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Air Quality of the Black Sea Region: Local and Long Range Transported Pollutants

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Abstract

Catalysis has manifested its role as a fundamental tool in pollution prevention. While catalysis has long been utilized in increasing efficiency, yield, and selectivity, it is now also recognized as accomplishing a wide range of green chemistry goals. Air pollutants produced by industrial and man-made emissions possesses a unique property that it could affect regional and global receptors. Measuring and defining the levels of pollutants and its sources whether it is local, regional or global should precede the precautions and measures that should be taken to reduce the levels of a particular pollutant. In this article the air quality at the Black Sea region of Turkey is being discussed. Moreover, it endeavors to locate the possible sources of the different pollutants at local, regional and long range transported scales. About 196 rainwater samples were collected over the Black Sea region of Amasra between 1995-1999 and analyzed for major and trace ions.

Although statistical tools do provide information on the type of sources and processes affecting the site, they do not provide information on where these sources are located. A back trajectory has to be included in the evaluation to incorporate geographical information in analytical results. To compute the PSCF for each ion the back trajectories were computed using ECMWF model, which is an isentropic 3-D model. Then number of 1 hour-long segment of the 3.5 daylong trajectories in each defined sub-region is determined. This study shows that, the Black Sea region receives different amounts and types of anthropogenic pollutants via long-range transport according to trajectory models. The highest PSCF values for H^+ are calculated for central Europe and Russia have fairly high contribution to observed free acidity in our samples. The main source areas for SO_4^{2-} were found to be central Europe and Northwestern Turkey (Marmara region or Istanbul–Kocaeli industrial area).

Introduction

The driving force behind much of the research in the atmospheric sciences today is the recognition that anthropogenic activity may be altering (perturbation) Earth's climate

Scientists have discovered that air pollution from the burning of fossil fuels is the major cause of acid rain. Acidic deposition, or acid rain as it is commonly known, occurs when emissions of sulfur dioxide (SO_2) and oxides of nitrogen (NO_x) react in the atmosphere with water, oxygen, and oxidants to form various acidic compounds. This mixture forms a mild solution of sulfuric acid and nitric acid. Sunlight increases the rate of most of these reactions [1, 3].

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The recognition that man has started to perturb the atmosphere on a global scale has provoked wide spread attention to this problem. The discovery of the ozone hole and the world wide discussion of the greenhouse effect have generated a public interest for atmospheric chemical processes, environmental mechanisms and equilibria. The basis for any such discussion is, however, rather rudimentary due to a lack of relevant analytical data in many areas around the globe [1].

Source Oriented Models

Trajectory models, which describe the paths air parcels take, have been used to study dynamical processes in the atmosphere for several decades now.

Applications vary from synoptic meteorology, for instance to investigate air-mass flow around mountains, to climatology, for instance to identify pathways of water vapour transport or desert dust, to the environmental sciences, for instance to establish source-receptor relationships of air pollutants. They may be even used to detect illegal cultivation of marihuana by combining pollen measurements in the ambient air with back trajectories [2].

Many workers to predict the ambient concentrations of air pollutants used emissions inventories and dispersion models. Many researchers have criticized these models because they are inadequate in many aspects. For the limitations possessed by the later models, receptor modelling has attracted many workers in the last decades because it is based on source contribution by various source regions.

Potential Source Contribution Function (PSCF)

Several methodologies using trajectory analyses have been applied to study emitter-receptor relationships for acidic species collected in precipitation and, in particular, a receptor-oriented methodology called *PSCF*. Since its creation in 1985, the receptor-oriented methodology has been developed by several authors and successfully applied to various atmospheric species. A previous study has shown that the receptor-oriented methodology developed by Seibert et al. (1994) provides maps of potential sources, which could be used to examine the quantitative relationships between concentrations in rain and emissions [3-5].

In this technique, meteorological data is used to draw trajectories in order to predict and correlate the composition of collected rainwater by matching the time of arrival of each trajectory at the receptor site. The PSCF were calculated every one hour trajectory segment for each single grid cell (5° longitude by 5° latitude) by counting each end point that terminates within that grid cell [2,6].

The number of end points of segments of trajectories in each of the defined sub-regions was used to calculate *PSCF*. If we assume that N is the total number of trajectory segment end points for the whole study period and the number of end points that fall in the j^{th} cell is n_j, then the probability of an event at the receptor site is related to that cell, A_j, over entire study period T is given by the relation:

$$P(A_j) = \frac{n_j}{N}$$

$P(A_j)$ is the residence time of a randomly selected air parcel on the j^{th} sub-region relative to the time period T.

By the same manner, for the same cell, if there are m_j end points whose arrival times of air parcels correspond the events with pollutant concentrations (concentrations with high values than geometric mean), the probability of that polluted event "matched" event, B_j is given by;

$$P(B_j) = \frac{m_j}{N}$$

Then we can define thee PSCF for the j^{th} as:

$$PSCF = P(B_j)/P(A_j) = \frac{m_j}{n_j}$$

The *PSCF* is the probability of a polluted air mass with a specific concentration to arrive at the receptor site. These *PSCF* are indication of areas of high potential contributions to the pollution at a receptor site. It is important to note that the exact location of the source(s) within the high potential areas is unknown in the present analysis because of the fundamental limitation of the *PSCF* methodology that cells must be large enough to have a reasonable number of counts in them, and the uncertainty involved in calculating the backward air parcel trajectories [2, 7-9].

Material and methods

Air quality monitoring station was established in 1992 at the Western Black Sea Coastal site of Turkey (41° 47' N and 32° 29' E), 20 km to the east of Amasra town (Fig. 1) and 3.5 km far from the Black Sea shore. The station is located approximately 150 m above sea level.

Rainwater is a good indicator about the quality of atmosphere in a specific region. It could provide information on the local and long range-transported pollutants to the study area.

Rainwater samples were collected using modified Anderson rain sampler. The collected rain events were stored in 1-liter polyethylene bottles and analyzed for pH using slandered pH meter and pH electrode (Orion), Cl^-, SO_4^{2-} and NO_3^- using HPLC (Varian 2010 (Vydac column with Jasco 875 UV/VIS detector). Trace metals (Cr, V, Pb, Cd and Ni) were analyzed by GFAAS (GF-AAS (Perkin Elmer 1100B Spectrometer coupled with HGA 700 Atomization unit).

Fig. 1. Sampling site at the Black Sea region of Turkey.

Results and Discussions

Concentrations of pollutants in the Black Sea precipitation show fairly well defined seasonal variations. Similar variations are also observed in the eastern and western Mediterranean aerosol and rainwater [7].

The average pH value in rainwater is 5.21. Very similar to annual pH found in the eastern Mediterranean [7]. Such pH indicates that the rainwater is not acidic. The interaction between the water droplets and the carbon dioxide in the atmosphere gives rain a pH of 5.6 [10], making even clean rain slightly acidic. For that reason pH values between 5.0-5.6 do not considered highly acidic.

Trajectories of hydrogen ion indicate that Europe contributes for low pH values whenever there is any wind blow from northern or western sectors (Fig. 2). It is known that these sectors include the most industrialized countries in Europe in addition to former-USSR, where controlled industry is rare. Contrary to this observation, when the sampling site receives air masses from north west the pH values are higher than those obtained from northern and western sectors

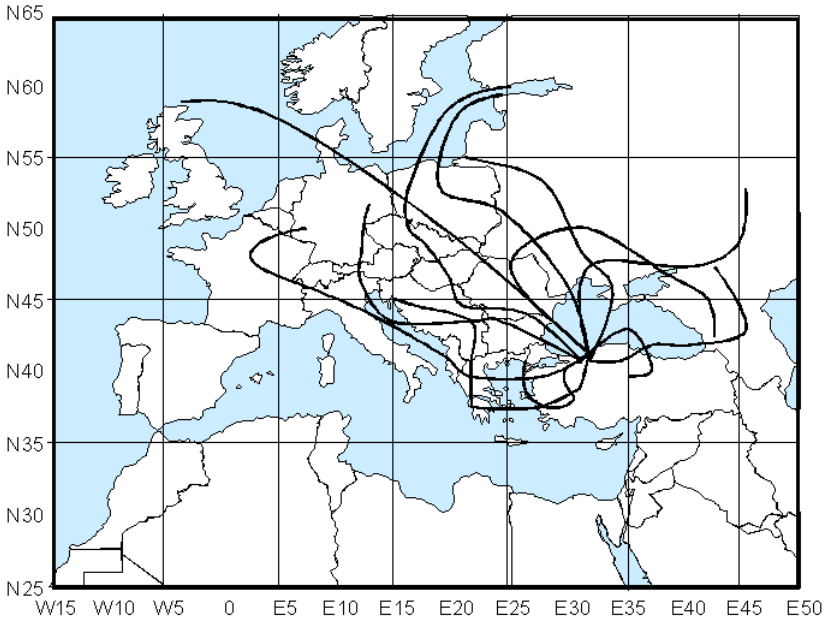

Fig. 2. Trajectories Corresponds to pH<5 values.

Potential Source Contribution Function (PSCF)

Investigation of trajectories that correspond to high factor scores provides preliminary information about the general wind directions from where these pollutants components are transported. One of the key questions that should be answered in this study is that "from where pollutants affecting the sampling site originates?"

Trajectory calculations are a common tool to relate concentrations of pollution-derived parameters with geographical information. The simplest approach that can be used for this purpose is to visually assign each polluted trajectory (trajectory that corresponds to samples with high concentrations of one of the anthropogenic elements) to a wind sector and try to determine common directions where polluted air masses originate. Which is an approach we used in identifying factors in the previous section. This simplistic approach can only provide qualitative results as a first approximation, because most of the trajectories do not stay in one sector during whole transport time, but crosses sectors which makes assigning trajectories to one of the sectors a difficult task. Another drawback of this approach is that all the countries and regions in a sector should be considered as one source area, because there is no way to differentiate between them.

In recent years source region apportionment in regional scale is being done by a more sophisticated approach called "trajectory statistics". In trajectory statistics, each trajectory is divided 1 hr long segments (commonly called trajectory end points) and each segment is treated separately in secular approach.

There are a number of statistical techniques used for this purpose [6,2,9,8,11-14]. The most commonly used technique, which is also the technique used in this study is Potential Source Contribution Function (*PSCF*). In *PSCF*, the study area (which covers a region from west of the UK on the west to the middle of Asia and From Siberia to the middle of Africa) is divided into sub regions and potential contribution of each sub region on each of the elements is calculated. Each of the country in Europe is assigned as a sub region. Turkey was divided into 4 separate sub regions as west, northwest central and east Turkey. The sub regions that lie to the east and south of the station are kept larger. The following considerations were taken into account in selecting sub regions:

1. Each country in Europe was selected as a sub region, because ultimately we would like to know contribution of each country on observed pollution levels on the Black Sea coast. The 150 km × 150 km EMEP grid system was the starting point for calculations. The trajectory segments in each EMEP grid was counted using a technique developed at our group, then grids are combined to form countries. The EMEP interest area is the continental Europe. Consequently, the grid system does not cover all of our study area, which includes parts of Asia, Middle and Africa. The formulation that was used to calculate grid coordinates was obtained from EMEP Coordinating center-west (NILU, Norway) and their grid system was extended to cover our study area.
2. The sub regions should be large enough to have statistically significant number of trajectory segments. The reliability of the contributions of sub regions depends on the availability of statistically significant number of trajectory segments (or end points) in each sub region. For example if there is only one trajectory segment in a given sub region, and if that segment corresponds to a polluted trajectory, then that particular sub region may appear as having the highest contribution to the observed pollution at our receptor site. To avoid this significance problem, sub regions with fewer than 10 segments are either is not included in the *PSCF* calculations or combined with other sub regions. Some small countries in Europe are combined with this reasoning. Since the air mass transport to the Black Sea is not frequent from east and south wind sectors, the sub regions in these sectors had to be larger in size to have adequate number of trajectory end points. This did not cause a resolution problem, because the countries lying to the east and south of the sampling point are not industrialized countries and identification of regions but not individual countries was sufficient.

To calculate the *PSCF* of an element or ion first, fractional residence time of air masses [$P(A_j)$] was calculated using the following formulation

$$P(A_j) = \frac{n_j}{N}$$

Where, n_j is the number of trajectory segments in a sub region and N is the total number of trajectory segments in the whole study area.

In the second step, fractional residence time of polluted air masses [$P(B_j)$] were calculated using the following equation:

$$P(B_j) = \frac{m_j}{N}$$

Where, m_j is the number of polluted trajectory segments in sub region *j*, and *N* is the total number of trajectory segments. The polluted trajectory is a trajectory that corresponds to "high concentration" of the test element. High concentration is a tentative term. In this study, a concentration of an element that is higher than its geometric mean is considered to be high. It should be noted that the elements are log normally distributed and their population is represented correctly by geometric mean. The arithmetic mean is approximately 2.0 to 2.5 times higher than geometric mean. Approximately 30% of the data are higher than arithmetic mean value of an element.

Finally the *PSCF* is calculated by dividing $P(A_j)$ with that of $P(B_j)$.

$$PSCF = P(B_j)/P(A_j) = \frac{m_j}{n_j}$$

There were approximately 30 sub regions and for each element n_j and m_j values must be determined by simply counting number of segments in each sub region, which was a tedious task if done manually. Most of the counting was done by software developed in our group. The software counted the segments in each EMEP grid and combined the grids to determine number of segments in countries or sub regions.

It should be pointed that, for sub regions consisting of countries (Europe) there was a small problem. In most cases, the borders of the countries do not exactly match with the borders of the grids. In these cases the closest possible match was performed. This was not a serious problem when the sub region is not a country, because in those cases sub region boundaries were adjusted to be the same with grid boundaries.

The ECMWF trajectory model, which is used in this study, calculates back trajectories in three levels 900 mb (ground level), 850 mb which corresponds to 1500 m altitude and 700 mb level which corresponds to 3000 m. In this study, the segments from both 850 mb and 700 mb in each sub region is counted and summed up. Consequently the approach used in this study is 3D *PSCF* rather than simple *PSCF*, which refers to calculations based on single layer (either 850 mb or 700 mb). The ground level (900 mb) trajectories were not included in the calculations, because it is well documented that long-range transport is not possible at the ground level due to rapid deposition of pollutants at the boundary layer.

The distributions of *PSCF* for anthropogenic elements and ions SO_4^{2-}, H^+, Ni, and NO_3^- are given in Figs. 3-6, respectively. The highest PSCF values for H^+ are calculated for Germany and Poland. United Kingdom, former Czechoslovakia, Hungary and Russia also have fairly high contribution to observed free acidity in our samples.

The main source areas for SO_4^{2-} are: Germany-

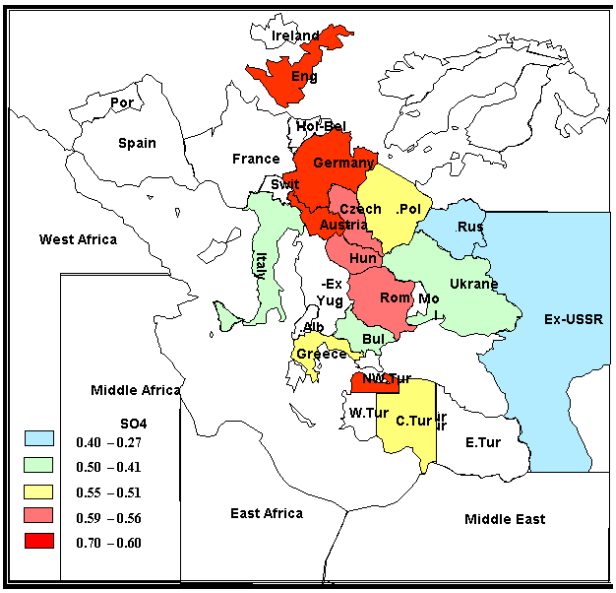

Fig. 3. Potential Source Contribution Function for SO_4^{2-} at 850 mb.

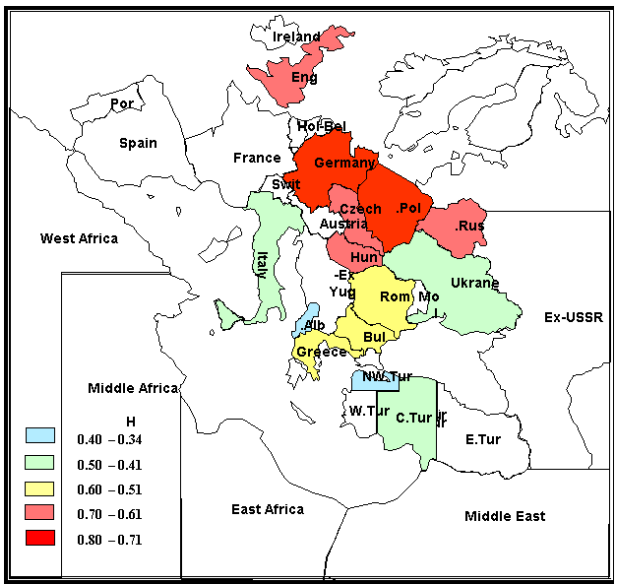

Fig. 4. Potential Source Contribution Function for H^+ at 850 mb.

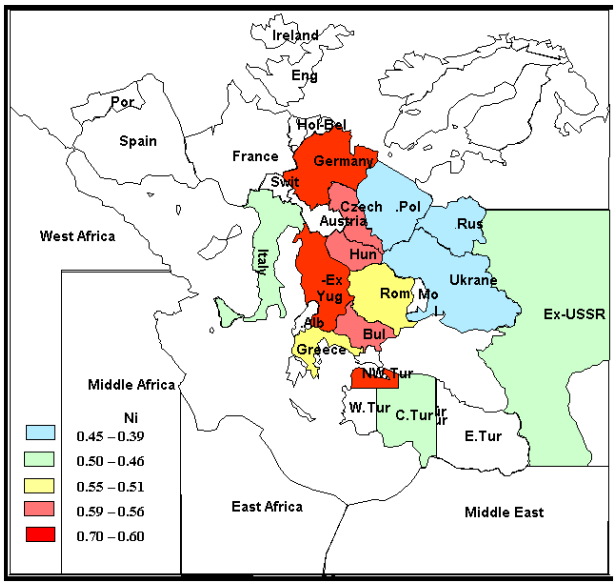

Fig. 5. Potential Source Contribution Function for Ni at 850 mb.

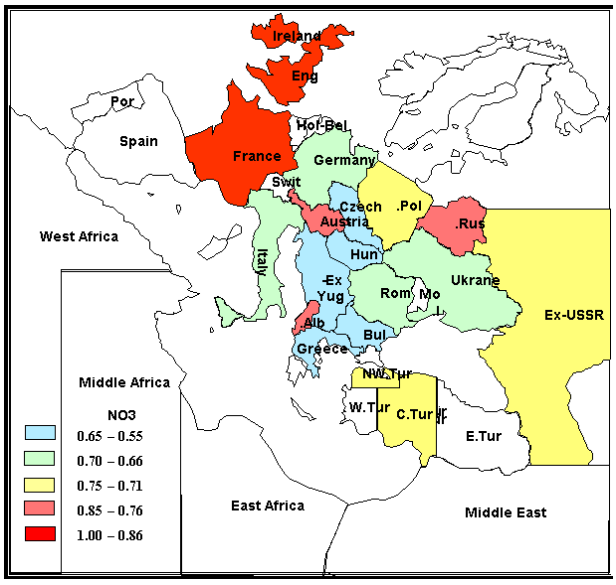

Fig. 6. Potential Source Contribution Function for NO_3^- at 850 mb.

Austria, UK and Northwestern Turkey (Marmara region or Istanbul–Kocaeli industrial area). Former Czechoslovakia, Hungary and Romania are the secondary SO_4^{2-} sources effecting Black Sea atmosphere. One of the most important species among those found in rainwater is H^+. Potential source regions for acidity are Germany and Poland followed by Russia, Austria and Hungary. The main sources for NO_3^- are France, England, and Ireland in addition to Russia. These countries are one of the most industrialized countries in Europe. Although they have many restrict regulations about emission levels, yet they emit large quantities of acid forming species into the atmosphere due to the huge industries they have. Cadmium has local sources in addition to other strong sources from Greece and to a less extent from former USSR, Ukraine, Hungary and Romania. The local emissions belong to the western part of Turkey, where most of the big industry is located. Pb is known to be related to the automobile emissions. It has a big contribution from Europe namely, Germany, former Yugoslavia, Romania Russia and former USSR. Central and western Turkey are local source regions for this element. Most of the European countries are less industrialized countries, the use of un-leaded gasoline is common among all the developed countries in Europe, while undeveloped countries still using leaded gasoline or both of them. Ni is known to be used in many industries including batteries industry. The main source regions for this element are Germany, former Yugoslavia and western Turkey.

In general, Europe is seem to be the potential source region for the most high levels of toxic elements found in rainwater collected at Black Sea region. Furthermore, western turkey is a potential source for acidity forming species, namely SO_4^{2-}. The crustal elements are originated mainly from middle Africa, former USSR and central Turkey.

Conclusion

During the period between April 1995 and December 1999, the chemical characteristics of the rainwater and the aerosol have been studied at Amasra, an agricultural area located in the Black Sea region. A total of 196 rain samples were collected by means of Anderson wet and dry only rain sampler. The elucidation of rainwater composition includes the determination of 20 different ions in soluble and insoluble fractions of rain.

The average pH value in rainwater is 5.21. Very similar to annual pH found in the eastern Mediterranean. Such pH indicate that the rain water is not acidic. Trajectories of hydrogen ion indicates that Europe contributes for low pH values whenever there is any wind blow from northern or western sectors

Potential Source Contribution Function (*PSCF*) statistical techniques were used in this study to identify the source region of the different rain components. The highest PSCF values for H^+ are calculated for Germany and Poland. United Kingdom, former Czechoslovakia, Hungary and Russia also have fairly

high contribution to observed free acidity in our samples. The main source areas for SO_4^{2-} are Germany-Austria, UK and Northwestern Turkey (Marmara region or Istanbul–Kocaeli industrial area). Former Czechoslovakia, Hungary and Romania are the secondary SO_4^{2-} sources effecting Black Sea atmosphere. The potential source regions of the first factor of factor analysis results are Eastern Africa, Middle East, and Middle Africa. This factor is identified in factor analysis as a pure crustal factor. This is further conformed by PSCF model. The second factor was identified as a mixed anthropogenic and crustal one. From the PSCF calculations, it is clear that this factor has loadings from crustal source regions such as Middle and Eastern Africa in addition to anthropogenic contributions from industrialized European countries such as, Italy, Austria and Hungary.

Acknowledgment

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