4. COMPOSITION OF ESTONIAN ATMOSPHERE

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Introduction

Atmospheric study, particularly that of its chemical composition, has a long tradition in Estonia. Since middle of this century, in addition to meteorological observations, some chemical compounds in precipitations have been regularly measured in many meteorological stations. The main aim was to acquire information about the state and dynamics of the atmosphere. Therefore, main attention was paid to monitoring chemical compounds which have a direct impact on the human environment.

As energy production developed intensively and SO_2 and NO_x increased drastically in the atmosphere in acidic rock areas, like Scandinavia, the problem of acid rain became the most important environmental problem in Europe and North-America. As a consequence, monitoring the compounds of sulphur in precipitation was organized in Estonia. In the 1970s, as related to large operating oil shale-based power plants, Estonia became a country , where emissions of sulphur compounds per capita were extreamly high. In 1979, Estonia became a participant in the European Monitoring and Evaluation Programme – the network created to study transboundary air pollution.

The aims of the precipitation chemistry study and the related problems of the formation and transformation of the atmospheric composition have varied over the years. But monitoring of pollutant (in particular, sulphur compound) loads has been a central issue. Over recent years, an attempt was made to estimate the spatial regularities of atmospheric impurities and their impact on the pH of mean monthly precipitations (Frey et al., 1991). Furthermore, calculations were provided to find out the origin of atmospheric impurities washed out in Estonia (Roots, et al., 1992; Punning,1993).

Until the 1990s, CO_2 and some other greenhouse gas (GHG) emissions were not studied in Estonia. The first inventory of GHG for Estonia was provided in 1995 using the Intergovernmental Panel on Climate Change (IPCC) methodology. The principles of this methodology are based on the following considerations:

1. The emission and removals were calculated for the sectors directly caused by human activities or as a result of natural processes affected by human activities.

2. Energy and industrial sector carbon dioxide emissions were calculated using Carbon Emission Factors (IPCC Guidelines, 1994), amounts of fuels and the carbon content of fuels.

3. In forestry, the methodology was based on the assumption that the flux of CO_2 to or from the atmosphere be equal to the changes in carbon stocks in the existing biomass, and soil. Changes in carbon stocks be estimated by the rates of change in the land use.

4. Since the main GHG source in agriculture is animal husbandry and the use of fertilizers, calculations of CH_4 and NO_2 emissions were made.

5. In the GHG budget calculations for wetlands, the mean values of carbon accumulation and the decay of natural and drained peatlands and for lakes were used.

The resultant GHG budget contained very valuable information, but it is rather complicated to use the results to characterize Estonia's atmosphere. There are some other processes that have a significant influence on the composition of the atmosphere, such as:

1. The chemical processes with different GHG in the fuel burning process, their interaction with the atmosphere, their outwash from the atmosphere and the absorption by the surface of land or waterbodies.

2. Transboundary processes (import-export).

Therefore, to obtain an objective picture about the Estonian atmosphere, it is neccessary to conduct an additional study and compare the GHG inventory data with the results of direct measurements of atmospheric compounds.

Estonian Greenhouse Gas Inventory

The GHG Inventory for Estonia was compiled for the energy, industry, transport, agriculture, forestry, and land-use sectors. Thus, all directions of human activities related to GHG emissions were covered.

In the Estonian GHG Inventory, six gases were found to have direct or indirect impact on the greenhouse effect: carbon dioxide (CO_2), methane (CH_4), carbon monoxide (CO), nitrous oxide (N_2O), nitrogen oxides (NO_x), and non-methanous volatile compounds (NMVOC). In addition, there are other groups of compounds that contribute to the greenhouse effect, for instance, chlorofluorocarbons – CFCs, hydrofluorocarbons – HFCs, and sulphur hexafluoride – SF_6, which are not included in this inventory because their share in Estonia's GHG emissions is insignificant.

Energy-related activities are the most significant contributors to greenhouse gas emissions. Estonia's primary sources of energy are fossil fuels, in particular, oil shale, whose share in the total fuel consumption is approximately 68% (Punning, et al., 1995).

Estonia's oil shale field is the largest commercially exploited deposit in the world. The deposit has been exploited since 1916, and its total output exceeds 800 million tons of shale. Oil shale has a low caloric value; the calorific value of dry material is approximately 7.5-18.8 MJ/kg (1800-4000 kcal/kg). The main components of oil shale are organic matter or kerogen (15-46%); carbonate matter (26-57%) and clastic material (18-42%). Oil shale contains a relatively small amount of sulphur, which mainly occurs in a sulphide form (Jürgenfeld et al., 1994).

In the context of GHG emissions, the high content of carbonate rocks is particularly important, because they dissociate at high temperatures in boiler houses. The content of carbonate CO_2 varies in different seams from 14 up to 23% (Ots, 1977), and therefore the total quantity of carbon dioxide increases up to 25% in the flue gases of oil shale.

This type of fuel is not common in the world, and therefore in the IPCC methodology, the carbon emission factor for oil shale was absent and was calculated by A.Martins as 29.1 tC/TJ (Punning, et al., 1995). This value exceeds that of other common fuels and is comparable with the emission factors of some lignites and peat.

Apart from GHG emissions, the oil shale-fired power production and industry are major contributors to atmospheric pollution. In 1990-1991, the quantity of air pollutants in north-eastern Estonia (where the main oil shale operating industry is located) might have been 440-470 thousand tons. During this period, only six thermal power plants have emitted annually about 180 thousand tons of fly-ash, 200 thousand tons of SO_2 and 16 thousand tons of NOx (Liblik and Rätsep, 1994) ranking among the six largest pollution sources in Europe. The emissions by TPP were the largest in the late 1970s. Then the new purification systems (electrofilters) were established, and emissions decreased markedly. Since the 1990s, energy production has decreased considerably due to economic decline. The history of air pollution is recorded by peat and lake sediment sequences, where the distribution of heavy metals and spherical particle content closely follows the history of oil shale consumption (Varvas and Punning, 1993).

Table 1. Estonian GHG emissions from the energy and industry sector in 1990 and 1994, based on the IPCC methodology, Gg (Punning et al., 1995)

Compound	1990	1994
CO_2	39,597	23,714
CH_4	322	187
N_2O	2,3	1,3
NO_x	93	50
CO	185	101
NMVOC	22.9	12.5

Apart from the energy production and industry (such as mining, gas transmission), waste decomposition contributes measurably to the methane emissions in the atmosphere. According to preliminary calculations, the total amount of methane emitted by landfills and wastewaters was approximately 42 Gg CH_4 in 1990.

In addition to direct GHG, solid matter (fly-ash) and sulphur dioxide emitted by oil shale-operated power plants and industry are substantial. According to the reports of the Environmental Data Centre (Estonian Environment, 1991), in 1990 278 thousand tons of fly ash and 233 thousand tons of SO_2 were emitted to the atmosphere from stationary sources. Due to a decline in oil shale consumption and power production, the emissions were some 130 and 120 thousand tons in 1994. There are plenty of other pollutants (for instance, nitrogen oxides, polycyclic aromatic hydrocarbons and other organic compounds, heavy metals) emitted into the atmosphere, but, as a rule, their distribution is mainly restricted to the vicinity of the source.

The calculation and prediction of pollutant dispersion in the atmosphere is complicated because of various factors, such as the parameters of the sources (for instance, height above ground level), emissions (temperature, flow-out velocity, and intensity per time unit), meteorological characteristics (wind speed, direction, and atmospheric stratification), surface profile and temperature, chemical reactions in the atmosphere. Therefore, even today only such models have been elaborated that characterize a short-time pollution level, formed by wind parameters above certain points of the landscape (Liblik & Rätsep,1994). Isolines of the concentrations of fly-ash and sulphur dioxide around the pollution sources show that the concentration of pollutants decreases quickly in relation to the distance from the emission source. On the basis of these models alone, it is complicated to estimate the share of long-transported pollutants.

In the non-energy sector (dispersed emission sources), the changes in emissions and sinks of GHG are related to changes in land-use. Calculations performed by M.Mandre (Punning, et al., 1995) showed that over the last fifty years, as the forest stands area has more than doubled, forest is essential in the sequestration of CO_2. Consequently, CO_2 uptake by forests in 1990 exceeded 3.3 times its emission, and the annual net removal of CO_2 was approximately 7950 Gg.

The main GHG sources in Estonia's agriculture are animal husbandry and the use of fertilizers. The calculations made by H.Roostalu showed that in 1990 the methane emissions from livestock were 60 Gg, and the nitrogen oxide from the mineral fertilizers used 0.91 Gg. Over the years since then, the decrease in these gas emissions has been significant (Punning, et al., 1995).

Wetlands are a particular problem in providing the GHG inventory for Estonia. About one million ha or ca 22% of Estonia's territory is covered by wetlands (peatlands and lakes). Peat contains a huge amount of accumulated carbon. According to M.Ilomets (Ilomets et al., 1995), the mean peat organic matter accumulation on fens may be about one ton per hectare and 1.6 tons per hectare on ombrotrophic bogs (dominated by *Sphagnum*). During the Holocene (the last 10,000 years), this value has varied depending on the temporal-spatial development of peatlands. Up to the last century, the carbon balance was determined by natural processes. Due to amelioration activities, the carbon cycling of wetlands is greatly influenced by a human.

There are two consequences resulting from the human impact on peatlands:

1. As a result of the drainage of peatlands, CO_2 accumulation has ceased, and due to the intensive decay processes, the mineralization of organic matter and emission of CO_2 has started.

2. In general, the drainage of peatlands has decreased CH_4 emissions.

The calculations performed by M. Ilomets showed that in peatlands, strongly affected by amelioration work, carbon accumulation in 1990 was lower than in 1970 by approximately 300 Gg, and CH_4 emissions had decreased approximately 5 Gg (Punning, et al.,1995).

Summarized results of the GHG budget in Estonia for the years 1990 and 1994 are illustrated in Table 2.

Table 2. GHG budget in Estonia in1990 and 1994

| GHG Sources and Sink Categories	Emissions, Gg											
	CO_2		CH_4		N_2O		CO		NO_X		NMVOC	
	1990	1994	1990	1994	1990	1994	1990	1994	1990	1994	1990	1994
Fuel Combustion	37184	21413	3	2	1.4	0.8	184	100	93	50	22.9	12.5
Fugitive Fuel Emissions	NO	NO	217	109	NO	NO	NO	NO	NO	NO	NO	NO
Industrial Processes	613	215	NA	NA	NA	NA	NA	NA	NA	NA	NO	NO
Agriculture	NO	NO	60	46	0.9	0.5	NO	NO	NO	NO	NO	NO
Land Use Change & Forestry	-7950	-7660	NO	NO	NO	NO	1	1	NO	NO	NO	NO
Wetlands	9746	9746	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO
Wastes	NO	NO	42	30	NO	NO	NO	NO	NO	NO	NO	NO

NA – not available   NO – not occurring

Because of drastic changes in the Estonian economy and political life since 1990, strong trends towards the decrease of GHG emission have prevailed. As a result, within the recent 3-4 years, the total GHG emission in Estonia has diminished by about 40%. It is obvious that the decreasing trend of GHG emissions is partly related to the economic decline and cannot continue at such a rate indefinitely. After economic recovery, a period of stabilization and an increase in energy use will follow.

Accumulation of CO_2 by alkaline matter

Due to the high carbonate content in oil shale, the content of alkaline oxides, in particular, CaO, in combustion products is very high. According to the data reported by Ots (1977), the carbonate fraction contains 90.5% $CaCO_3$; 9.2% $CaMg(CO_3)_2$; 0.3% $FeCO_3$.

Of oil shale combustion technologies, pulverized fuel combustion is the most common. Approximately 45% of the total amount of fired oil shale will be converted to ash. The bulk of the ash falls to the bottom of the furnace and is carried by hydrotransport to the ash fields, which cover some 10.6 km^2. The water (8-10 million m^3) in the closed system of hydrotransport has a pH value of about 13 and a mineral content up to 11 g l^{-1}. In this way, ca 7000 million tons of furnace bottom ash will be transported to the ash fields annually. This quantity contains approximately 3.1 million tons of free CaO. CaO will hydrolyse and react with atmospheric CO_2 according to the following formulas:

$$CaO + H_2O = Ca(OH)_2$$

$$Ca(OH)_2 = CaOH^+ + OH^-$$

$$CaOH^+ = Ca^{2+} + OH^-$$

$$Ca^{2+} + CO_3^{2-} = CaCO_3.$$
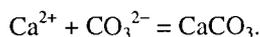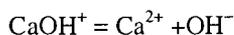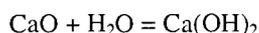
To calculate the share of free CaO which will react with atmospheric CO_2, such limitations have to be considered as the diffusion coefficient of CO_2 in water and temperature, furthermore the fact that after a certain time, part of the CaO-rich ash will be buried by new layers of ash.

if we presume that the share of reacted CaO is between 0.1 and 0.5, then the sink of CO_2 in ash fields is 0.25-1.25 million tons per year (Table 3). This amount equals 1-5% of the total yearly emission of CO_2 by thermal power plants in Estonia.

Approximately 160 thousands tons of solid pollutants were emitted into the air in 1994. More than 95% of that was fly-ash emitted by plants operating on oil shale. The content of earth and alkali metals in fly-ash is even higher than in furnace bottom ash due to thermal destruction of clay minerals in the furnace with the volatilization of potassium (Öpik, 1989). The concentrations of fly-ash in the atmosphere of Estonia vary greatly. Naturally, the highest concentrations has been found in north-eastern Estonia. Based on the results of numerical modelling (Liblik & Rätsep, 1994), it is possible to distinguish three zones. The first zone, comprising the area within a radius of 9-12 km from the Baltic TPP, is characterized by a dust level exceeding 300 μg m^{-3} of solid dust in the atmosphere. The second zone extends for 20-25 km to the west and south of the Estonian TPP with a maximum surface dust concentration of 100-300 μg m^{-3}. The remaining territory of the Ida-Virumaa County belongs to the third zone, where the concentration of dust in the air is below 100 μg m^{-3} (Liblik & Rätsep, 1994).

Therefore, the pH values of precipitation in north-eastern Estonia are high troughout the year, the mean values in the summer months being 5.9-7.5 (Punning, 1991). The pH value of the fly-ash precipitated on the electric filters is in the interval of 12.3-12.6 (Mandre, 1995). In general, free CaO content in the fine grain ash from cyclones and electrical precipitators is 40.0 % (Pets et al., 1985). Its proportion decreases with the reduction of the disintegration level. Therefore, we can presume that CaO content in fly-ash is ca 30%, and its content in the annual emissions into the atmosphere totals 50 thousand tons.

Table 3. Amounts of ash and CaO transported to ash fields and CO_2 neutralized by CaO

Emission year	Amounts of ash transported to ash fields, Gg	Amounts of CaO in the ash, Gg	Neutralized CO_2, Gg		
			Share of reacted CaO		
			0.1	0.25	0.5
1990	7.32	3.11	0.24	0.61	1.22
1991	7.45	3.20	0.25	0.63	1.26
1992	7.09	3.12	0.24	0.61	1.22
1990-1992	21.87	9.42	0.74	1.85	3.70

In the atmosphere, CaO is in a very dispersed form, and therefore an active reaction with CO_2 will proceed intensely, depending mainly on the moisture content. Most probably in the case of the wet outwash, the reaction might be complete. If we again presume 0.5, 0.25 and 0.1 share of neutralization of CaO by CO_2, the chemically bounded amount of CO_2 (as $CaCO_3$) is from twenty thousand tons up to four thousand tons annually or less than 0.1% of the total amount of CO_2 emitted by oil shale combustion.

Fly-ash will deposit and reach the soil surface as dry and wet sediments. The study of the transect located in northern Estonia near the Kunda Cement Plant demonstrates explicitly that the accumulation of earth and alkaline oxydes causes alkalization and an increase in the pH values of soil. The hydrolytic acidity of the soil has decreased but the level of saturation with alkali has become very high, reaching 99% in the litter horizon and 75-85% in deeper horizons. In the vicinity of the cement plant, the pH of litter layer was above 7, being 4.5 units higher than the control. Moreover, the pH of subsoil water has increased, having values higher than 7 (Annuka & Mandre, 1995).

In those conditions, CO_2 will react with free CaO. Considering that about half of the free CaO is hydrolyzed and reacts with CO_2 in the atmosphere, the remaining half would then react during some interval with CO_2 in soil. It means that theoretically some 20 thousand tons of CO_2 would be absorbed by this part of fly-ash.

Summarizing all sinks related to combustion products of oil shale, we obtain a maximum value of CO_2 of 1.25 million tons annually or approximately 6% from the total emitted CO_2 from oil shale combustion. This facilitates the reduction of CO_2 emissions if the amount of bonded CO_2 can be increased. This can be accomplished by:

1. Reducing the amount of CO_2 released in oil shale combustion from the mineral part of oil shale;

2. Increasing the share of CO_2 neutralized by free CaO.

Long transported pollutants in Estonia's atmosphere

As a result of the geographical position and open landscape of Estonia, its atmosphere is influenced both by local pollution sources and, to a great extent, by contaminants transferred from the neighbouring areas. The best indicators of that process are the distribution curves of heavy metals in snow cover and lichens, because there are no metallurgy industries in Estonia.

The spatial distribution of industry in the territory of Estonia and the heavy metal isolines show that the majority of the elements studied (Zn, Cd, Cu, Pb) reach Estonia by long-distance transportation. The input is constant from the south-west and west and less explicit from the south-east (Punning et al., 1991). The influence of local pollution sources is more evident only in north-eastern Estonia near large industrial centers.

The share of long-transported gaseous compounds is difficult to estimate. Within the European Monitoring and Evaluation Programme framework, it has been calculated that in 1980 71,000 tons of sulphur precipitated on the surface of Estonia, 26,000 tons of which originated from within Estonia (Roots et al., 1992). According to the data reported by Frey et al. (1988), 90,000 tons of sulphur precipitated in Estonia in 1987 half had a transboundary origin. Both estimates seem to be exaggregated, because the real precipitated amounts of sulphur were considerably lower (Punning, 1993).

Model calculations provided by Tuovinen et al.(1990) showed that approximately 1/3 of the total amount of sulphur compounds deposited in Estonia originated from outside Estonia.

These examples demonstrate that budget calculations for different atmospheric constituents are complex. In addition to the compounds transported over long distances, in the case of a rather

small country such as Estonia, difficulties will also arise of how to calculate the contribution of gases emitted by long-distance vehicles like airplanes and ships, and overflying flights.

Conclusions

To obtain a real picture of the composition of the atmosphere is an extremly complex task. Based on the IPCC methodology for the GHG Inventory, the first serious attempt was made to establish the fluxes of some gases (mainly GHG) to the atmosphere and from the atmosphere to the biosphere. The data show that in the Baltic Sea region in 1990 Estonia had the highest emissions of major GHG per capita. Due to the restructuring of Estonia's economy since 1990, the total emission of GHG has diminished approximately by 40%.

In addition to the CO_2 fluxes to the biosphere, the flux to alkaline environments (such as soil, waterbodies), typical of those surrounding oil shale-fired factories, is still substantial. Preliminary calculations show that up to 5% of the total emitted CO_2 might be bound by CaO into carbonate.

Because of the open landscape, the transboundary exchange of pollutants is active. Rough estimates demonstrate that about half of the sulphur compounds precipitated in Estonia have a long-transported origin. Due to the dominating winds, southwestern and western Estonia are particularly influenced by long-transported airborne pollutants and to lesser extent, the south-eastern areas of the territory.

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