Nitrogen and sulfur cycles and how they are affected by human interference: the example of Greece

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ABSTRACT

With the development of technology over the past twenty years' human kind has solved most of its biggest problems that were considered unsolved before. Unfortunately, though, the consequences of this industrial and technological development affect to a great extend the major factor of life, the environment. The aim of this article is to begin with a theoretical review of the importance of the cycles for humans and to analyze the way we intervene in them and what will the consequences (long or short term) be for our lives. Furthermore, we explain phenomena like acidification, particle and photochemical cloud and how they affect our health. Moreover, we quote the substances and chemical reactions that are produced by human activity and penetrate in the cycles creating the above phenomena. We also mention especially in Greece, how human activity has changed its environment through years and we compare it with other countries from different backgrounds.

Key Words

Sulfur cycle, nitrogen cycle, NOx emissions, SOx emissions, acidification, nitrification, European Union

1. Introduction

1.1 Nitrogen and sulfur cycle:

It is widely known that almost 79% of the atmospheric air consists of nitrogen which undergoes a process in order to be absorbed by plants. This process is called fixation (biological and atmospheric). In the first ammonia is produced as atmospheric nitrogen is connected with hydrogen[1].Atmospheric fixation takes place when electric shocks happen, necessary energy releases and nitrogen forms nitrogen ions that reach the ground through rain entering the plants.

Sulfur is an abundant element which maintains the climate balance. The greatest quantities of sulfur exist in rocks and minerals in the form of sulfites. The biogeochemical cycle of sulfur consists of both atmospheric and terrestrial procedures. During the terrestrial procedures the cycle begins with the corrosion of the rocks releasing the stored sulfur which comes in touch with air producing sulfate SO4 which is finally absorbed by plants. Some sulfur remains in the atmosphere, and along with the one that is released by volcanoes or humans, ends in the ground through the rain in a procedure called deposition.

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[1] $N_2 + 8H \rightarrow 2NH_3 + H_2$

<u>1.2 Toxic compounds derive from both cycles:</u>

The main toxic compounds are those which contain nitrogen, like NO, NO_2. Nitrogen monoxide reacts with oxygen or ozone producing nitrogen dioxide. In this way half-life time of nitric acid reaches one week and reaches the ground in the form of acid rain. Apart from nitrogen oxides ammonia is considered a pollutant due to its high concentration in the atmosphere because it forms aerosols.
Other pollutants apart from NO_x are HNO_2, HNO_4, N_2O_5, NH_4NO_3 and PAN. The sulfur pollutants are sulfur oxidants SO_x like SO_2 and also H_2S, CH_3SCH_3, CS_2, OCS which are dangerous for flora, fauna and wetlands. The sources of sulfur compounds mainly come from human activity as we add 73 to 80 $\frac{T\ \ S}{Y}$ in the atmosphere.

<u>2. The consequences of human interference in the environment</u>

<u>2.1 Nitrogen oxidants NOx</u>

The origin of those oxidants are 99% based on human activity (industry, power plants). The consequences are the appearance of bronchitis and the dramatic reduction of agriculture as they don't let the plants to grow.

<u>2.2 Acid deposition</u>

This process affects flora and it refers to the transfer of toxic compounds from the atmosphere to the ground. These compounds are mostly NO_2, HNO_3 and SO_2. As soon as they reach the ground they change the pH as they form strong oxidants. The direct effect of acid deposition is reduced crops and also corrosion of the surfaces.

<u>2.3 Eutrophication</u>

The main causes of eutrophication is the input of large amounts of nitrogen compounds in the aquatic ecosystem which cause imbalance in the food web and the creation of phytoplankton.

During eutrophication the concentration of oxygen carbon and nitrogen in the bottom is increased which means that there is not enough oxygen left for the living organisms such as fish. This phenomenon is 90% by human industrial activity near the aquatic ecosystems and affects the liver, the nerves as well as the skin.

<u>3. Time evolution of pollutants in Greece</u>

<u>SO_2 emissions in Greece from 1940 to 2005 in Tn/year</u>

The above table shows us the time evolution of SO_2 emissions in tons per year [tnSO_2/year] in Greece. We notice that the emissions have increased dramatically since 1950* especially the carbon ones. This happens because of the beginning of electricity production in Greece taking advantage of the abundant deposits of lignite of the area. The burning of lignite is a process that releases huge amounts of pollutants in the atmosphere. Using results from the *Socioeconomic Data and*

Applications Center, 'Historical Anthropogenic Sulfur Dioxide Emissions', 1970 and 2005 we notice that despite the reduction of the SO_2 emissions across Europe, Greece is the only country that despite the regulations has increased theirs since 2005.

Year	1940	1950*	1960	1980	2000	2005
Emissions from Carbon	8	14	54	248	278	313
Emissions from melting	4	2	3	11	2	3
Emissions from oil burning	7	23	43	137	205	220
Other burning	6	9	8	4	6	7
Total	18	48	109	400	493	543

Fortunately after 2005 the data is encouraging, since 2009 our emissions were $426\frac{t \quad z}{y}$ and 2012 $244\frac{t \quad z}{y}$. The reason is that the government took advantage of the geographic position of the country and made a turn in renewable sources of energy. Moreover clean technologies were applied by the industries (mostly energy) since 2008. Apart from SO_2 emissions NO_x is also a problem in Greece as their concentration is stable but in high levels. As we see in table 2 during the years 1990 and 2009 it ranges between $326\frac{tn \quad z}{y}$ to $379\frac{tn \quad z}{y}$. However post 2009 data are more encouraging as we managed to cope with the European standards in our NO_x emissions. Most of these pollutants come from fuel combustion and energy production.

NO_x emissions in Greece from 1990 to 2012

Year	1990	1995	2005	2009	2012
Total NO_x emissions	326	329	416	379	258

(Table 2.)

4. Comparison of Greece's NOx and SO2 emissions with Italy, Croatia and Sweden.

A comparison between some European countries that have signed the Kyoto protocol is essential in order to be able to understand the progress that has been done throughout

Europe. We chose to compare Greece with a country of the European North (Sweden), one of the South Europe (Italy) and one country from the Balkans (former USSR) (Croatia) keeping in mind the financial differences of each case.
The data we used come from the below sectors.
Fuel combustion activities (Energy industries, Manufacturing industries, Transportation), Emissions from fuels (Oil, Solid fuels). The information collected are from 1990 to 2012 and are measured in Ggr.

(Table 3)

NO_x (Ggr)							% total change
Year	*1990*	*1995*	*2000*	*2005*	*2010*	*2012*	
Italy	2000	1871	1420	1208	942	839	**58%**
Sweden	250	227	193	161	134	117	**53%**
Greece	323	326	356	414	317	256	**20.7%***
Croatia	90	61	69	70	61	53	**41%****

(Table 4)

SO_2 (Ggr)							% total change
Year	*1990*	*1995*	*2000*	*2005*	*2010*	*2012*	
Italy	1710	1246	727	378	193	167	**90%**
Sweden	71	41	22	22	19	15	**78%**
Greece	467	532	488	531	260	240	**48%***
Croatia	170	80	59	61	34	24	**85%**

**Greece has increased its emissions until 2005*
***Croatia has stable NOx emissions since1995*

Greece's energy sector until 2006 was based almost 100% on lignite burning coal fired power plants. Apart from power generation coal was used in transportation as well. This is the main reason we notice an increase in NOx and SO2 emissions as those are the main products of diesel, lignite and petrol combustion. After 2006 Greece started to use Natural Gas in public transportation and power production. Natural Gas is known for its zero sulfur emissions. That's why we notice this dramatic decrease on SO2 emissions after 2005. Apart from transportation and electricity production NG started to be provided is sufficient quantities through the city net for home use. The promotion and support of renewable energy in Greece is also important. During this decade the impact of wind farms and small hydro stations in the reduction of emissions will be essential for further NOx and SO2 deterioration. The reduction of emissions has been also achieved due to technologies that have been used by the industry and energy sector (see reference 13, 16). The decreasing trend that is observed after 2010 in the emissions (basically in NOx) is due to the economic recession that country is facing.
Croatia seems to have done a reasonable reduction on its emissions since 1990 but post 1995 data are not encouraging as their NOx emissions are almost stable. Even if they have achieved a total 41% reduction since 1990, after 1995 only a 13% reduction has been made.

We have to mention here that Croatia is not a part of the European Union which target was a 20% GHG reduction.
Croatia's main power production comes from thermal power plants but there are many hydroelectric stations and two nuclear power plants as well. Their reduction in SO2 emissions is due to the use of Natural Gas for transportation.
Italy has a large primary sector. There is a high industrial and manufacturing activity which means a lot of GHG and NOx emissions. Although the largest contributor of NOx emissions is the energy industry which covers 70% of the total emissions.
As a part of the EU and an industrial country has committed with a 5, 5% GHG emissions reduction for the 2008-2010 period.
Italy has met its commitments towards EU as managed a 9,1% emissions reduction and 58% NOx reduction since 1990. The main reason is the NOx reduction technologies that the manufactory industries have applied and the fact that there was a great transition from internal combustion machines to electrical motors in transportation. Moreover the increased use of Natural Gas (in public buses, cars) instead of conventional fuel has led to a dramatic reduction on SO2 emissions.
In Sweden we notice an overall 53%, 78% reduction in both NOx and SO2 emissions respectively since 1990. A great breakthrough that has been adopted in this country since 1992 is the refunded emission payments in order to reduce NOx emissions. In this way the government motivated the large combustor plants of the country to develop deNOx technologies. Those technologies are based in post combustion NOx minimizing.
Apart from that since 1990 12TWatt of renewable energy production has been installed and 64TWatt of hydropower also operates. Moreover, Sweden is the only country that imports waste from other countries to burn it for electricity production.

Conclusion

Nitrogen and sulfur cycles are essential for human life and environmental sustainability. Nitrogen is installed in the ecosystems by fixation (biological and atmospheric) while sulfur is installed with the corrosion of the rocks or by volcanoes and oceans. Human activities intervene in those cycles and increase the concentration of both Nitrogen and Sulfur in the atmosphere. This intervene causes the appearance of toxic compounds like NOx, HNO_2, HNO_4, N_2O_5, NH_4NO_3 an d PAN or SO_x like SO_2 and also H_2S, CH_3SCH_3, CS_2, OCS. The increase of the above compounds in the atmosphere and the ecosystems cause phenomena like acid deposition, eutrophication that affect humans indirectly but there are also direct consequences like brochettes and skin diseases. Human activity inputs large amounts of NOx and SO_2 as those are the main products of combustion. In Greece in particular NOx emissions were in a systematic increase since 1990 due to the lignite burning power plants. Since 2006 Natural Gas and renewables have been widely introduced in the market and a total 20% NOx emissions reduction has occurred. General progress has been made overall in Europe since the past decay as we notice from the above tables. This progress is due to innovative applications that have been installed in industries and the turn to NG and renewables instead of coal as well as effective motives that governments applied to NOx reduction.

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