REPORT FOR 2013 ON AIR QUALITY AND ENVIRONMENTAL RADIOACTIVITY IN CĂLĂRAŞI, DOLJ, GIURGIU, MEHEDINŢI AND OLT COUNTY - " DANUBE WATER INTEGRATED MANAGEMENT " PROJECT

The assessment of ambient air quality in Romania is regulated by *Law 104/2011 on ambient air quality*.

The air pollutants considered for assessing air quality in the Project "Danube WATER integrated management" are:

- sulfur dioxide (SO_2),
- nitrogen dioxide (NO_2)
- particulate matter PM_{10}
- ozone (O_3),

2013 ambient air quality assessment in Calarasi, Dolj, Giurgiu, Mehedinti and Olt counties was achieved through 15 automated stations that are part of the National Network on Air Quality Monitoring (AQ-NMN) as follows:

- 4 urban and suburban background stations to assess the pollution background level for urban and suburban areas: CL-2 Călăraşi, Dj-2 Craiova, DJ-5 Işalniţa, GR-2 Giurgiu, TR-1 Alexandria;
- 6 industrial stations to assess the contribution of emissions from industrial sources: DJ-3 Craiova, Craiova DJ-4, GR-3 Giurgiu, MH-1Drobeta Turnu Severin, OT-1, Slatina, TR-2 Turnu Măgurele
- 3 traffic stations to assess the contribution of traffic emissions: CL-1 Călăraşi, DJ-1 Craiova, GR-1 Giurgiu;
- 1 rural fund station to assess the pollution fund level for rural areas: GR-4 Braniştea.

Below are the data and summary information on the results of air quality monitoring in 2013 to pollutants taken into account in this study.

The charts are based on measurements carried out in automatic air quality monitoring stations in compliance with the data quality objectives set out in Annex no. 4 to Law 104/2011, using the criteria of aggregation and calculation of statistical parameters, in accordance with Annex 3, B .1 and D.2 of Law. 104/2011.

Nitrogen dioxide (NO_2)

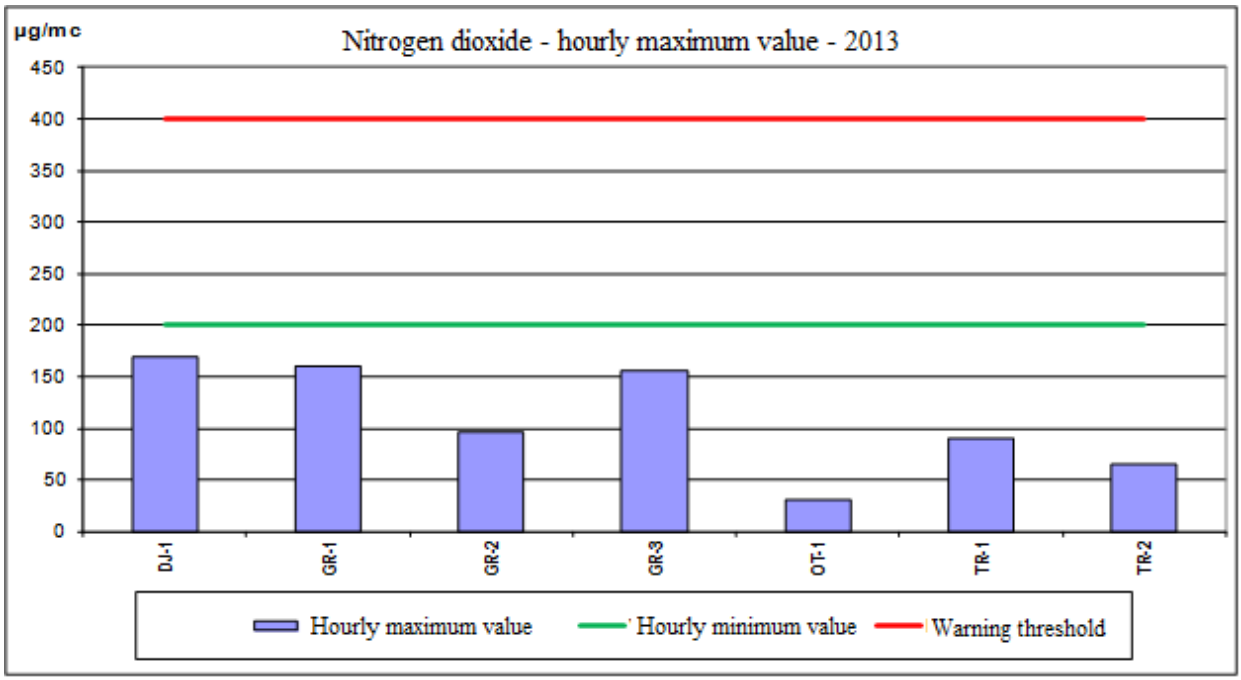
Nitrogen oxides come primarily from the burning of solid, liquid and gaseous fuels in different industrial, residential, commercial, institutional installations and from road transport. Nitrogen oxides have an effect of eutrophication on ecosystems and an effect of acidification on many environmental components such as soil, water, terrestrial or aquatic ecosystems, and also on buildings and monuments. NO2 is a gas that is transported on long distances and plays an important role in atmospheric chemistry, including in the formation of tropospheric ozone. Exposure to high concentrations of nitrogen dioxide causes inflammation of the respiratory airways and reduces lung functions, increasing the risk of respiratory diseases and worsening bronchial asthma.

NO2 concentrations in ambient air are measured using *the hourly limit value for human health protection* (200 $\mu g/m^3$), value that must not be exceeded more than 18 times / year and *the annual limit value for human health protection (40$\mu g/m^3$).*

No hourly limit value was exceeded for human health protection (200µg/m^3).

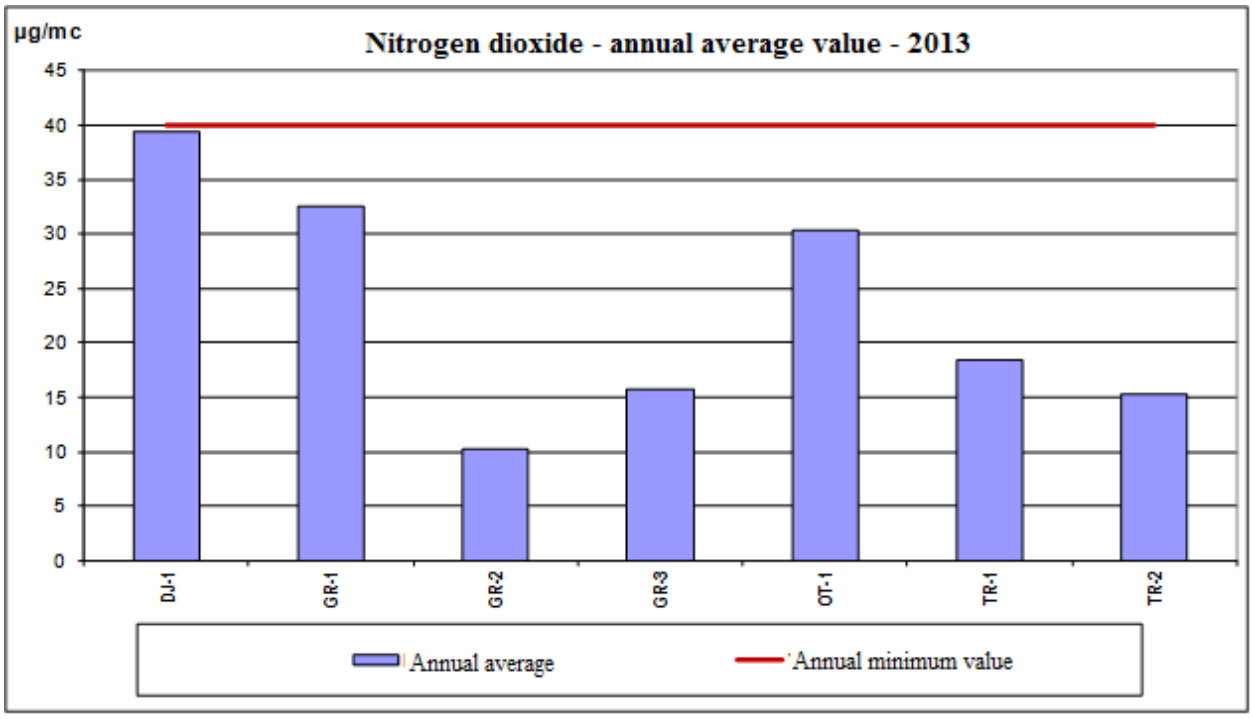
No exceedances of the warning threshold value *(400$\mu g/m^3$ concentration measured for 3 consecutive hours)* for nitrogen dioxide were recorded.

Fig.1 Nitrogen dioxide (NO_2)- hourly maximum value - 2013



The annual average value for human health was not exceeded (40µg/m^3)

Fig.2 Nitrogen dioxide (NO2) - annual average value - 2013



Sulfur dioxide (SO_2)

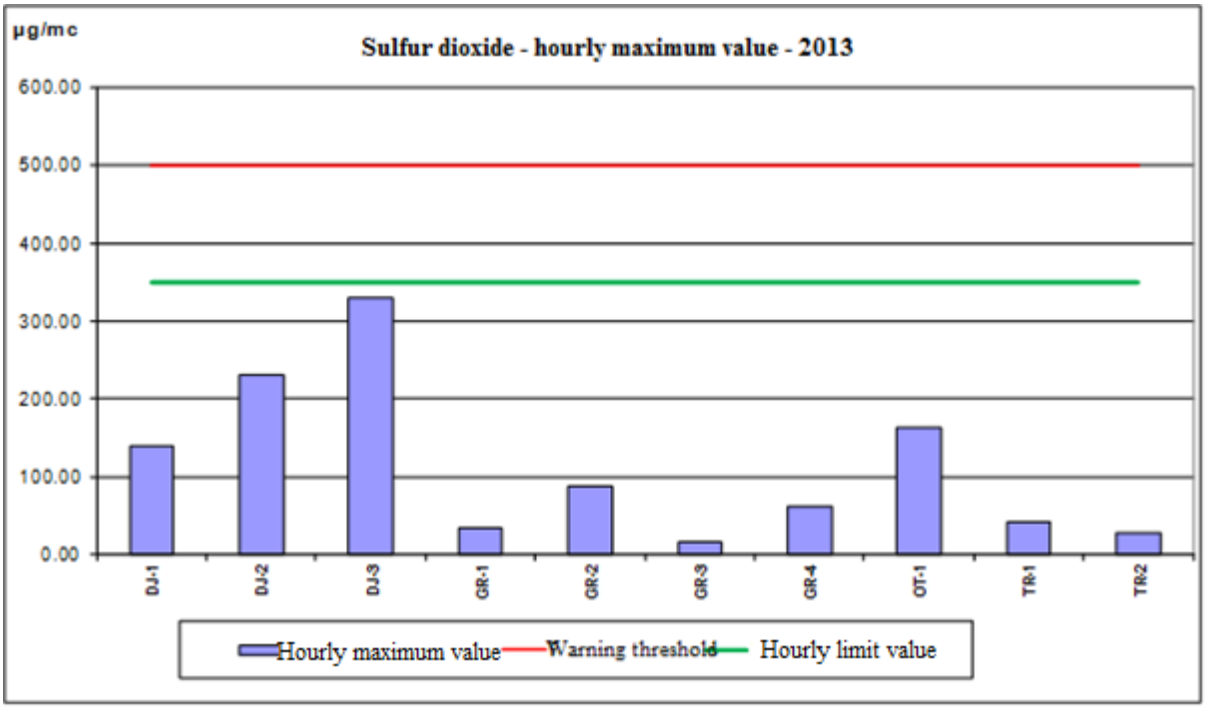
Sulfur dioxide is a highly reactive gas, that comes mainly from burning sulur fossil fuels (coal, oil) in order to produce electricity, heat and liquid fuels (diesel) in the internal combustion engines of road vehicles. Through the effect of acidification, sulphur dioxide can affect both human health through its effects on the respiratory system as well as the environment in general (ecosystems, materials, buildings, monuments).

SO_2 concentrations in ambient air can be evaluated using the *hourly limit value for human health protection* ($350 \mu g/m^3$), which must not be exceeded more than 24 times / year and *the daily limit value for human health protection* ($125 \mu g/m^3$) which must not be exceeded more than 3 times / year.

There were no exceedances of the hourly limit value.

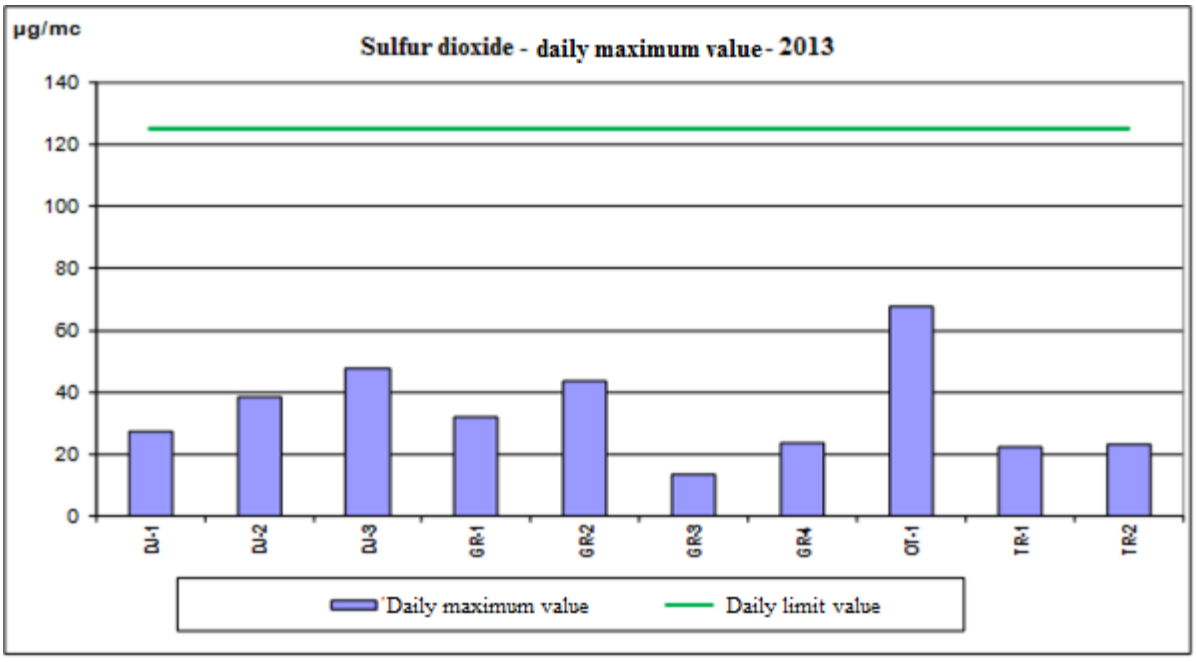
There were no exceedances of the threshold value *($500 \mu g/m^3$ concentration measured for 3 consecutive hours)* for sulfur dioxide.

Fig.3 Sulfur dioxide (SO_2)- hourly maximum value - 2013



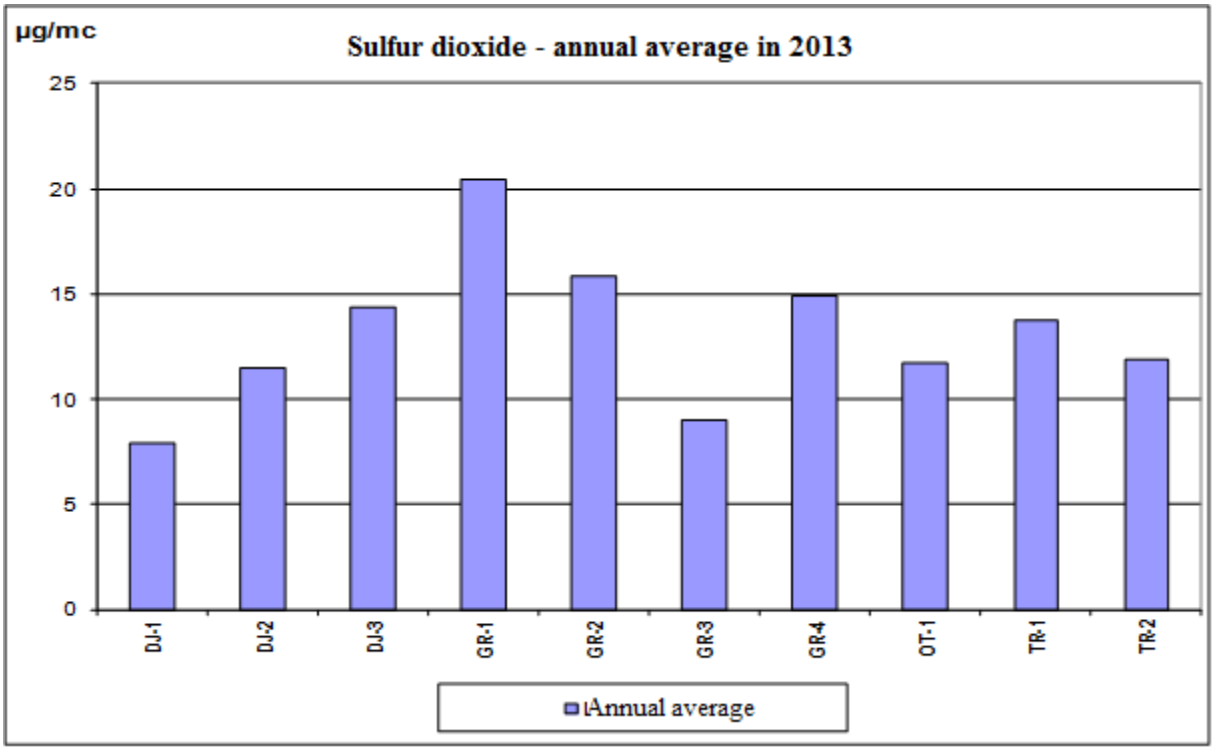
There were no excedances of the daily limit value.

Fig.4 Sulfur dioxide (SO_2)- daily maximum value - 2013



The annual average values for SO_2 are presented in the following table:

Fig.5 Sulfur dioxide (SO_2)- annual average - 2013



Ozone (O_3)

Ozone is found naturally in very low concentrations in the troposphere (lower atmosphere). Unlike stratospheric ozone that shields life forms from the action of ultraviolet radiation, tropospheric ozone (between ground area and 8-10km height) is highly toxic, with a strong irritant action on the respiratory airways, eyes and has carcinogenic potential. Also, ozone is toxic to vegetation, causing inhibition of photosynthesis and produces foliar injuries, necrosis.

Ozone is a secondary pollutant because, unlike other pollutants, it is not emitted directly from any source of emission, but is formed under the influence of ultraviolet radiation through photochemical chain reactions between a number of primary pollutants (ozone precursors - NO_x, volatile organic compounds (VOCs), carbon monoxide).

Ozone precursors originate from both anthropogenic sources (fuel combustion, traffic, industrial activities) and natural sources (biogenic VOCs emitted by plants and soil, mainly isoprene emitted by forests, these biogenic

compounds, difficult to quantify, can contribute substantially to the formation of O_3). Another natural source of ozone at low pressure is represented by small amounts of O_3 in the stratosphere which occasionally migrates, under certain weather conditions, to the surface of the earth.

Photochemical O_3 formation depends mainly on meteorological factors and concentrations of precursors, NO_x and VOC. Complex chain reactions occur in the atmosphere, many of these competitors, in which the O_3 is formed and consumed, so the O3 concentration at a given time depends on many factors, such as the ratio between NO and NO_2 in the atmosphere, the presence of volatile organic compounds required to initiate the reaction, and meteorological factors.

As a result of the complexity of physical and chemical processes in the atmosphere and their close dependence on weather conditions, the spatial and temporal variability of precursor emissions, transport increase of ozone and its precursors at a great distance, including at inter-continental scale in the northern hemisphere, as well as the variability of the stratosphere and troposphere exchange, the ozone concentrations in the lower atmosphere are highly variable in time and space, and are difficult to control.

The concentration of ozone in ambient air can be evaluated using *the information threshold (180$\mu g/m^3$)* calculated as the hourly average, *the alert threshold (240$\mu g/m^3$* measured for 3 consecutive hours) calculated as an hourly average and the *target value for the protection of human health* (120 *$\mu g/m^{3,}$)* calculated as the daily maximum 8-hour average (moving average), which must not be exceeded more than 25 times / year.

There were no exceedances of the threshold value, the information threshold was exceeded for 1 hour at DJ-3 station and the target value for the protection of human health was exceeded at DJ-4 and TR-2 stations.

Fig. 6 Ozone (O_3) hourly maximum value - 2013

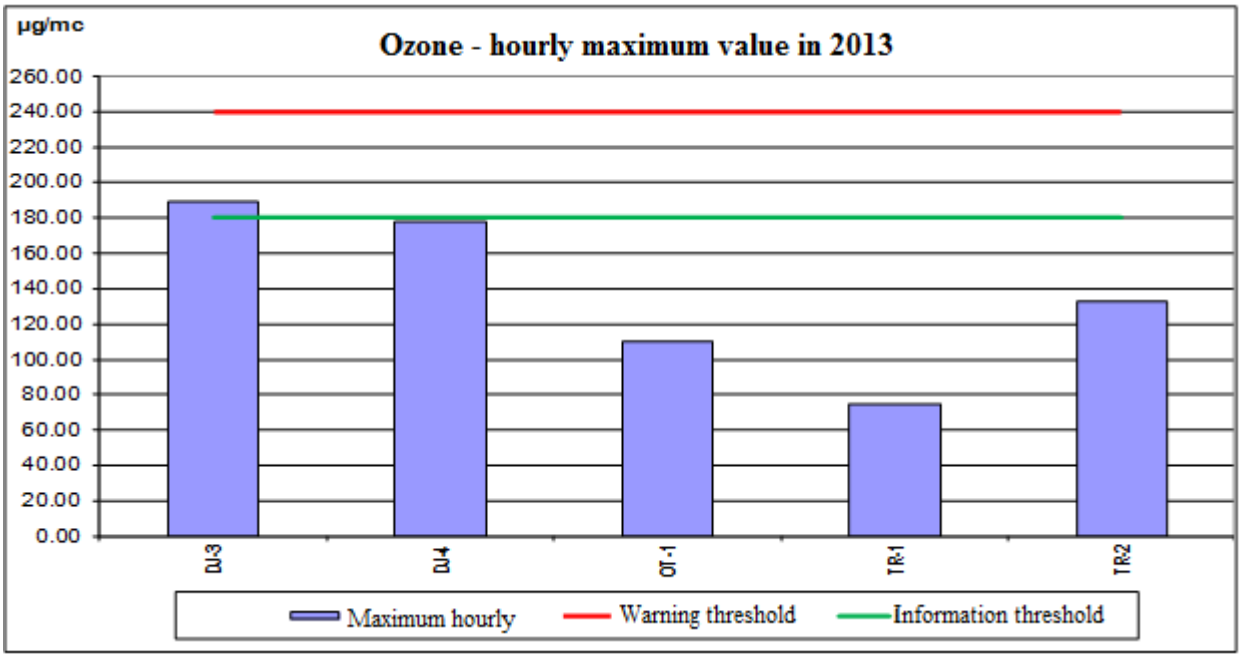
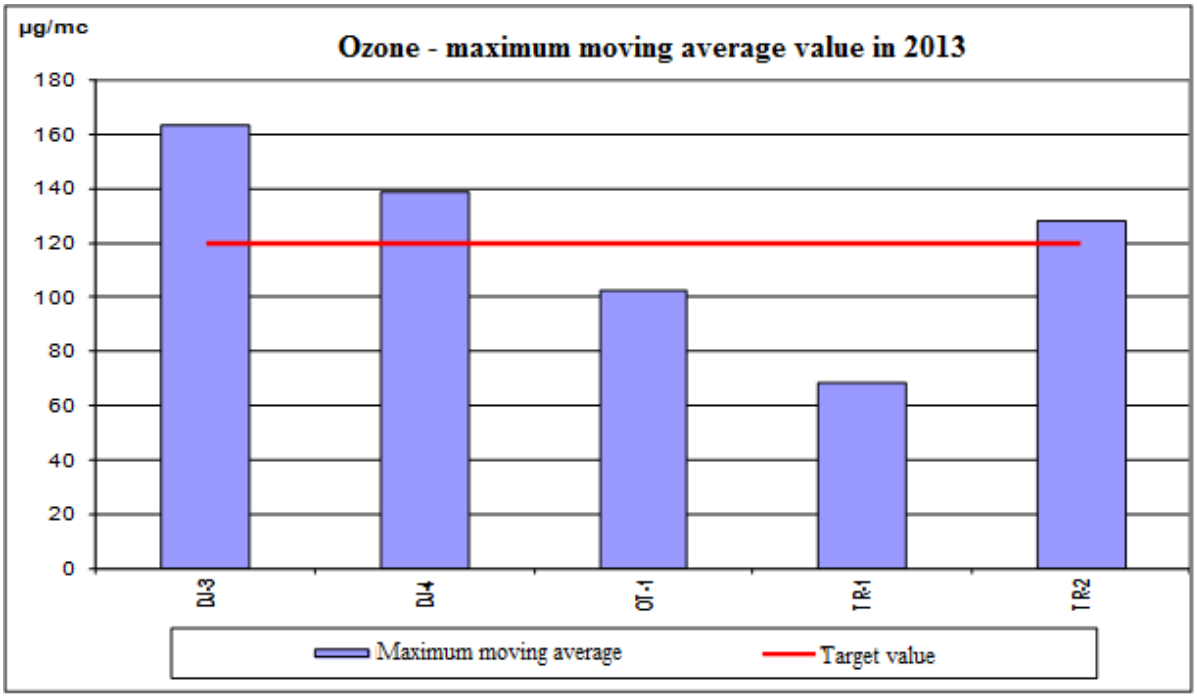
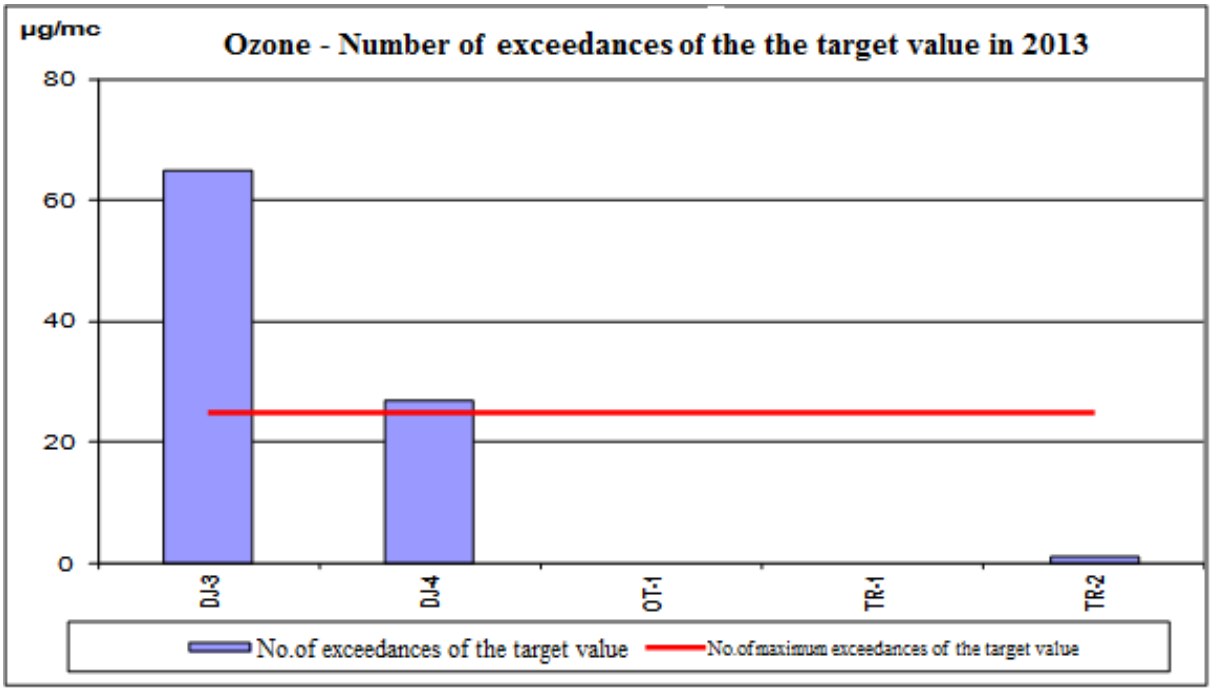


Fig. 7 Ozone (O_3) maximum moving average value - 2013



The number of exceedances of the target value for the protection of human health is represented in the chart below.

Fig. 8 Ozone (O_3) - number of exceedances of the target value - 2013



Particulate Matter PM_{10}

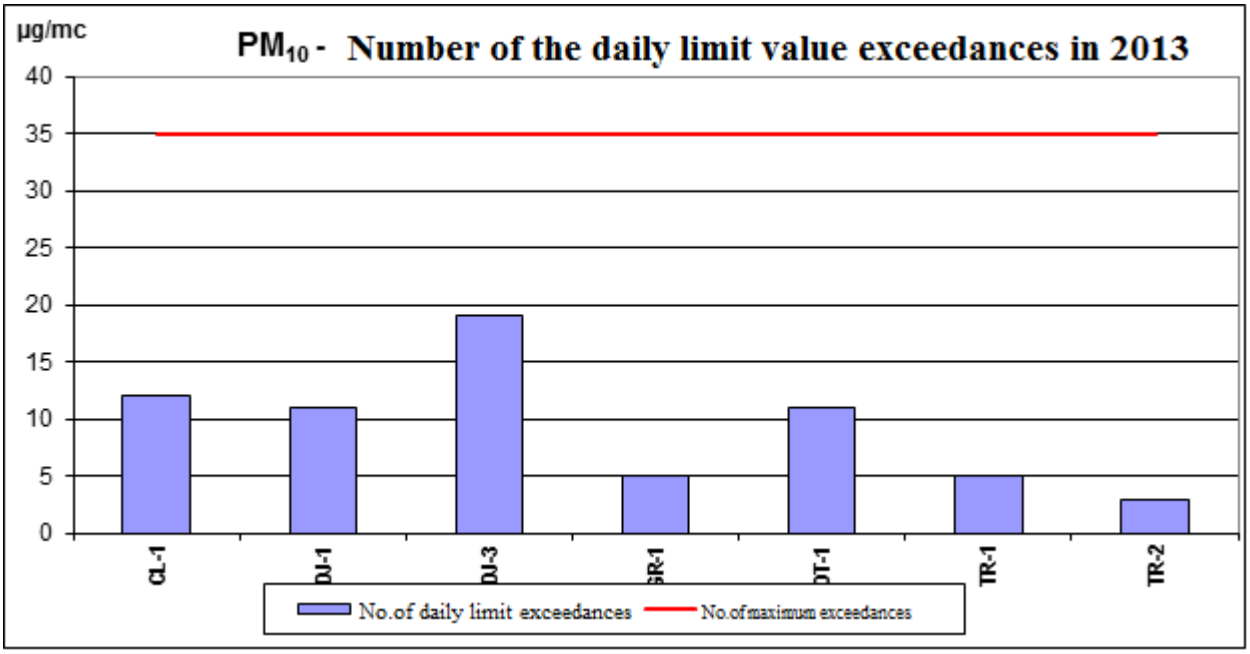
Particulate matter in the atmosphere, are pollutants that are transported on long distances, derived from natural causes, such as particles on the surface stirred up by the wind, volcanic eruptions, etc. or from anthropogenic sources such as combustion in the energy sector, manufacturing processes (metallurgy, chemical industry, etc.), construction sites, road traffic, industrial and municipal dumps and waste landfills, individual heating systems, especially those using solid fuels, etc..

The nature of these particles is varied. Thus, they may contain carbon particles (soot), heavy metals (lead, cadmium, chromium, manganese, etc.), iron oxides, sulphates, as well as other toxic emissions, some of which are carcinogenic effects (such as persistent organic pollutants - PAHs and polychlorinated biphenyls compounds – PCBs, adsorbed on the surface of solid aerosol particles).

The concentrations of particulate matter with a diameter less than 10 microns in ambient air are evaluated using *the daily limit value ,(50µg/m^3)*, which must not be exceeded more than 35ori/an and *the annual limit value (40µg/m^3)*.

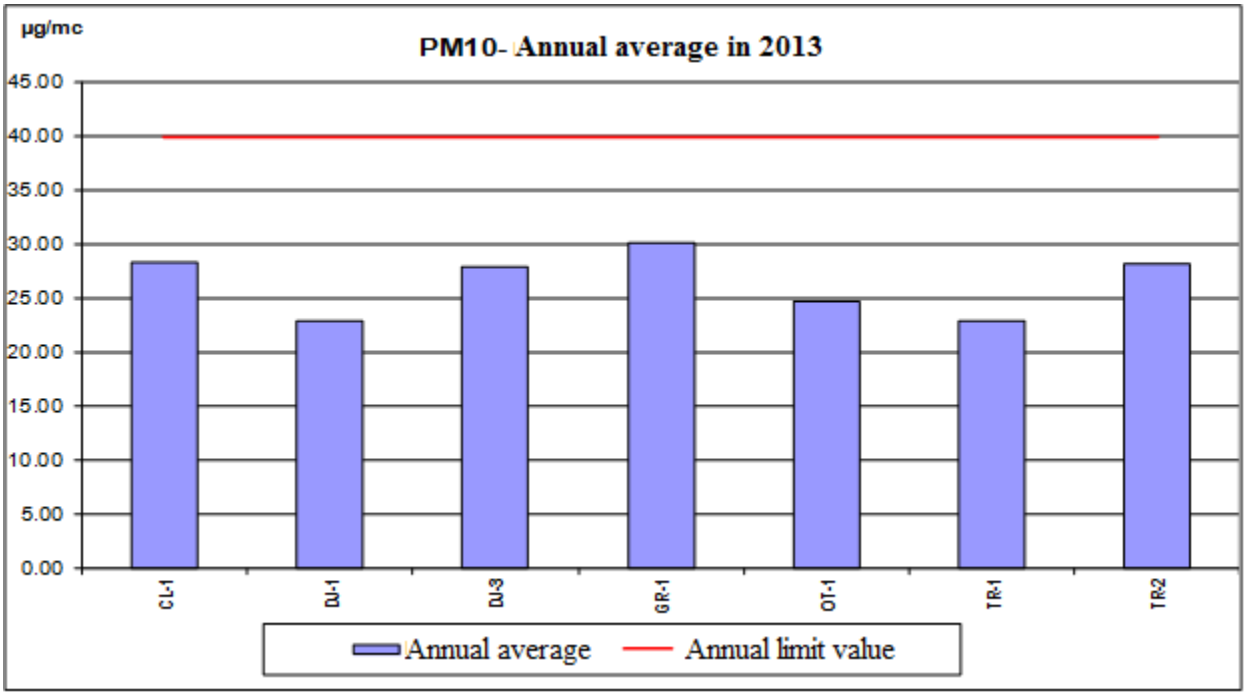
The number of exceedances of the daily limit value for particulate matter PM10 is shown in the following chart:

Fig. 9 Particulate matter (PM_{10}) _ number of exceedances of the daily limit value - 2013



There were no exceedances of the annual limit value:

Fig. 10 Particulate matter (PM_{10}) –annual average concentrations 2013



Conclusions

Following an analysis of the air quality evolution in Calarasi, Dolj, Giurgiu, Mehedinti and Olt county, and based on the measurements for SO_2, NO_2, O_3 pollutants and particulate matter PM_{10}, the following are observed:

- For the SO_2, NO_2 pollutants no exceedances of the limit values were recorded.
- For O3 exceedances were recorded in the information threshold for 1 hour (DJ-3) and the target value (DJ-3 DJ-4).
- For particulate matter PM_{10} the exceedances of the daily limit values were below the maximum number accepted at all stations considered in the analysis.

REPORT FOR 2013 ON ENVIRONMENTAL RADIOACTIVITY IN MEHEDINŢI , DOLJ, OLT, TELEORMAN, GIURGIU AND CĂLĂRAŞI COUNTY - " DANUBE WATER INTEGRATED MANAGEMENT " PROJECT

Radioactivity is the property of some chemical elements cores to emit by spontaneous decay corpuscular and electromagnetic radiation. This is a natural phenomenon that occurs in the environment.

Natural radioactivity is determined by the land-based radioactive substances (such as U-238, U-235, Th-232, Ac-228, etc.), to which are added the radioactive substances from cosmic sources (H-3, Be-7, C -14 etc.) and cosmic radiation. Land-based radioactive substances exist in nature from ancient times, and their abundance is dependent on the geological conformation of different areas, varying from one place to another. The extra-terrestrial component of natural radioactivity consists of cosmic radiation originating from outer space and the Sun. Radioactive substances from cosmic sources are formed in the higher layers of the atmosphere through the interaction of cosmic radiation with stable elements. It follows that all living organisms are exposed to ionizing radiation of natural origin, which all together form the natural background radiation.

All ionizing radiation, of terrestrial or cosmic origin, represent the natural background radiation that acting on living organisms.

Along with the natural radionuclides there are also artificial radionuclides that have entered the environment in different ways:

- intentionally after nuclear tests and discharges from various nuclear facilities
- accidentally due to malfunctioning at nuclear facilities (eg. the Cernobyl, Fukusima nuclear accidents).

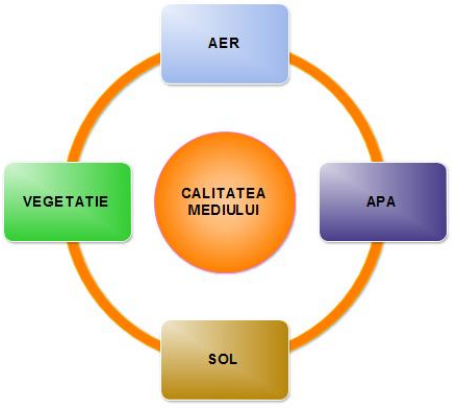
The National Environmental Radioactivity Surveillance Network (NERSN) is part of the Environmental Pollution Integrated Surveillance System in Romania, within the Ministry of Environment and Climate Change (MECC).

The NERSN scientific, technical and methodological coordination is provided by the National Reference Laboratory for Radioactivity (NRLR) of the National Environmental Protection Agency (NEPA).

In 2013, the assessment of the environmental radioactivity along the Danube River in Mehedinţi, Dolj, Olt, Teleorman, Giurgiu and Călăraşi, was carried out by 4 ERSS (Environmental Radioactivity Surveillance Stations) laboratories, found in the organizational and administrative structure of the County Environmental Protection Agencies and with 18 automatic monitoring stations of the gamma absorbed dose rate in air (Figure 1).

Fig.1. National Environmental Radioactivity Surveillance Network

Of the 4 ERSS, one operated on a 24 hours / day work schedule (ERSS Bechet), and the rest on an 11 hours / day work schedule.



Under the coordination of NRLR – NEPA, in 2013 NERSN conducted, two types of environmental radioactivity monitoring programs, along the Danube River. These were:

- The National Environmental Radioactivity Monitoring Program, consistently carried out by all ERSS within NERSN. This program is ongoing and monitors the evolution in time of environmental radioactivity factors;
- Monitoring program of the areas with

anthropogenic modified natural background – specific for each area; the National Environmental Radioactivity Monitoring Program.

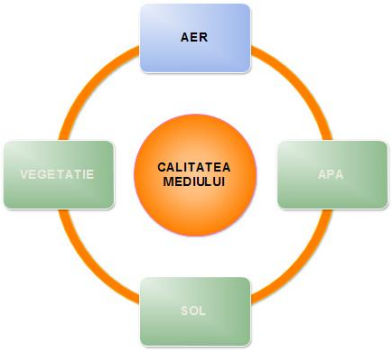
The analyses performed to monitor environmental factors (air - by aerosols, wet and dry atmospheric depositions, water - by surface water and groundwater, unsown land, spontaneous vegetation) were: global beta, beta spectrometry and gamma spectrometry as well as, determination of the gamma dose rate.

The environmental radioactivity monitoring objectives are:

- early detection of any significant radiological increase in environmental radioactivity levels on the national territory;
- early notification of decision makers in case of radiological emergency and support, with field data, the decisions to implement protection measures in real time;
- control of the operation of radioactive pollution sources with environmental impact, in line with legal requirements, and the nationally authorized limits;
- assessment of the doses received by the population as a result of additional exposure to radiation due to practices or radiological accidents;
- continuous monitoring of the natural radioactivity levels, important in assessing the consequences of a radiological emergency;
- providing information to the public.

NATIONAL ENVIRONMENTAL RADIOACTIVITY MONITORING PROGRAM

AIR RADIOACTIVITY



Air quality monitoring in terms of radioactivity is the first way to identify the presence of natural and artificial radionuclides in the atmosphere, above the natural background.

To this end are carried out gamma dose rate measurements, global beta and gamma spectrometry on atmospheric aerosols and on the total atmospheric depositions (wet and dry), as well as global beta

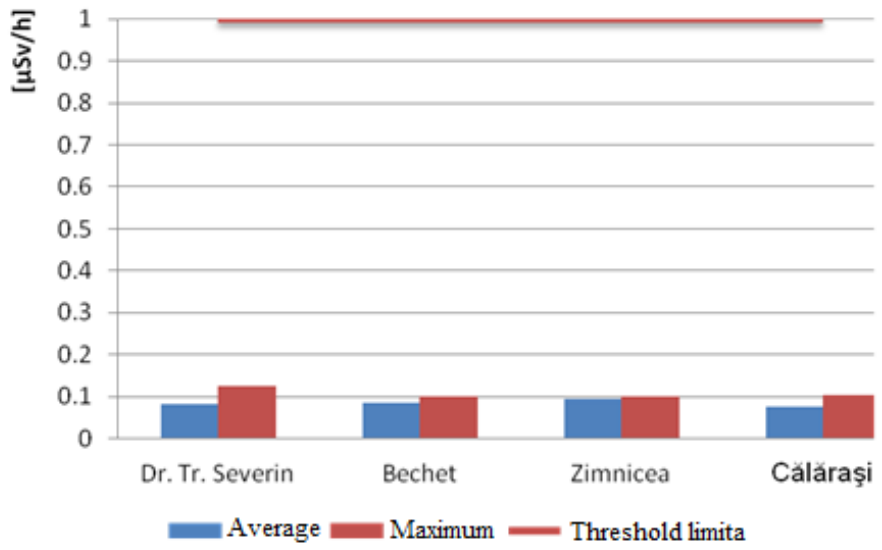
measurements on wet atmospheric depositions.

➢ *Gamma dose rate*

The determination of gamma dose rate is achieved with an hourly frequency. The values give a first indication of the radioactivity in the atmosphere.

Annual variation of gamma dose rate recorded in 2013 is shown in Figure 2..

Fig. 2. Annual average variation of the gamma dose rate in 2013



Note: The warning limit of the gamma dose rate (in accordance with M.O. no. 1978/2010) is of 1 µSv/h.

The chart shown in Figure 2 was obtained by averaging the dose rate value, hourly recorded 2013. The error associated with this analysis is less than 15%.

➢ *Atmospheric aerosols*

Samples of atmospheric aerosols are removed by suction filters, which are analysed by global beta and gamma spectrometry.

Sampling of atmospheric aerosols is achieved in the ERSS depending on the specific operating schedule, as follows:

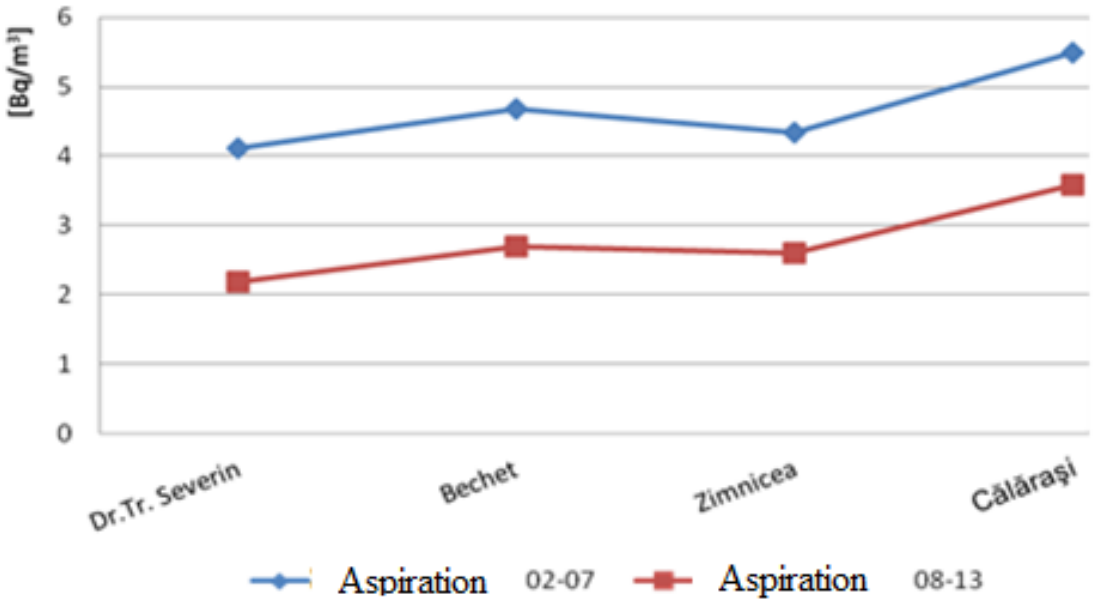
- 4 aspirations: 02 - 07, 08 - 13, 14 - 19 and 20 - 01;
- 2 aspirations: 02 - 07 and 08 - 13.

Global beta analysis on the atmospheric aerosols filters were performed on individual filters. Each filter was measured three times at well set time intervals: 3 minutes after sampling to 20 hours, or 24 hours, respectively (depending on the operating schedule of the station, in order to determine the radon and thoron in the atmosphere), and 5 days after cessation of aspiration.

The total number of global beta tests conducted in 2013, on the atmospheric aerosols filters, was of 10950.

In the case of immediate global beta tests of atmospheric aerosols samples, the influence of diurnal variation of air currents on the activity of aspirated atmospheric aerosols in the ERSS is observed through higher values recorded at night and morning samples (aspiration 20-01, aspiration 02-07 respectively), which are higher than those observed during the day (aspiration 08-13, 14-19 respectively), the maximum was reached within the aspiration range of 02-07, due to the low dispersion conditions in the atmosphere and the minimum was reached within the aspiration range of 14-19.

Fig. 3. Comparison between global beta activity values obtained in the aspiration range of 02-07 and 08-13



Note: The warning limit for atmospheric aerosols by analysing the immediate global beta (according M.O. no.1978/2010) is of 50 Bq/ m^3.

Delayed beta global analysis of atmospheric aerosols samples are performed at 20 hours, or 24 hours respectively (depending on the working

schedule of the station, in order to determine the radon (Rn-222) and thoron (R-220) in the atmosphere), and 5 days after cessation of aspiration. The specific activity of radon and thoron was indirectly determined by global beta analysis of filters on which were aspirated the atmospheric aerosols.

The radon (Rn-222) and thoron (Rn-220) are decay products of U-238 and Th-232 , found in gaseous state. They get into the atmosphere by exhalation from soil and rocks, where are subject to atmospheric dispersion phenomena. The Rn-222 and Rn-220 concentrations vary seasonally in the atmosphere, depending on the weather conditions which influence both the emanation rate of gas from the soil, and the dilution / their dispersion into the atmosphere.

Fig. 4. Variation of the annual average specific activity of radon in the atmosphere in 2013

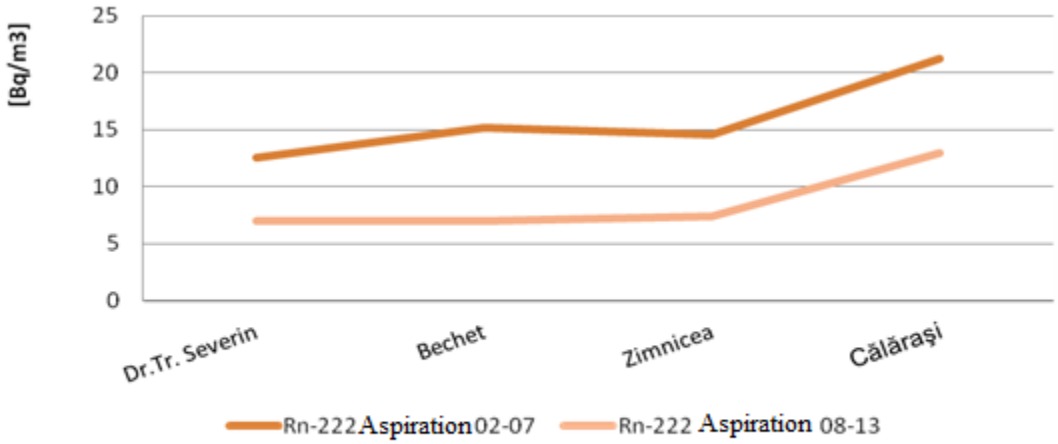
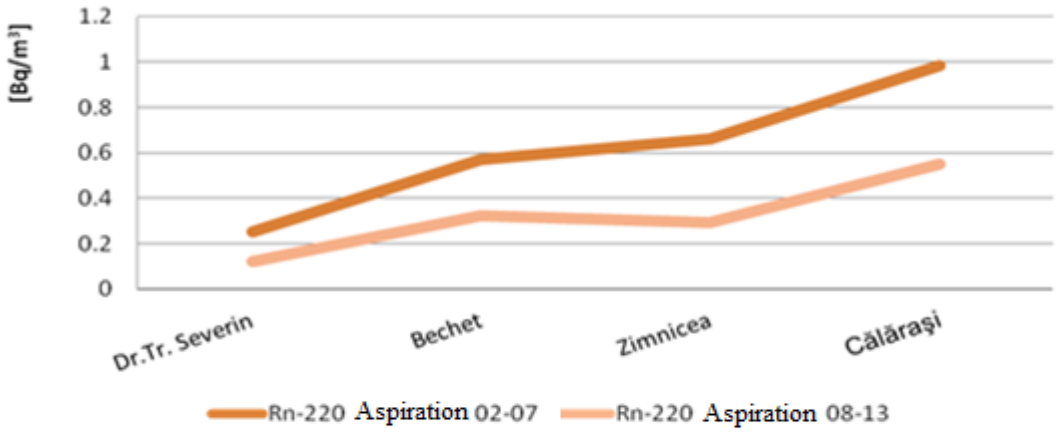


Fig. 5. Variation of the annual average specific activity of thoron in the atmosphere in 2013

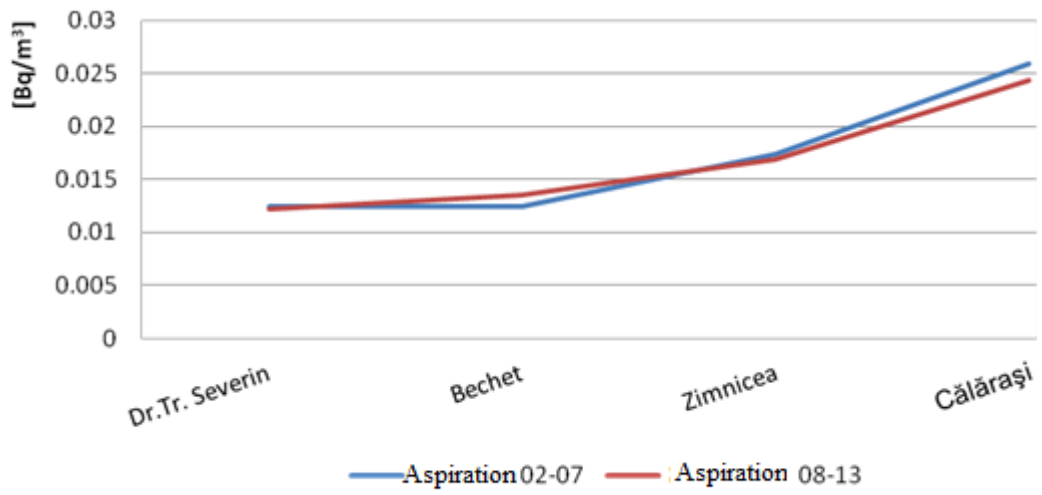


Atmospheric radon and thoron concentration follows the same trend as atmospheric aerosols, both for diurnal and seasonal variation and for variation in altitude, being strongly influenced by the air currents movement.

Variation in the concentrations of Rn-222 and Rn-220 in the country is heavily influenced by the altitude of the sampling point. The average annual value, of the two aspirations (the sampling range of 02-07 and 08-13 sampling range) was of 12.22 Bq/ m^3 for Rn-222 and of 0.47 Bq/ m^3 for Rn-220.

Figure 6 shows the variation of the annual average global beta activity of atmospheric aerosols measured at 5 days after sampling. The variation range of the annual average values for atmospheric aerosols measured at 5 days is of 0,012 ÷ 0,026 Bq/ m^3, with an average value of 0.017 Bq/ m^3.

Fig. 6. Variation of the annual average global beta activity of atmospheric aerosols – measurement at 5 days



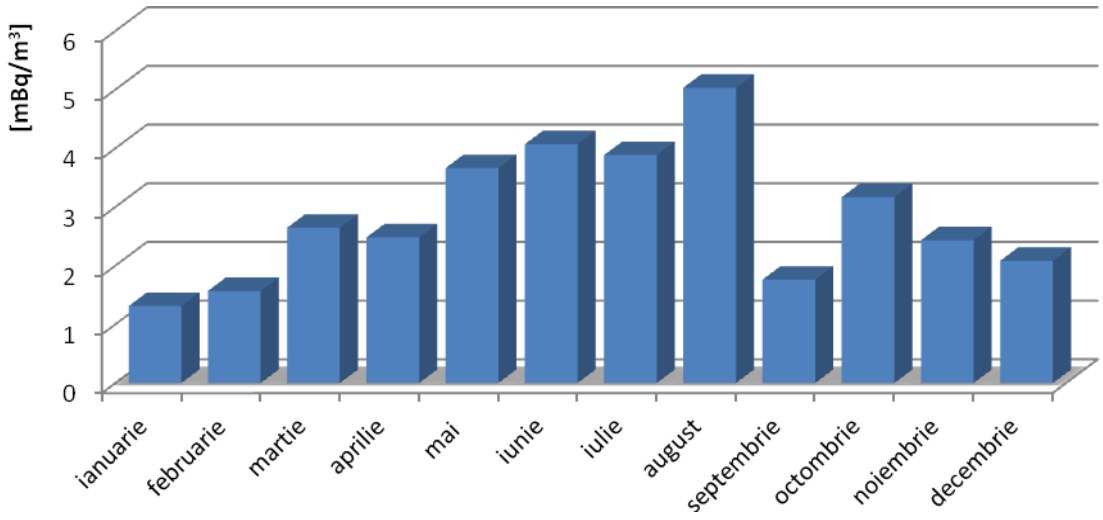
Gamma spectrometric analysis of atmospheric aerosols samples

In normal circumstances gamma spectrometric analysis of the atmospheric aerosols samples is carried out on a cumulated sample containing all samples collected by an ERSS over a month.

In the atmospheric aerosols samples collected throughout the year was highlighted also the presence of the natural radionuclide of cosmic origin, Be-7 its monthly average concentration ranging between 1,310 and 5,032 mBq/ m^3. (Figure 7.).

The analysis of the variation of Be-7 monthly averages has showed an upward period between March to August, followed by a period of declining values, the lowest values being recorded in winter, in January and February.

Fig. 7. The variation of Be-7 monthly average activity in samples of atmospheric aerosols



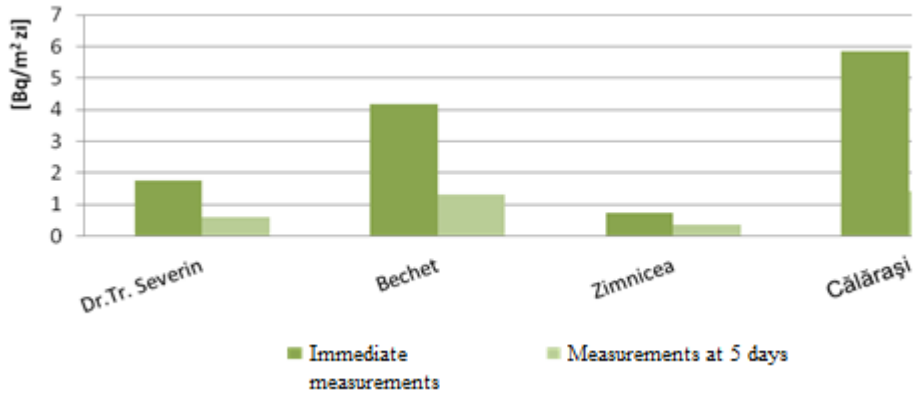
Total atmospheric deposition and precipitation

Atmospheric deposition samples are obtained by daily sampling the sediments and precipitation, on an area of 0.3 m^2.

After sampling and preparation, the total deposition samples are measured to determine the immediate global beta activity, and also after 5 days from the sampling.

Global beta analysis of the total atmospheric deposition samples highlighted the variation of the global beta activity of this type of sample, in 2013 (Figure 8). The values shown were obtained by averaging the daily values recorded in 2013. The overall number of analysis performed in 2013 at the 4 ERSS, for atmospheric depositions was 2920.

Fig. 8. The global beta annual average activity of the total atmospheric depositions recorded in 2013



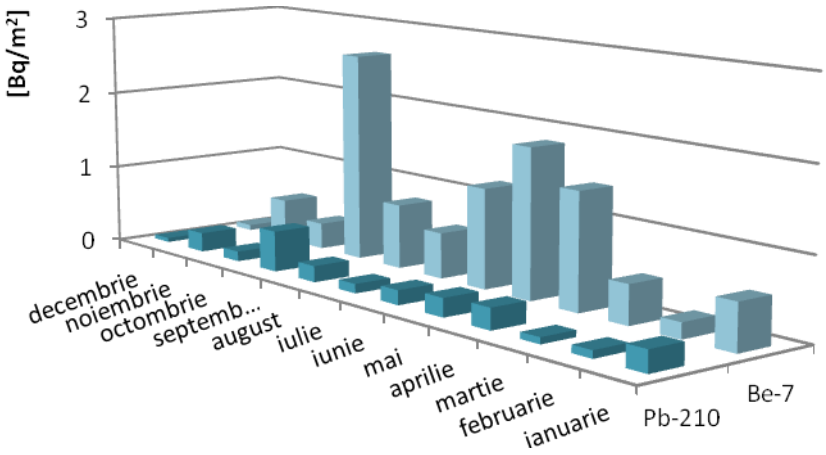
Note: The warning limit for total atmospheric depositions (wet and dry) through the immediate global beta analysis (according with M.O. 1978/2010) is of 1000 Bq/ m^2 day.

Gamma spectrometric analysis of the total atmospheric deposition samples

The samples collected daily are monthly cumulated and measured by gamma spectrometric measurements.

Gamma spectrometric analysis results with significant values, conducted on atmospheric deposition samples collected in 2013 are shown in Figure 9.

Fig. 9. Variation of the monthly average specific activity of natural and artificial radionuclides identified in samples of total atmospheric depositions in 2013



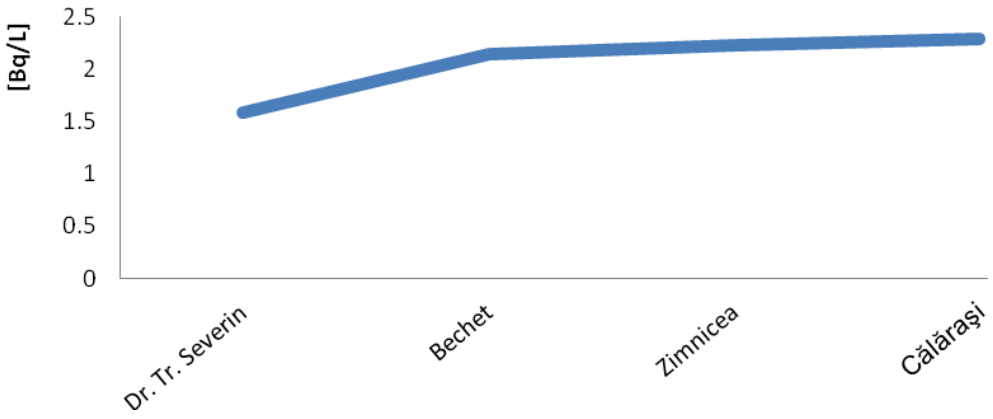
The fission product Cs-137 is absent in atmospheric deposition samples, hovering in 2013 under the detection limit.

Beta spectrometric analysis of atmospheric precipitation samples

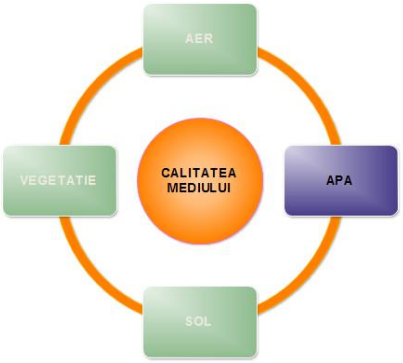
Samples of precipitation are obtained by collecting all types of precipitation. After collection and preparation, the samples are analysed beta spectrometric by a liquid scintillation analyser in order to determine the tritium concentration.

Figure 10 shows the tritium levels of precipitation samples collected in 2013 from the 4 ERSS. The monthly values presented below were obtained by cumulating precipitation samples collected throughout a month.

Fig. 10. Annual average volume activity of tritium in atmospheric precipitation samples, in 2013



Water radioactivity

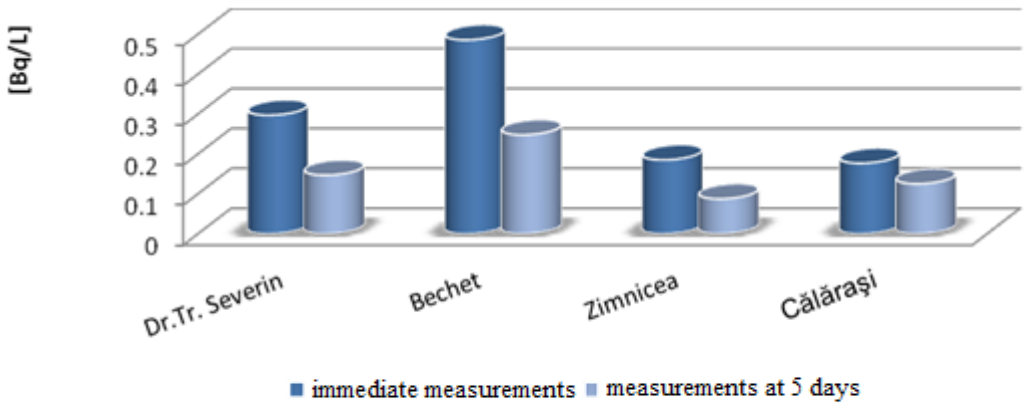


In order to supervise the main river flows in the country, samples from rivers located near the ERSS are collected on a daily basis. The samples are prepared for analysis and immediate global beta activity measurements are performed also after 5 days. Daily samples are monthly cumulated and submitted for gamma spectrometric analysis. The total number of global beta analysis (immediate and delayed) for surface water samples collected from the Danube and performed by the 4 ERSS in 2013 was 2920.

Global beta analysis of water samples collected from the surface water

Figure 11 shows the global beta radioactivity level in surface waters, annual average values recorded in 2013 for the immediate and delayed measurements. The values were obtained by averaging daily values of the immediate measurements in 2013, performed by the 4 ERSS.

Fig. 11. Variation of annual average global beta activity of surface waters in 2013

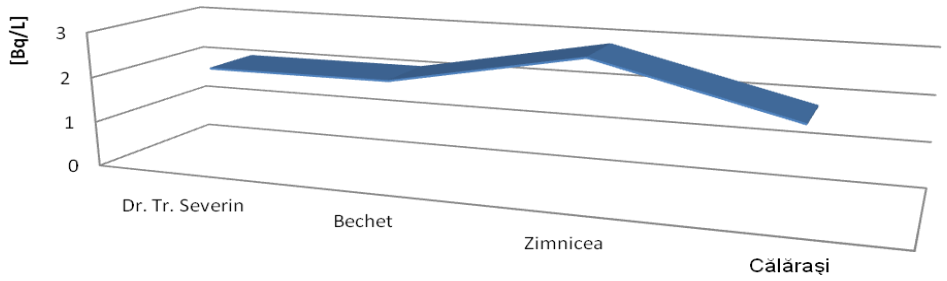


Note: The warning limit for surface water by immediate global beta analysis (according to M.O. 1978/2010), is of 5 Bq / L.

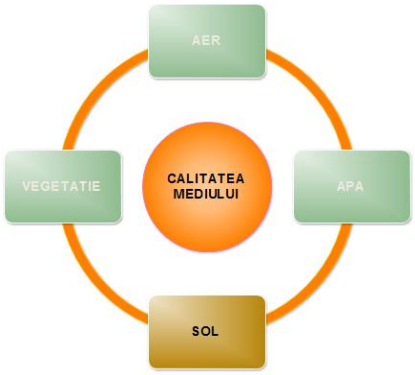
Beta spectrometric analysis of surface water samples

Annual average concentrations of tritium (for significant values) in surface water samples ranged in 2013 between 1.872 to 2.890 Bq / L.

Fig. 12. Variation of the specific activity of tritium in surface waters in 2013



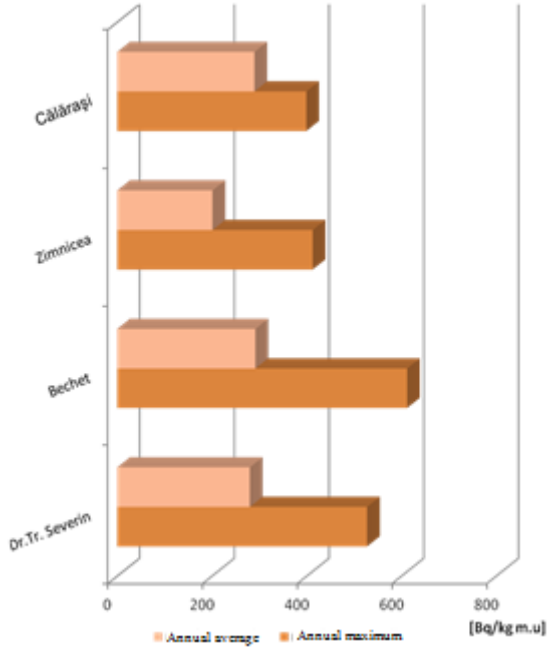
Soil radioactivity



The soil samples are collected from unsown areas of at least 10 years. Soil sampling is performed weekly and global beta samples measurement is performed after 5 days.

The annual average results values of the **global beta analysis of unsown soil samples,** collected in the four ERSS in 2013, are shown in Figure 13. The values in the chart were obtained by averaging the samples values collected weekly. The total number of measurements performed in the 4 ERSS within NERSN is about 206.

Fig. 13. Variation of annual average global beta activity of unsown soil samples collected in 2013



Variation of annual average global beta activity of unsown soil samples is shown in Figure 13, along with the maximum annual variation.

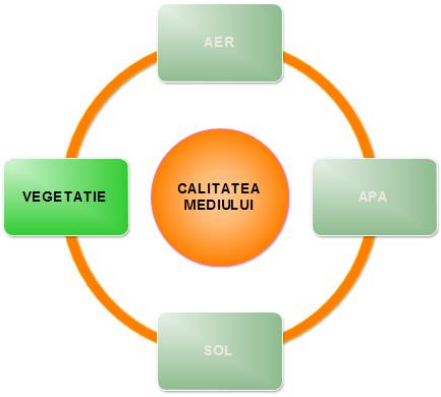
From **the gamma spectrometric analysis of soil samples**, collected annually, was obtained information on the distribution and concentration level of radionuclides in the laboratories area of the NERSN. The variation of the concentrations of radionuclides in soil samples collected from the four ERSS is given by the soil type - for natural radionuclides and by radioactive contamination peculiarities during the Chernobyl nuclear accident – for the artificial radionuclide Cs-137.

Table 1 shows the average concentrations in Bq / kg d.w. (dry weight – d.w.) of Ra-226 (descendant of U-238), Ac-228 (descendant of Th-232) K-40 and Cs-137, determined in unsown soil samples.

Table 1. Variation of natural radionuclides concentrations

Radionuclide	**Minimum Bq/kg (d.w.)**	**Average Bq/kg (d.w.)**	**Maximum Bq/kg (d.w.)**
Ra-226	14,36	41,00	87,11
Ac-228	19,89	32,20	42,80
K-40	418,71	471,80	536,48
Cs-137	2,02	5,26	9,13

9.2.3. Vegetation radioactivity

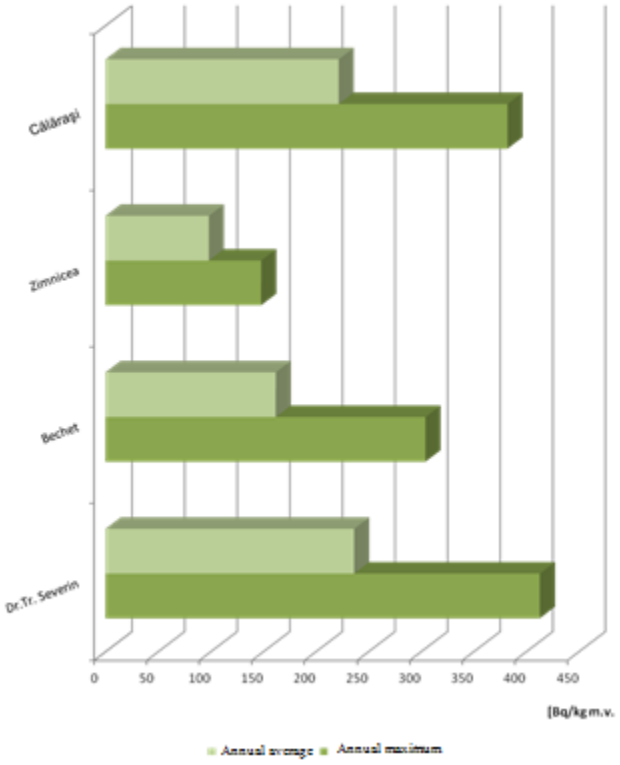


Spontaneous vegetation samples are collected weekly and the measurement of global beta samples is performed at 5 days after collection. The chart in figure 14 shows the global beta radioactivity level in the spontaneous vegetation samples collected from April to October, 2013.

The values shown in this chart were obtained

by averaging the monthly average values, in 2013.

Fig. 14. Variation of annual average global beta activity of the spontaneous vegetation, recorded in 2013, compared to the green weight (g.w.)



ENVIRONMENTAL RADIOACTIVITY MONITORING IN THE KOZLODUY NPP, ON THE ROMANIAN TERRITORY

Environmental radioactivity surveillance program conducted by NERSN in the influence area of Kozloduy NPP aimed at identifying possible radioactive emissions into the environment, in 2013. There was not identified the presence of gamma emitting artificial radionuclides whose source is Kozloduy NPP.

All values recorded in 2013 at the environmental radioactivity surveillance stations (Bechet ERSS, Craiova ERSS, Zimnicea SSRM and Dr. Tr. Severin SSRM) in the influence area of the plant were within the operational warning / alarm limits of the National Environmental Radioactivity Surveillance Network.