the chaotic behavior of the time series. The largest Lyapunov exponents were calculated on MATLAB for all stations. The largest Lyapunov exponent example of Nitrate concentration for Amasra station is shown in Figure 4.5.

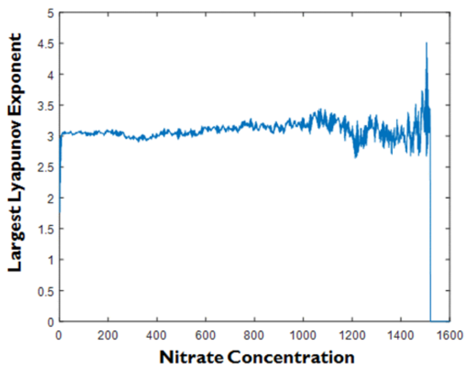

Figure 4.5 Largest Lyapunov exponent of Nitrate concentration for Amasra station

The largest Lyapunov Exponent graphics for each station are presented in Appendix A2. For Amasra station the largest Lyapunov exponents of nitrate, sulfate concentration and pH degree are shown in Figures A2.1 through A2.3, respectively. Figures A2.4 through A2.6 in Appendix A2 show the largest Lyapunov exponents of nitrate, sulfate concentration and pH degree for Antalya station. For Balıkesir station the largest Lyapunov exponents of nitrate, sulfate concentration and pH degree are demonstrated in Figures A2.7, A2.8, and A2.9, respectively. Finally, Figures A2.10 through A2.12 in Appendix A2 show the largest Lyapunov exponents of nitrate, sulfate concentration and pH degree for Çatalca station. All stations have at least one positive Lyapunov exponent and according to the graphics it can be said that this dynamic system has chaotic behavior and it is not possible to make long-term prediction. It means that neighbor orbits in the phase space are diverging each other and they are sensitive to initial conditions.

4.3.2 Power Spectrum

Power spectrum analysis is another method for detecting chaotic signals of a dynamic system. The continuity of the peaks in the power spectrum indicates the presence of chaotic behavior in the time series. Power spectrum graphics for all stations were drawn on MATLAB. The Power spectrum graphic of Nitrate concentration for Amasra station is shown in Figure 4.6.

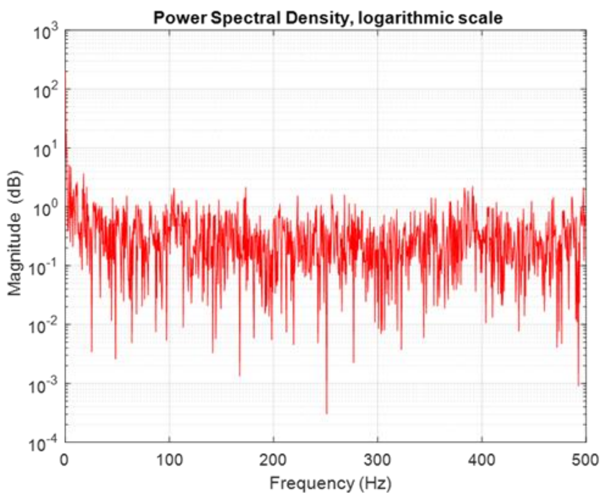

Figure 4.6 Power spectrum graphic of Nitrate concentration for Amasra station

Power spectrum graphics for each station are shown in Appendix A3. For Amasra station, Power spectrum of nitrate, sulfate concentration and pH degree are shown in

Figures A3.1 through A3.3, respectively. Figures A3.4 through A3.6 in Appendix A3 demonstrate Power spectrum of nitrate, sulfate concentration and pH degree for Antalya station. For Balıkesir station, Power spectrum of nitrate, sulfate concentration and pH degree are displayed in Figures A3.7, A3.8, and A3.9, respectively. Finally, Power spectrum of nitrate, sulfate concentration and pH degree for Çatalca station are shown in Figures A3.10 through A3.12 in Appendix A3. According to the power spectrum graphics, it can be said that this dynamic system has chaotic behavior due to significant peaks.

CHAPTER FIVE
CONCLUSION AND FUTURE RESEARCH

The nature we live inside is inevitable for the continuation of the ecological balance. It is necessary to determine the reasons of the changes in order to understand the nature we live in and to make the estimation possible. For many years, people have polluted the environment unconsciously and caused irreversible environmental damages. One of the kinds of pollution occurring in the atmosphere is acid rain. Acid rains have adverse effects on air, soil and living organisms. Acid rains can show their effects by long distance transport at thousands of kilometers. Therefore, pollution has become a growing problem between countries and international agreements have been signed for the purpose of prevention cross-border pollution. The demonstration that acid rain shows chaotic behavior is also important for future modeling studies. Thus, it will be easier to make forecasts for air pollution.

Chaotic structure can be observed at the every part of the natural systems. Acid rain is one of the natural systems where chaos can be examined. There is no study conducted on the chaotic structure of acid rain in the literature within our knowledge. Demonstration that acid rain has a chaotic structure like many other natural systems will be another proof that nature is controlled by chaos.

In this study, we aimed to investigate the chaotic structure of the acid rains which pours in Turkey. General information about acid rains and their effects, background information of the analyzed time series, mathematical explanation of the chaos theory and chaotic analysis methods were given in the content of thesis.

Sulphate and nitrate concentrations and pH degree on wet precipitation samples collected from four rain water collection stations in Turkey (Amasra, Antalya, Balikesir, Catalca) for the period between February 2004 and February 2016 were analyzed with chaotic analysis methods. Largest Lyapunov Exponent, reconstruction of the phase space, and power spectrum analysis methods were used as chaotic analysis methods. The most important criterion of the existence of chaos is having at least one positive Lyapunov exponent. This is also condition of the sensitivity to initial conditions. In this study, Lyapunov exponents were calculated on MATLAB. According to our calculations largest Lyapunov exponents of all the time series have at least one positive Lyapunov exponent. Thus, it can be observed that analyzed time series have chaotic structure. Power spectrum analysis is another criterion for detecting chaotic behavior. The continuity of the peaks in the power spectrum indicates the presence of chaotic behavior in the time series. Power spectrums were interpreted by drawing on MATLAB. Power spectrum graphs of all the analyzed time series shows continuity and wide band structure. These are other evidences of the existence of the chaotic behavior in the acid rains which pour in Turkey.

Based on the result of the study, we can conclude that acid rains showed chaotic structure like many natural phenomena in nature. This study is the first to examine the chaotic structure of acid rains to the best of our knowledge. The implementation results show that, it will be possible to obtain more accurate results in the estimation of acid rains in accordance with the chaotic structure and to take measures in the long term in order to prevent the possible negative consequences of air pollution. For the future research, other variables that influence the formation of acid rains can be used in order to better determine the chaotic structure of acid rains and/or this study can be extended to other geographically areas in the world.

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APPENDICES

APPENDIX A1. Time Series Graphics of Amasra, Antalya, Balıkesir and Çatalca Stations

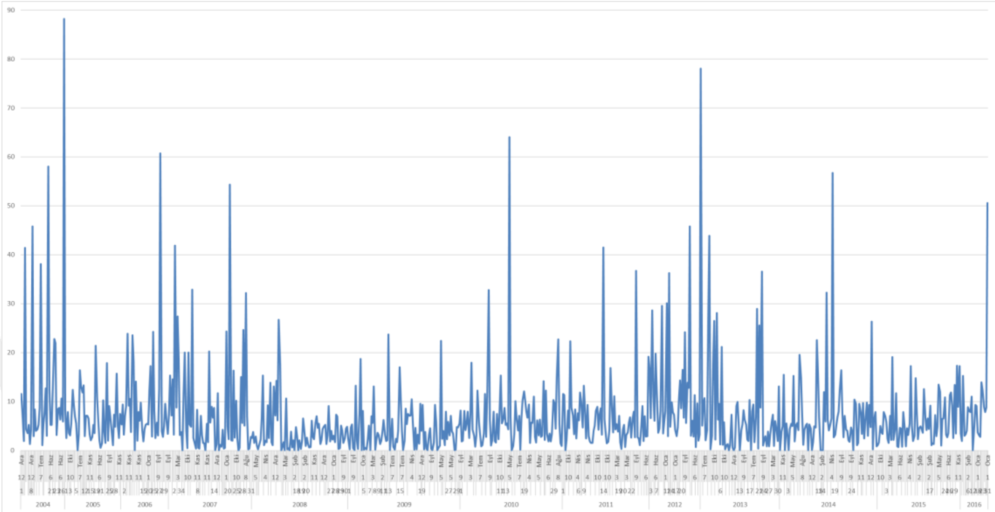

Figure A1.1 Time series graphic of Nitrate concentration (ppm) for Amasra station

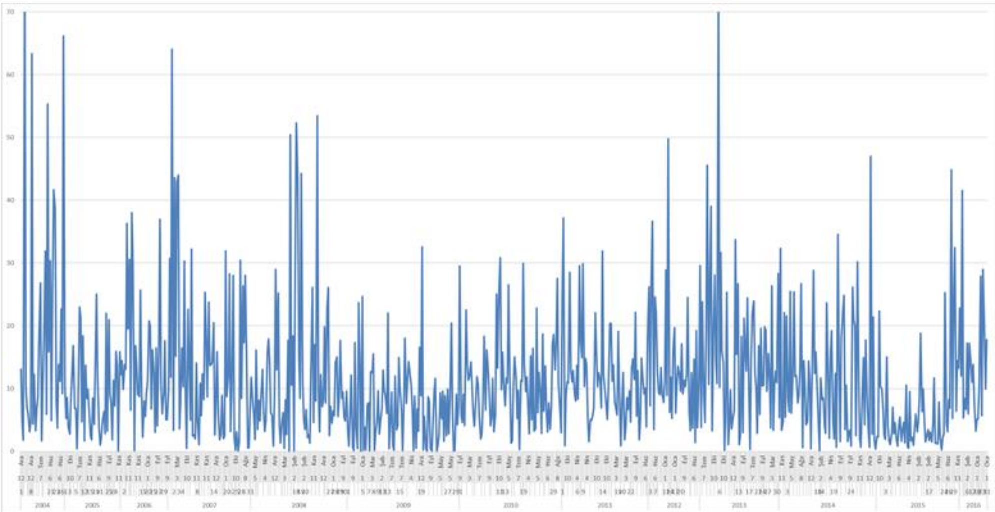

Figure A1.2 Time series graphic of Sulfate concentration (ppm) for Amasra station

Figure A1.3 Time series graphic of pH degree for Amasra station

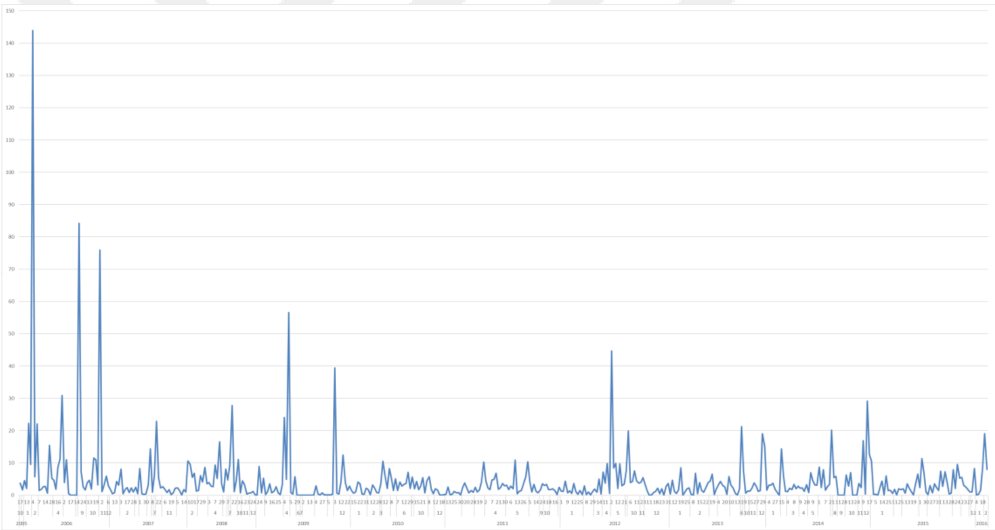

Figure A1.4 Time series graphic of Nitrate concentration (ppm) for Antalya station

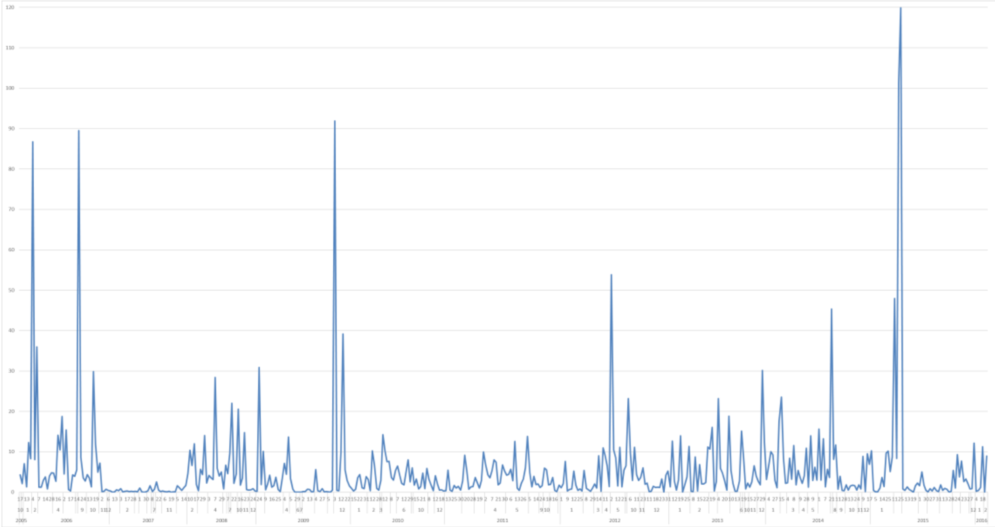

Figure A1.5 Time series graphic of Sulfate concentration (ppm) for Antalya station

Figure A1.6 Time series graphic of pH degree (Antalya station)

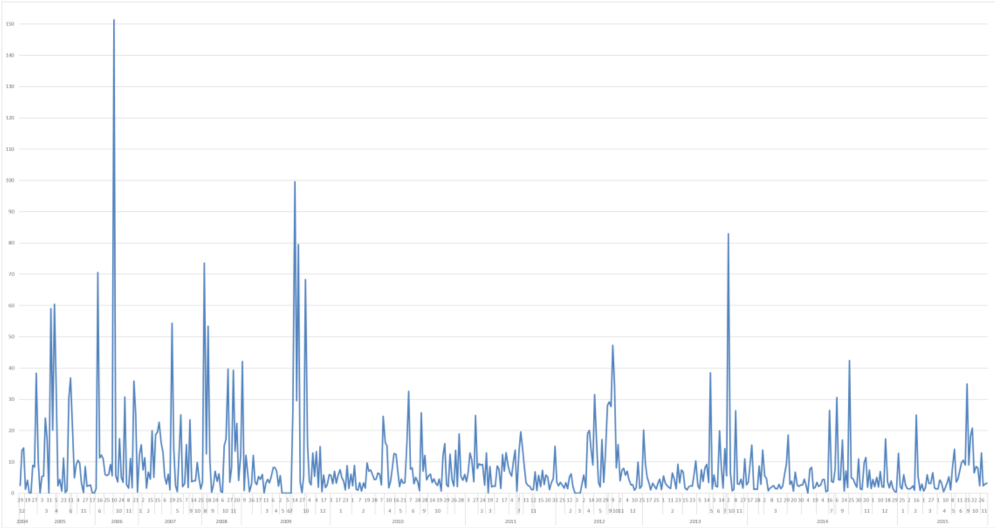

Figure A1.7 Time series graphic of Nitrate concentration (ppm) for Balıkesir station

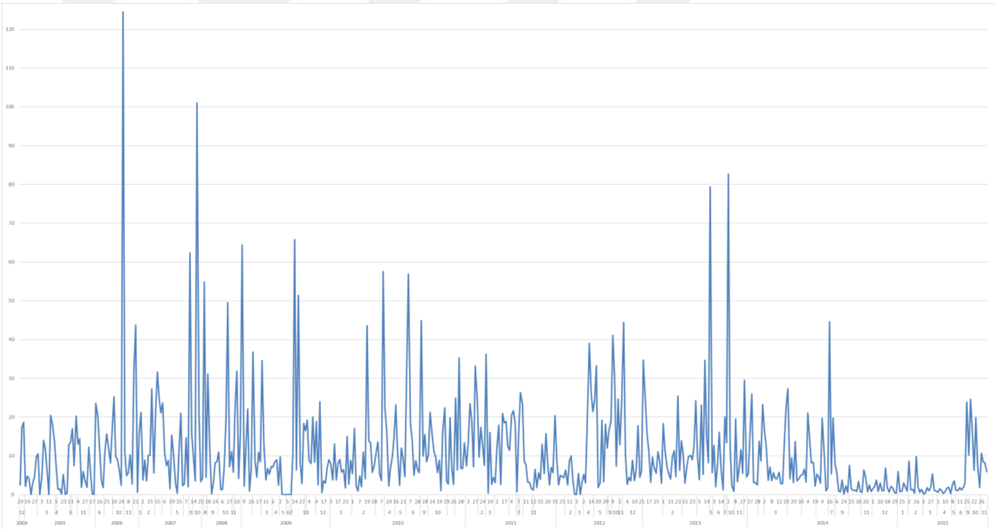

Figure A1.8 Time series graphic of Sulfate concentration (ppm) for Balıkesir station

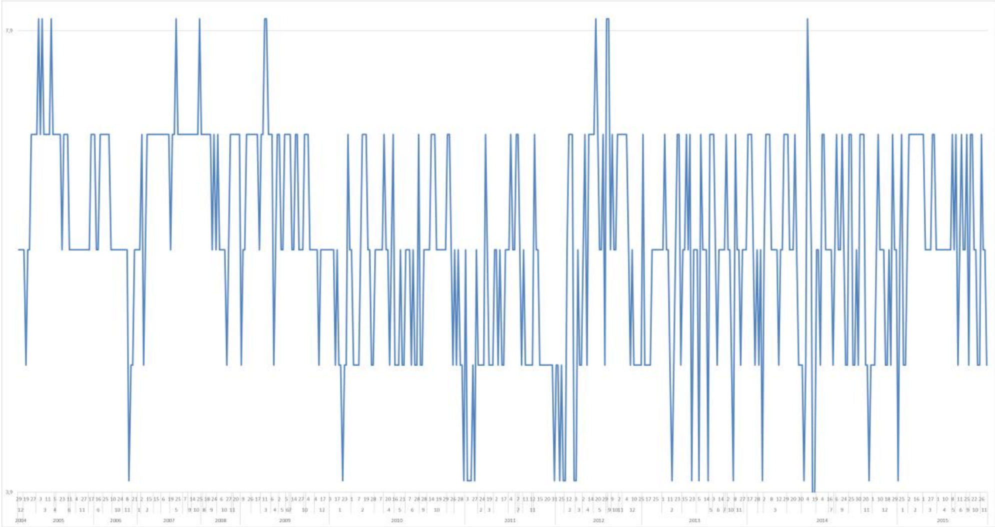

Figure A1.9 Time series graphic of pH degree for Balıkesir station

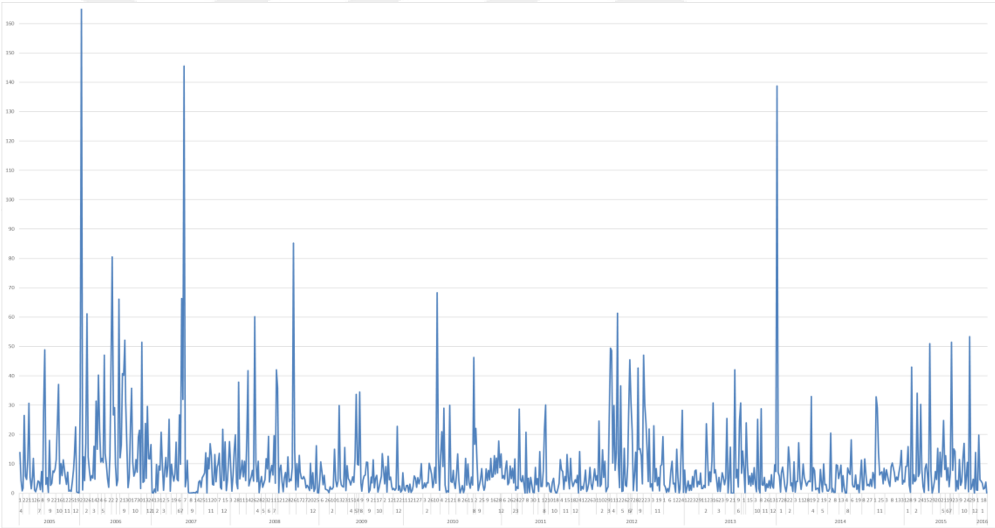

Figure A1.10 Time series graphic of Nitrate concentration (ppm) for Çatalca station

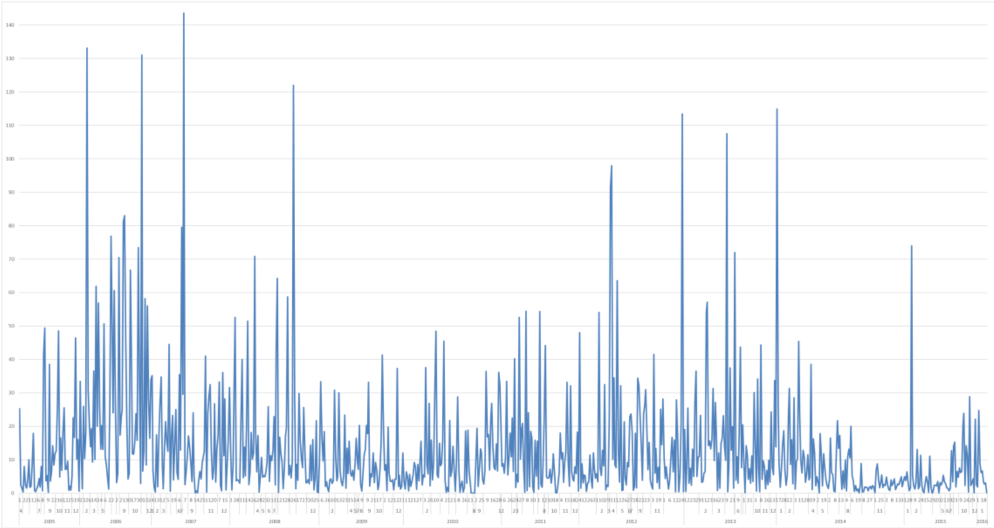

Figure A1.11 Time series graphic of Sulfate concentration (ppm) for Çatalca station

Figure A1.12 Time series graphic of pH degree for Çatalca station

APPENDIX A2. Largest Lyapunov Exponents Graphics of Amasra, Antalya, Balıkesir and Çatalca Stations

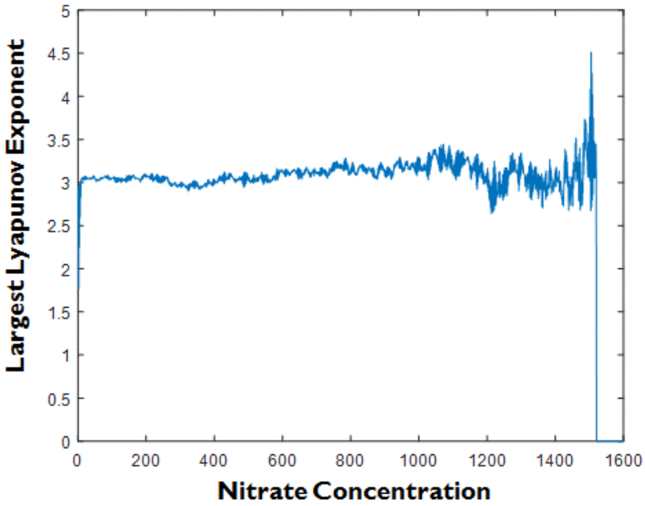

Figure A2.1 Largest Lyapunov Exponent of Nitrate Concentration for Amasra station

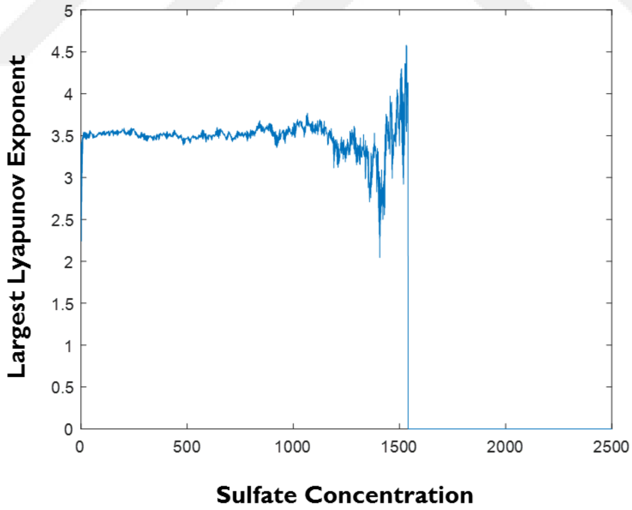

Figure A2.2 Largest Lyapunov exponent of Sulfate concentration for Amasra station

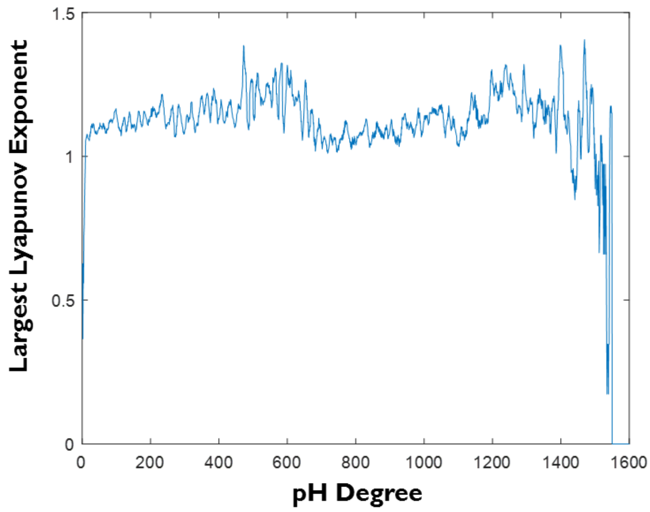

Figure A2.3 Largest Lyapunov exponent of pH degree for Amasra station

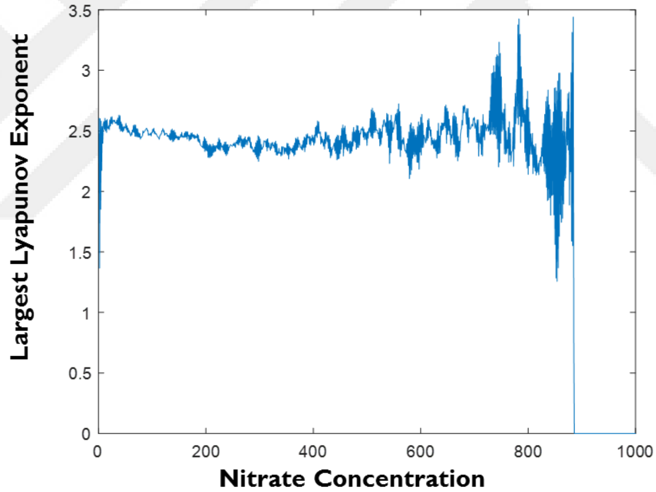

Figure A2.4 Largest Lyapunov exponent of Nitrate concentration for Antalya station

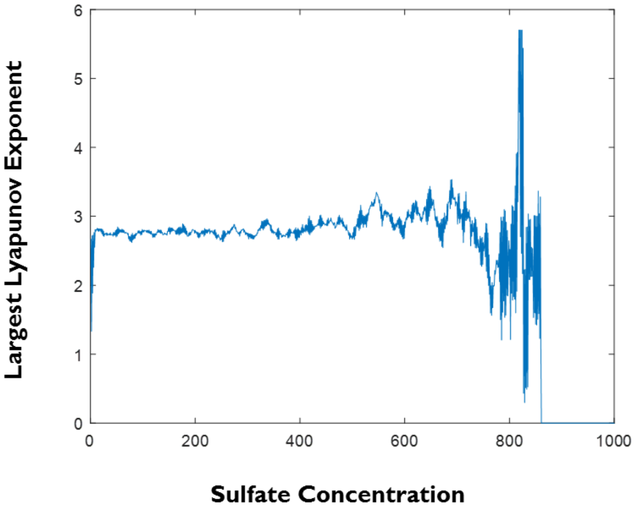

Figure A2.5 Largest Lyapunov exponent of Sulfate concentration for Antalya station

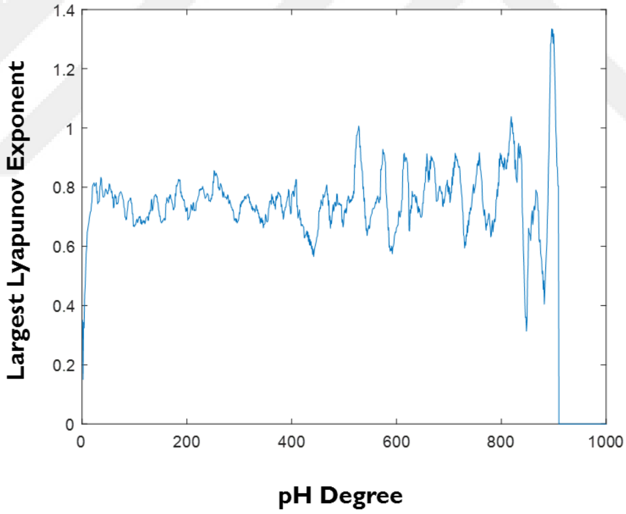

Figure A2.6 Largest Lyapunov exponent of pH degree for Antalya station

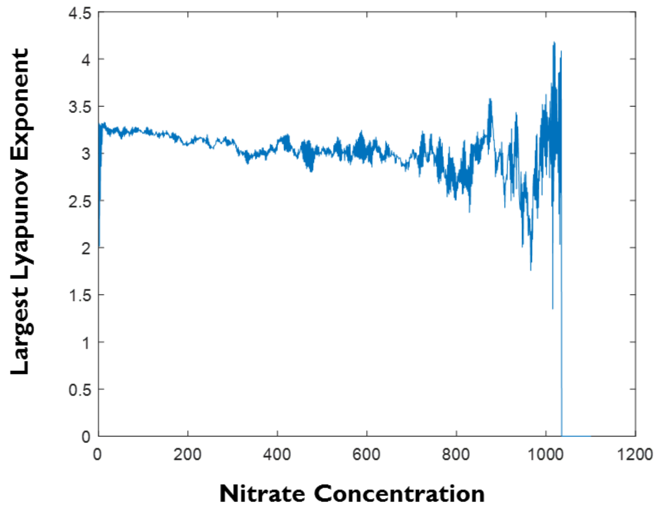

Figure A2.7 Largest Lyapunov exponent of Nitrate concentration for Balıkesir station

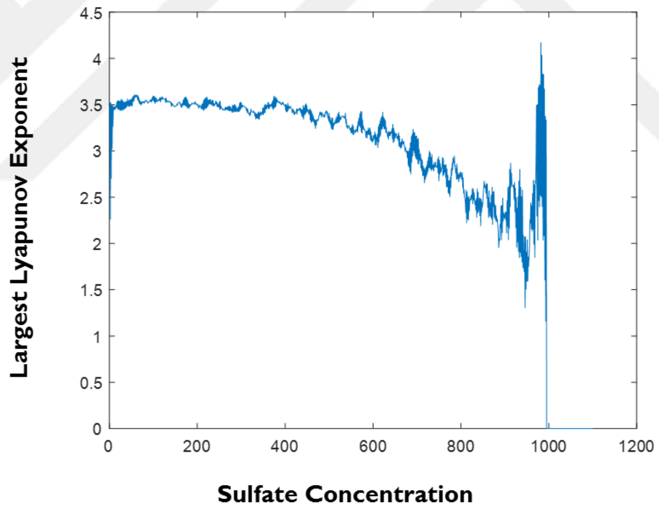

Figure A2.8 Largest Lyapunov exponent of Sulfate concentration for Balıkesir station

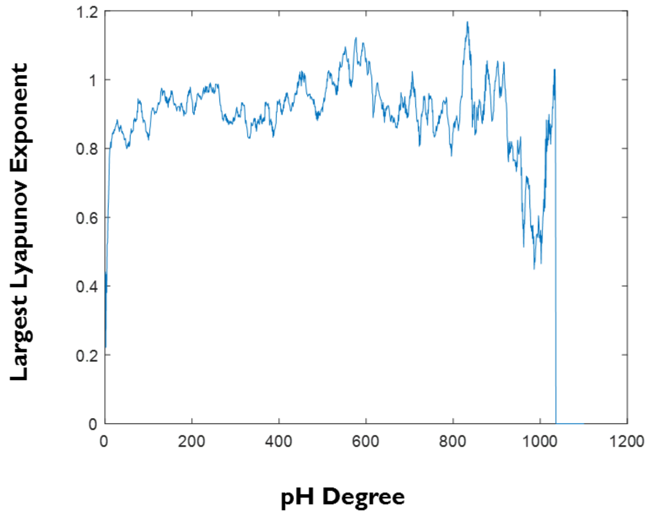

Figure A2.9 Largest Lyapunov exponent of pH degree for Balıkesir station

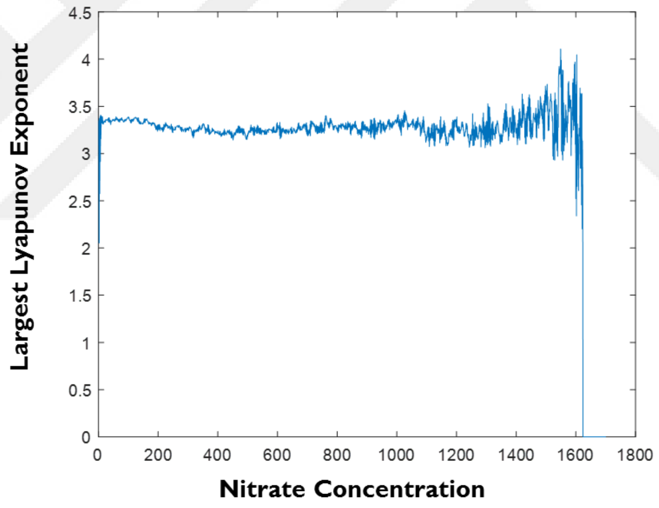

Figure A2.10 Largest Lyapunov exponent of Nitrate concentration for Çatalca station

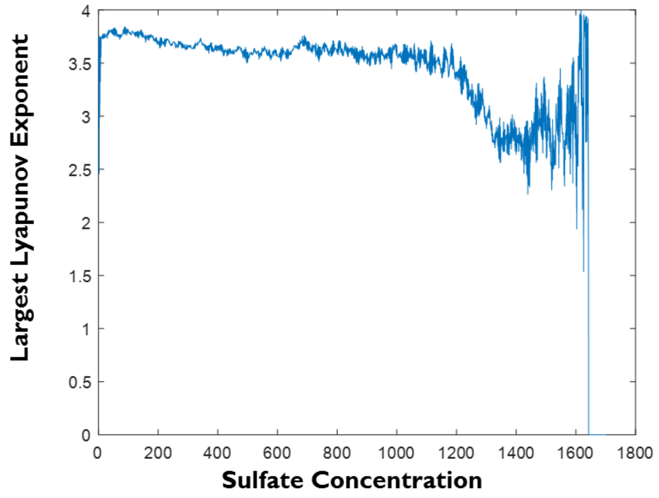

Figure A2.11 Largest Lyapunov exponent of Sulfate concentration for Çatalca station

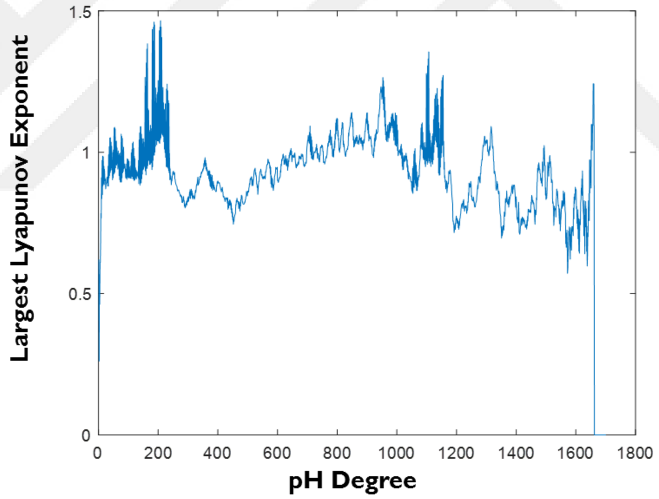

Figure A2.12 Largest Lyapunov exponent of pH degree for Çatalca station

APPENDIX A3. Power Spectrum Graphics of Amasra, Antalya, Balıkesir and Çatalca Stations

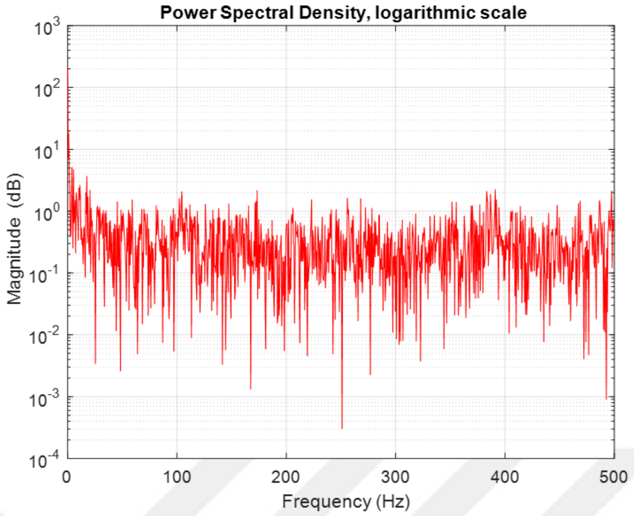

Figure A3.1 Power spectrum graphic of Nitrate concentration for Amasra station

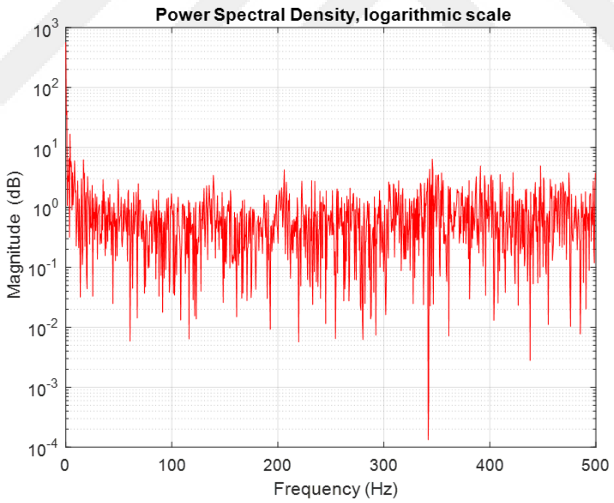

Figure A3.2 Power spectrum graphic of Sulfate concentration for Amasra station

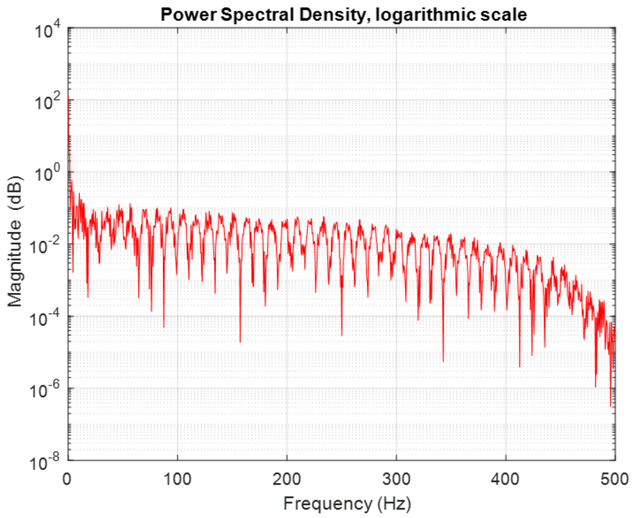

Figure A3.3 Power spectrum graphic of pH degree for Amasra station

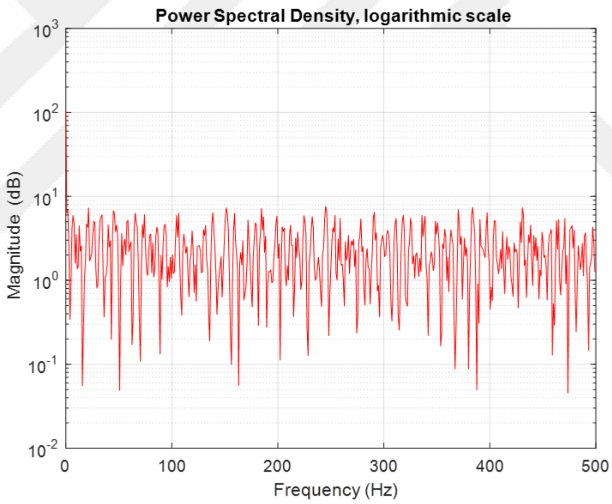

Figure A3.4 Power spectrum graphic of Nitrate concentration for Antalya station

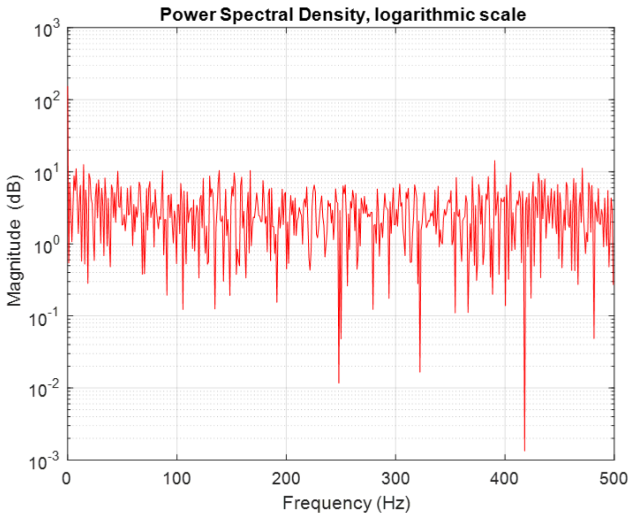

Figure A3.5 Power spectrum graphic of Sulfate concentration for Antalya station

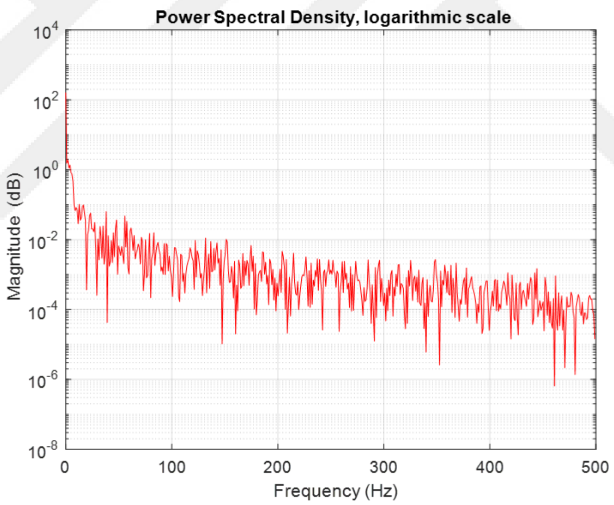

Figure A3.6 Power spectrum graphic of pH degree for Antalya station

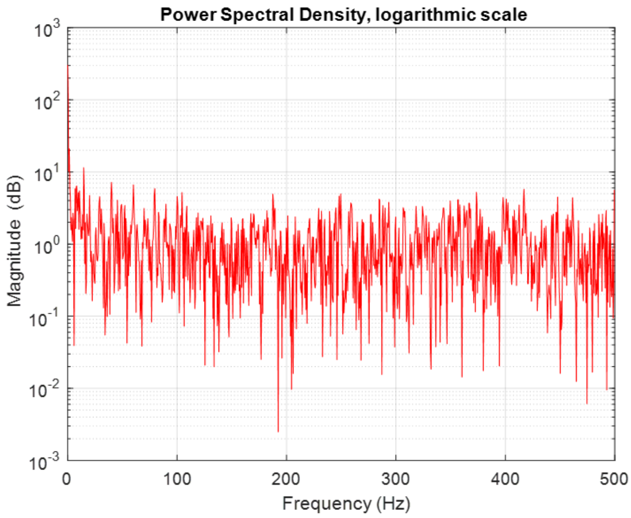

Figure A3.7 Power spectrum graphic of Nitrate concentration for Balıkesir station

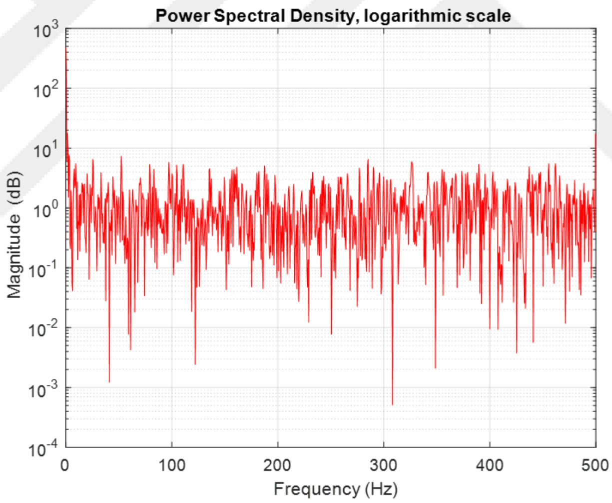

Figure A3.8 Power spectrum graphic of Sulfate concentration for Balıkesir station

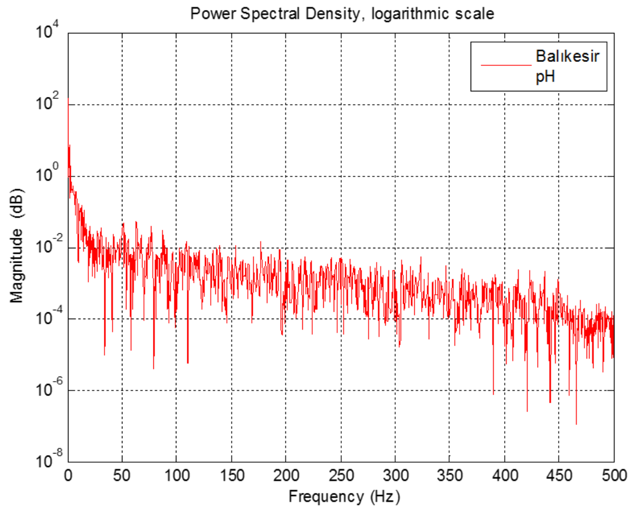

Figure A3.9 Power spectrum graphic of pH degree for Balıkesir station

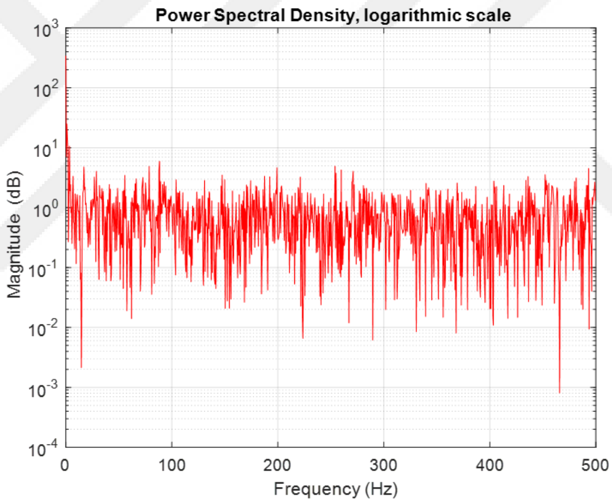

Figure A3.10 Power spectrum graphic of Nitrate concentration for Çatalca station

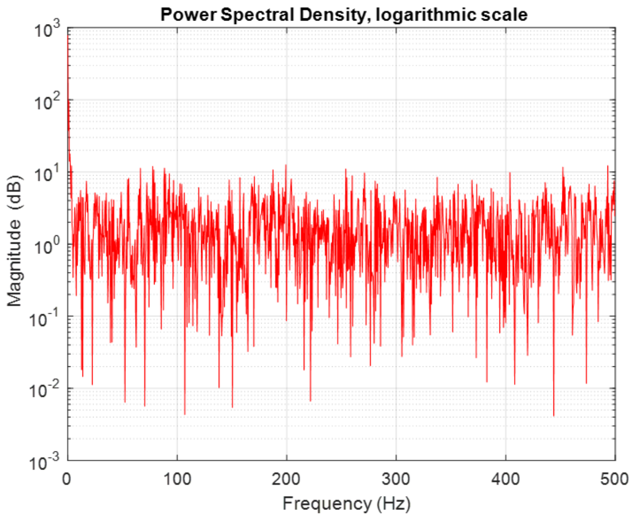

Figure A3.11 Power spectrum graphic of Sulfate concentration for Çatalca station

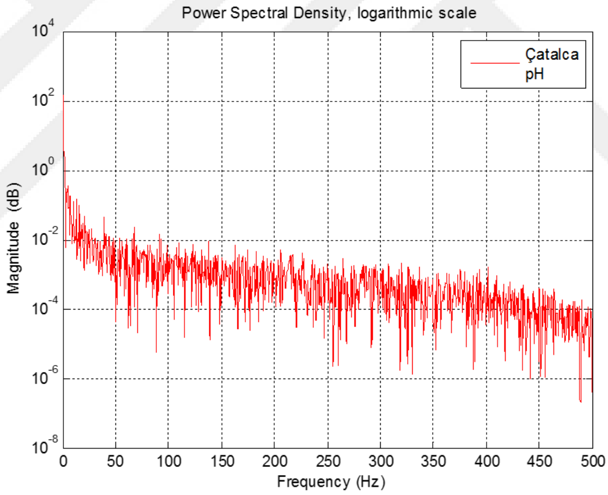

Figure A3.12 Power spectrum graphic of pH degree for Çatalca station