CONCEPT OF MODERNISATION AND OPTIMISATION OF DEPOSITION MEASUREMENTS IN POLAND

Task 1. Analysis of Polish and foreign documents and studies, monitoring systems and data of the State Environmental Monitoring in order to design a new system of research and assessment of atmospheric deposition

Report commissioned by the Chief Inspectorate of Environmental Protection for the implementation of the project **“Strengthening of atmospheric deposition assessment in Poland based on Norwegian experience”** under the Environment, Energy and Climate Change Programme, the Climate Change Mitigation and Adaptation sub-programme, financed by the European Economic Area Financial Mechanism 2014-2021

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WARSAW, 2022

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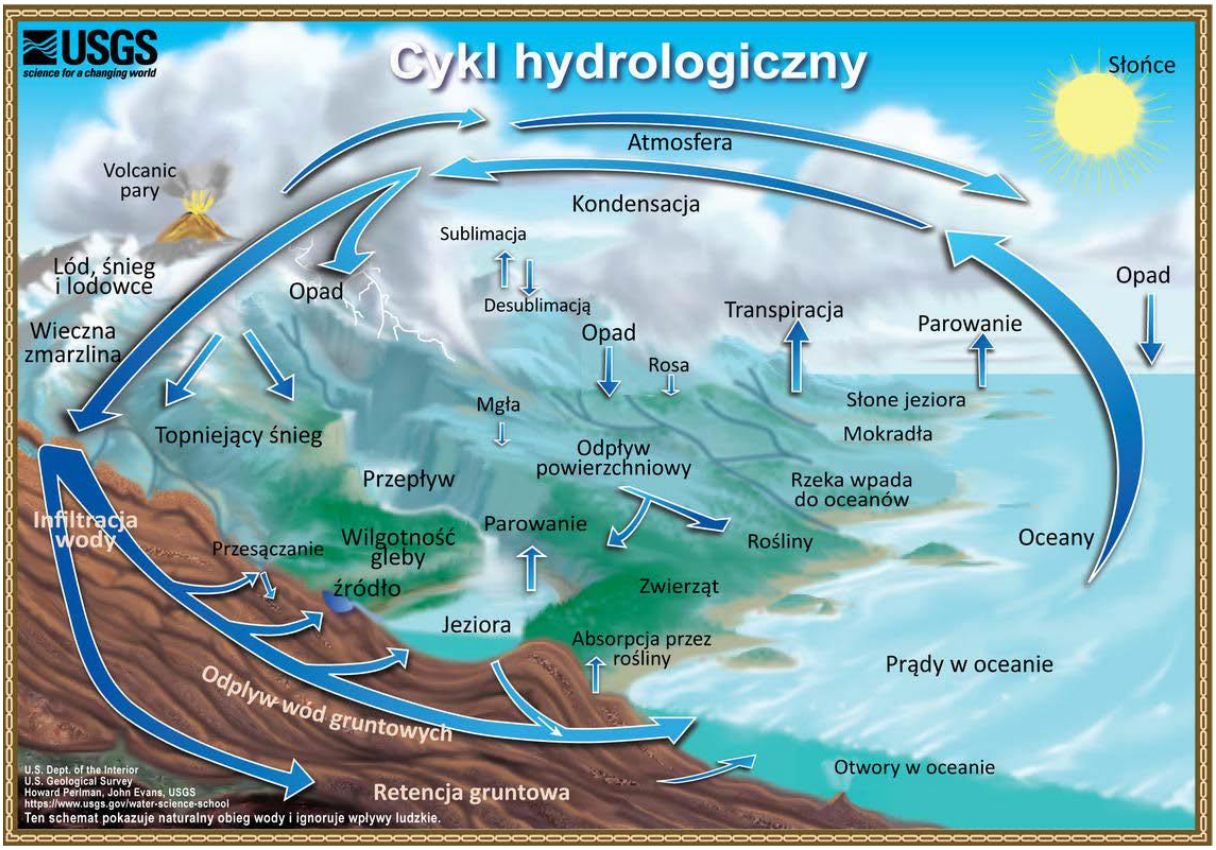
1. Introduction

Assessment of dry and wet deposition in regional and international terms is a very important task undertaken by various organizational and scientific units all over the world. Conducting research on the quality of precipitation water makes it possible to assess the chemical composition of the atmosphere and contributes to the knowledge of the sources of its pollution or the way in which chemical compounds move under the influence of meteorological or anthropogenic factors. In the process of planning the atmospheric deposition monitoring system, it is also necessary to take into account factors related to climate change which influence the amount of deposited substances.

Precipitation, which is an important part of the hydrological cycle as shown in Figure 1.1, can be a factor affecting ecosystems due to the variable chemical composition of precipitation and deposition rates.



The Water Cycle
Volcanic steam / Ice and snow / Precipitation / Snowmelt runoff
Sublimation / Desublimation / Fog drip
Atmosphere / Condensation / Evapotransporation / Evaporation / Surface runoff / Dew
Infiltration / Seepage / Streamflow / Evaporation / Seepage / Spring / Freshwater / Plant uptake / Floar and fauna
Groundwater flow / Groundwater storage / Vents and volcanos / Oceans

Figure 1.1 Hydrological cycle, source: https://www.usgs.gov/media/images/cykl-hydrologiczny-natural-water-cycle-polish

Precipitation chemistry in Poland is studied at national and international level within the following programmes:

1) State Environmental Monitoring (SEM);
2) Convention on Long Range Transboundary Air Pollution of 13 November 1979, known as the Geneva Convention and the Protocol to the Convention on EMEP (European Monitoring and Evaluation Programme);
3) Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, nickel, mercury and polycyclic aromatic hydrocarbons in ambient air;
4) Convention on the Protection of the Marine Environment of the Baltic Sea Area (HELCOM).

2. Purpose of the Project

The purpose of the project is to develop a concept for the modernisation and optimisation of atmospheric deposition in Poland using the Norwegian experience as part of the project entitled "Strengthening of atmospheric deposition assessment in Poland based on Norwegian experience" under the Environment, Energy and Climate Change Programme, the Climate Change Mitigation and Adaptation sub-programme, financed by the European Economic Area Financial Mechanism 2014-2021.

3. Basis of the Study

The basis for the study is Agreement No. GIOŚ/ZP/380/2021/DMŚ/MFEOG, concluded on 22 December 2021 between the State Treasury – Chief Inspectorate of Environmental Protection and the Institute of Meteorology and Water Management – National Research Institute.

4. Scope of the Study

The study covers analyses of Polish and foreign documents and studies, as well as monitoring systems and the data of the State Environmental Monitoring, for the purpose of designing a new system of research and assessment of atmospheric deposition. For the purposes of the study, elements of the current domestic monitoring of precipitation chemistry and international programmes are discussed.

4.1 Information on the functioning of the current precipitation chemistry monitoring system (wet and total precipitation), including EMEP sites, based on documents and studies of the Chief Inspectorate of Environmental Protection (annual national and regional reports, synthetic reports, reports of monitoring studies)

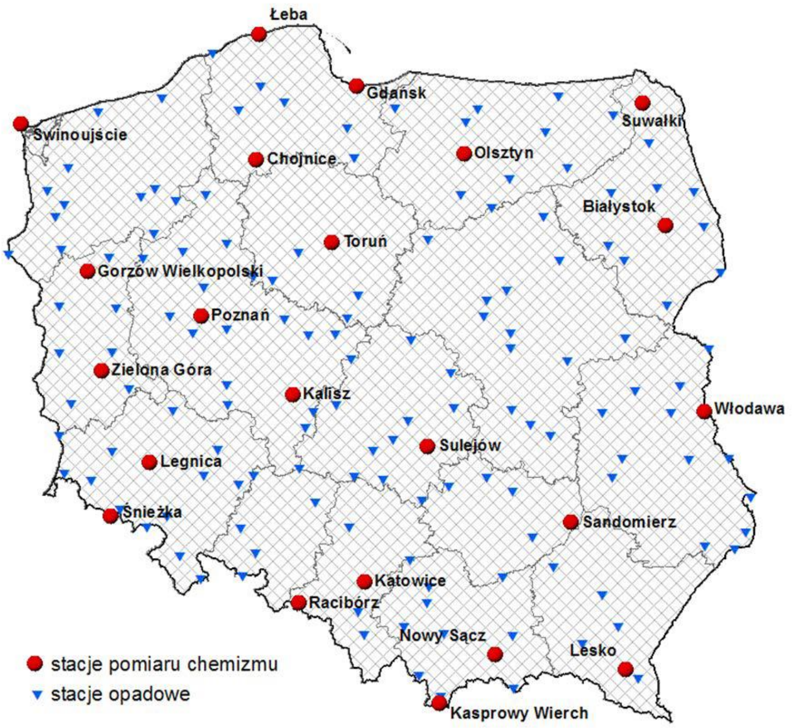
The current monitoring system of atmospheric precipitation chemistry in Poland consists of stations conducting measurements within the framework of: monitoring of precipitation chemistry and assessment of deposition of pollutants to the ground; background monitoring of atmospheric pollution for the needs of EMEP, GAW/WMO, HELCOM and the European Commission and regional background stations conducting measurements of total deposition of heavy metals, including mercury, and polycyclic aromatic hydrocarbons, in accordance with the provisions of Article 4(9) of Directive 2004/107/EC.

Monitoring of precipitation chemistry and assessment of pollution deposition to the ground

The programme for monitoring of precipitation chemistry and assessment of pollutant deposition to the ground is an element of the State Environmental Monitoring. It was implemented in 1999 in order to determine, at the national scale, the spatial and temporal distribution of pollution loads deposited with wet precipitation to the ground. The information on the loads of acidifying compounds, biogenic compounds and heavy metals deposited from the air on forest areas, soils and surface waters can provide a basis for use in developing and evaluating the effectiveness of air emission reduction schemes and in developing fertiliser balances for water and forest management. Interpretation of deposition results in connection with circulation types makes it possible to estimate the share and influence of sources of pollution from outside of the territory of Poland on deposition in the country.

Monitoring studies are carried out by the Institute of Meteorology and Water Management – National Research Institute (IMWM-NRI), commissioned by the Chief Inspectorate of Environmental Protection (CIEP), under contracts financed by the National Fund for Environmental Protection and Water Management (NFEPWM). As part of the monitoring programme annual reports on precipitation chemistry studies in Poland and annual voivodeship reports are prepared. For the needs of monitoring, compilations of sectors of air mass inflow and occurrence of precipitation are prepared, taking into account their genesis at 22 monitoring sites, as well as compilations of data concerning inflow of tropical air masses over Poland.

At the beginning, the measurement programme for atmospheric precipitation chemistry monitoring was carried out at 25 monitoring sites located at synoptic stations of IMWM-NRI. In the period of 23 years of research, the number of monitoring sites and the scope of examined indicators have been modified. At present, the monitoring system operates at 22 monitoring sites representing the area of whole Poland, both coastal regions and lowland areas of central Poland as well as foothills and mountains (Fig. 4.1).



chemistry measurement stations / precipitation stations

Figure 4.1 Location of monitoring stations of the national monitoring of precipitation chemistry and assessment of deposition of pollutants to the ground and the network of precipitation stations representing the field of average precipitation totals in the area of Poland [Annual report Monitoring of precipitation chemistry and assessment of deposition of pollutants to the ground in 2020-2021*, 2021].*

Table 4.1 Summary data on geographical location of monitoring stations of the national monitoring of precipitation chemistry and assessment of deposition of pollutants to the ground [Annual report "Monitoring of precipitation chemistry and assessment of deposition of pollutants to the ground in 2020-2021", 2021]

No.	location/ monitoring station	Latitude	Longitude	altitude [m] above sea level
1.	Świnoujście	53°55'24,0 "N	14°14'32,3 "E	6
2.	Łeba	54°45'13,0 "N	17°32'05,3 "E	2
3.	Gdańsk-Świbno	54°20'01,2 "N	18°56'03,5 "E	7
4.	Suwałki	54°07'51,1 "N	22°56'56,2 "E	184
5.	Chojnice	53°42'54,7 "N	17°31'57,4 "E	165

No.	location/ monitoring station	Latitude	Longitude	altitude [m] above sea level
6.	Olsztyn	53°46'06,7 "N	20°25'16,9 "E	133
7.	Gorzów Wlkp.	52°44'28,2 "N	15°16'38,1 "E	72
8.	Torun	53°02'31,6 "N	18°35'42,6 "E	69
9.	Bialystok	53°06'26,2 "N	23°09'44,1 "E	148
10.	Zielona Góra	51°55'48,0 "N	15°31'28,9 "E	192
11.	Poznan	52°24'59,5 "N	16°50'04,6 "E	83
12.	Kalisz	51°46'52,4 "N	18°04'51,3 "E	138
13.	Sulejów	51°21'11,4 "N	19°51'58,4 "E	188
14.	Włodawa	51°33'12,8 "N	23°31'45,1 "E	177
15.	Legnica	51°11'33,2 "N	16°12'27,6 "E	122
16.	Snowball	50°44'10,7 "N	15°44'23,1 "E	1603
17.	Racibórz	50°03'39,7 "N	18°11'26,9 "E	205
18.	Katowice	50°14'26,3 "N	19°01'57,8 "E	284
19.	Nowy Sącz	49°37'37,8 "N	20°41'19,0 "E	292
20.	Sandomierz	50°41'47,8 "N	21°42'57,2 "E	217
21.	Kasprowy Wierch	49°13'57,0 "N	19°58'54,4 "E	1991
22.	Lesko	49°27'59,4 "N	22°20'30,2 "E	420

Among the 22 stations, representing the area of Poland, we distinguish two high-mountain sites (Śnieżka, Kasprowy Wierch). These stations are distant from human settlements, therefore it may be concluded that for the greater part of the year the measurement results provide information on pollution transported over long distances. They are disturbed only by periodical work of snowgroomers on ski trails and occasional repairs of infrastructure of mountain huts and the high-mountain observatory with access roads. Similarly, the coastal sites, at certain periods, depending on the direction of air mass inflow, may also be a source of information on pollution transported over long distances. The remaining stations for sampling of wet precipitation are most often located in urban areas in suburban or non-urban areas with low buildings being at least 100m away from the measuring stations in case of 11 stations, in case of 6 sites – at least 100m away from the measuring stations. 100m, and between 50m and 100m in the case of 6 sites. The sites are located both in areas with low pollution from industry and low population density (north-eastern and eastern parts of the country) and in highly industrialized areas in the south of the country with dense population (e.g. Upper Silesia) and with higher emission of pollutants from local sources.

Wet precipitation sampling

At the monitoring stations, except for high-mountain stations, the work is carried out on the basis of automatic wet precipitation collectors from ELMECO (Fig. 4.2, 4.3). The collectors collect wet precipitation only, the collecting vessel is exposed only during precipitation. In case of failure of the automatic collector, the precipitation is collected by a backup manual collector installed near the automatic collector (Figure 4.4). At high mountain stations, due to their location and difficult weather conditions, precipitation is collected by means of manual collectors. The correctness of sample collection is ensured by supervision of employees at synoptic stations, who perform sample collection only when there is precipitation. Additionally, daily precipitation samples are collected in separate collectors (Fig. 4.2) for pH measurement performed directly at the stations.

Figure 4.2 Automatic wet precipitation collector with open lid during precipitation, small precipitation collector for pH measurement in the background [photo by J. Biszczuk-Jakubowska].

Figure 4.3 Automatic wet precipitation collector with the lid closed during no precipitation [photo: J. Biszczuk-Jakubowska].

Figure 4.4 Backup manual collector [photo from IMWM-NRI archive].

Precipitation is collected continuously. The automatic collectors open the cover automatically, exposing the collecting vessel during precipitation and close it after the precipitation has stopped. In periods of negative temperatures (below 0^{o} C) they heat the collection vessel. The precipitation water is poured off immediately after each precipitation event into polyethylene bottles and stored in a refrigerator for one precipitation day. A precipitation day lasts from 6:00 UTC on a given day until 6:00 UTC on the following day, i.e. 8:00 in summer time and 7:00 in winter time. At the end of the day, the volume of precipitation is measured and the precipitation sample is frozen at the temperature below -20^{o} C, ensuring stability of the physical and chemical composition of samples until the end of the month, i.e. until the samples are transferred for analyses to Central Testing Laboratories (CTLs) branches of the Chief Inspectorate of Environmental Protection. Frozen samples in polyethylene bottles are collected by CTL employees after each measurement cycle, in the first days of the following month. Samples to laboratories are transported in thermal containers (bags).

The daily precipitation samples for pH value measurement are collected using a separate stationary collector, consisting of a one-litre polyethylene bottle and a funnel placed on it with a diameter that ensures the collection of sufficient precipitation water for pH value measurement when the daily precipitation totals a minimum of 1 mm. The measurement of the pH value is carried out directly at the station, after a precipitation day, with the use of a pH meter with an autocalibration function and recording of results.

Measurement of meteorological parameters

Parallel to wet precipitation sampling, the station staff conducts measurements and observations of meteorological parameters necessary for the evaluation and interpretation of the monitoring results. Measurements and observations are conducted in the following range:

- date and time of precipitation and the time interval of precipitation (06-12, 12-18, 18-24, 00-06),
- measuring the amount of precipitation four times a day (according to GMT time, at the following times: 12, 18, 24, 06),
- the prevailing wind direction at the time of precipitation,
- the daily amount and volume of precipitation collected,
- the average daily air temperature in the day with precipitation occurring.

Meteorological measurements are conducted with standard devices and instruments used in the IMWM-NRI station network. The amount of precipitation is measured automatically with a Seba or Astra device and with the Hellmann rain gauge. Hellmann's rain gauge indications are treated as control measurements due to snowfall. Wind directions and speed are measured with an ultrasonic Vaisala wind meter and air temperature with a Vaisala sensor. At the high-mountain stations the following parameters are measured: precipitation amount – with a Hellmann rain gauge, wind speed – with an anemorumbometer, air temperature – with a mercury thermometer.

The aforementioned data, together with data on the measurement of the pH value of daily precipitation samples, are recorded on an ongoing basis in the observer's sheet and after the end of the monthly cycle presented in a monthly report.

Chemical composition analyses

Analyses of the chemical composition of samples collected within the framework of precipitation monitoring carried out at the 22 stations are conducted in laboratories of the Central Research Laboratory of the Chief Inspectorate of Environmental Protection. The measurement range and scope of analyses performed are presented in Table 4.2.

Table 4.2 Measurement programme at precipitation chemistry monitoring stations and the scope of physicochemical analyses [own work based on Annual Report “Monitoring of *precipitation chemistry and assessment of deposition of pollutants to the ground in the years 2021-2022, 2021]*

No.	location/ monitoring station	measurement cycle of 6 hours	daily measurement cycle	measurement cycle per month*	other programmes
1.	Świnoujście	precipitation (mm), the prevailing wind direction at the time of precipitation (degrees),	precipitation (mm), sample volume (cm^3), daily average air temperature, pH,	pH, conductivity, Cl^- SO_4^{--} N- (NO_2^- and NO_3^-) N- NH_4^+ Na^+ K^+ Ca^{++} Mg^{++} Zn Cu Pb Cd Ni Cr $N_{(sum)}$ $P_{(sum)}$	-
2.	Łeba				EMEP
3.	Gdańsk-Świbno				-
4.	Suwałki				-
5.	Chojnice				-
6.	Olsztyn				-
7.	Gorzów Wlkp.				-
8.	Torun				-
9.	Bialystok				-
10.	Zielona Góra				-
11.	Poznan				-
12.	Kalisz				-
13.	Sulejów				-
14.	Włodawa				-
15.	Legnica				-
16.	Snowball				EMEP
17.	Racibórz				-
18.	Katowice				-
19.	Nowy Sącz				-
20.	Sandomierz				-
21.	Kasprowy Wierch				-

No.	location/ monitoring station	measurement cycle of 6 hours	daily measurement cycle	measurement cycle per month*	other programmes
22.	Lesko				-

* additionally, auxiliary: $N_{(Kjeldahl)}$, H^+ ion and alkalinity

Analytical methods used by the Central Research Laboratory of the Chief Inspectorate of Environmental Protection

The range of analytical methods used in 2022 is summarised in Table 4.3.

Table 4.3 Methods of physical and chemical analyses of precipitation samples used to perform measurements by the Central Research Laboratory of the Chief Inspectorate of Environmental Protection – updated on 23.01.2022 [source: own work based on the Annual Report Monitoring of precipitation chemistry and assessment of pollution deposition to the ground in the years 2021-2022*, 2021]*

indicator	method
Reaction	PN-EN ISO 10523:2012 – German version
specific electrical conductivity	conductivity method PN-EN 27888:1999 – Polish version, - measurement at 25° C
alkalinity	a) measurement of total alkalinity and alkalinity in relation to phenolphthalein – PN-EN ISO 9963-1:2001/Ap1:2004P – Polish version b) measurement of carbonate alkalinity – PN-EN ISO 9963-2:2001 – Polish version
chlorides	ion chromatography PN-EN ISO 10304-1:2009/AC:2012E – English version
sulphates	ion chromatography PN-EN ISO 10304-1:2009/AC:2012E – English version
nitrate nitrogen	(a) ion chromatography PN-EN ISO 10304-1:2009/AC:2012E – English version b) flow analysis method (CFA and FIA) with spectrometric detection PN-EN ISO 13395:2001 – Polish version
nitrite nitrogen	a) the Particle Absorption Spectrometry method PN-EN 26777:1999 – Polish version

indicator	method
	(b) ion chromatography PN-EN ISO 10304-1:2009/AC:2012E – English version c) flow analysis method (CFA and FIA) with spectrometric detection PN-EN ISO 13395:2001 – Polish version
ammoniacal nitrogen	a) direct nesslerization method PN-C-04576-4:1994 – Polish version b) manual spectrometric method PN ISO 7150-1:2002 – Polish version c) flow analysis methods (CFA and FIA) with spectrometric detection PN-EN ISO 11732:2007 – Polish version d) ion chromatography PN-EN ISO 14911:2002 – Polish version
sodium	a) atomic absorption spectrometry PN-ISO 9964-1:1994 + Akt 1997 + Ap1:2009 – Polish version (b) inductively coupled plasma emission spectrometry method (ICP-OES) PN-EN ISO 11885:2009 – English version (c) inductively coupled plasma mass spectrometry (ICP-MS) PN-EN ISO 17294-2:2016-11 – English version d) ion chromatography PN-EN ISO 14911:2002 – Polish version
potassium	(a) the atomic absorption spectrometry method PN-ISO 9964-2:1994 +Ak:1997P - Polish version b) the inductively coupled plasma emission spectrometry method (ICP-OES) PN-EN ISO 11885:2009 - English version (c) inductively coupled plasma mass spectrometry (ICP-MS) PN-EN ISO 17294-2:2016-11 - English version d) Ion chromatography PN-EN ISO 14911:2002 - Polish version
calcium	a) atomic absorption spectrometry method PN-EN ISO 7980:2002 – Polish version b) inductively coupled plasma emission spectrometry method (ICP-OES) PN-EN ISO 11885:2009 – English version (c) inductively coupled plasma mass spectrometry (ICP-MS) PN-EN ISO 17294-2:2016-11 - English version d) ion chromatography PN-EN ISO 14911:2002 – Polish version
magnesium	a) atomic absorption spectrometry method PN-EN ISO 7980:2002 – Polish version b) inductively coupled plasma emission spectrometry method (ICP-OES) PN-EN ISO 11885:2009 – English version

indicator	method
	(c) inductively coupled plasma mass spectrometry (ICP-MS) PN-EN ISO 17294-2:2016-11 – English version d) ion chromatography PN-EN ISO 14911:2002 – Polish version
zinc	a) inductively coupled plasma emission spectrometry method (ICP-OES) PN-EN ISO 11885:2009 – English version b) flame atomic absorption spectrometry method PN-EN ISO 8288:2002 – Polish version (c) inductively coupled plasma mass spectrometry (ICP-MS) PN-EN ISO 17294-2:2016-11 – English version
copper	a) graphite furnace atomic absorption spectrometry PN-EN ISO 15586:2005 – Polish version b) inductively coupled plasma emission spectrometry (ICP-OES) PN-EN ISO 11885:2009 – English version (c) inductively coupled plasma mass spectrometry (ICP-MS) PN-EN ISO 17294-2:2016-11 – English version d) flame atomic absorption spectrometry PN-EN ISO 8288:2002 – Polish version
lead	a) graphite furnace atomic absorption spectrometry PN-EN ISO 15586:2005 – Polish version b) inductively coupled plasma emission spectrometry (ICP-OES) PN-EN ISO 11885:2009 – English version (c) inductively coupled plasma mass spectrometry (ICP-MS) PN-EN ISO 17294-2:2016-11 – English version
cadmium	a) graphite furnace atomic absorption spectrometry PN-EN ISO 15586:2005 – Polish version (b) inductively coupled plasma mass spectrometry (ICP-MS) PN-EN ISO 17294-2:2016-11 – English version c) atomic absorption spectrometry method PN-EN ISO 5961:2001 – Polish version
nickel	a) graphite furnace atomic absorption spectrometry method PN-EN ISO 15586:2005 – Polish version b) inductively coupled plasma emission spectrometry method (ICP-OES) PN-EN ISO 11885:2009 – English version (c) inductively coupled plasma mass spectrometry (ICP-MS) PN-EN ISO 17294-2:2016-11 – English version

indicator	**method**
chrome	a) atomic absorption spectrometry method PN-EN 1233:2000 – Polish version b) graphite furnace atomic absorption spectrometry PN-EN ISO 15586:2005 – Polish version (c) inductively coupled plasma emission spectrometry (ICP-OES) PN-EN ISO 11885:2009 – English version (d) inductively coupled plasma mass spectrometry (ICP-MS) PN-EN ISO 17294-2:2016-11 – English version
Kjeldahl nitrogen	instrumental methods after mineralisation PN-EN 25663:2001 – Polish version, PN-EN ISO 11905-1:2001 – Polish version
total nitrogen	instrumental methods after mineralisation PN-EN 25663:2001 – Polish version; PN-EN ISO 11905-1:2001 – Polish version
total phosphorus	spectrometric method PN-EN ISO 6878:2006, p.7+ Ap1:2010 +Ap2:2010 recommended photometric measurement at 880 nm – Polish version

Last update of standards 23.01.2022

Compliance with the following document was verified:

REGULAITON OF THE MINISTER OF INFRASTRUCTURE of 25 June 2021 on classification of the ecological state, the ecological potential and the chemical state, as well as the way of classifying the state of the surface water bodies, and environmental quality standards for priority substances (Journal of Laws of 2021, item 1475)

Processing of measurement results and making calculations

Knowledge of air pollution transported from long distances and from local sources is of great importance for the assessment of threats to human health and quality of life, as well as the state of the natural aquatic and terrestrial environment. Knowledge of the parameters of atmospheric precipitation quality changes, identification of pollution sources and direction of their inflow connected with the observed inflow of air masses, combined with knowledge concerning local sources is of considerable importance for the assessment of the condition of the environment. The measurements carried out within the framework of wet precipitation chemistry monitoring provide information on the averaged chemical composition of wet precipitation in monthly periods.

Monthly data sets form the basis for the analysis. Mean values are determined for annual periods. Mean values of concentrations of the analysed indicators in wet precipitation were calculated as weighted averages, where the weight is the amount of precipitation in a given averaging period, on the basis of the formula:

$$C_{śr} = \frac{\sum C_i \cdot h_i}{\sum h_i}$$

where:

$C_{śr}$ – weighted average concentration of the respective component [mg/l, µg/l]

C_i – individual concentrations for which the average value is calculated [mg/l, µg/l].

h_i – particular precipitation amounts corresponding to the above concentrations [mm].

Σh_i – sum of precipitation amounts for which the ith component was determined, in the period for which the average value is calculated [mm].

In practice, this means that the weighted average concentration of a given component is calculated as the quotient of the sum of the loads from the individual precipitations and the sum of the amounts of these precipitations for which quantitative analyses of the component in question are carried out.

Hydrogen ion concentrations are used to calculate the average pH value. The pH value is converted to hydrogen ion concentration using the formula:

$[H^+] = 10^{3-pH}$ where: $[H^+]$ – hydrogen ion concentration [mg/l].

or $[H^+] = 10^{6-pH}$ where: $[H^+]$ – hydrogen ion concentration [µg/l]

A weighted average of the hydrogen ion concentrations is then calculated according to the formula given above and converted to an average pH value according to the formula:

$$pH_{śr} = 3 - \log[H^+]_{śr}$$

The data on concentrations of individual indicators combined with meteorological data on monthly precipitation at the measurement points make it possible to calculate deposition with precipitation at 22 monitoring stations.

The deposition of particular substances introduced with precipitation is calculated on the basis of the data obtained during the research process regarding the concentration values of particular substances in the samples of wet precipitation collected at particular time intervals and the data from the measurements of precipitation amounts from the same time intervals. The deposition of substances introduced with wet precipitation to the ground, for a given area, is calculated as the product of the concentrations of substances contained in the precipitation and the amount of precipitation according to the following formula

$$Di = \mathrm{Ci}' * \mathrm{h}/100$$

where:

Di – deposition of the ith substance to the ground with precipitation in the given measurement period [kg/ha].

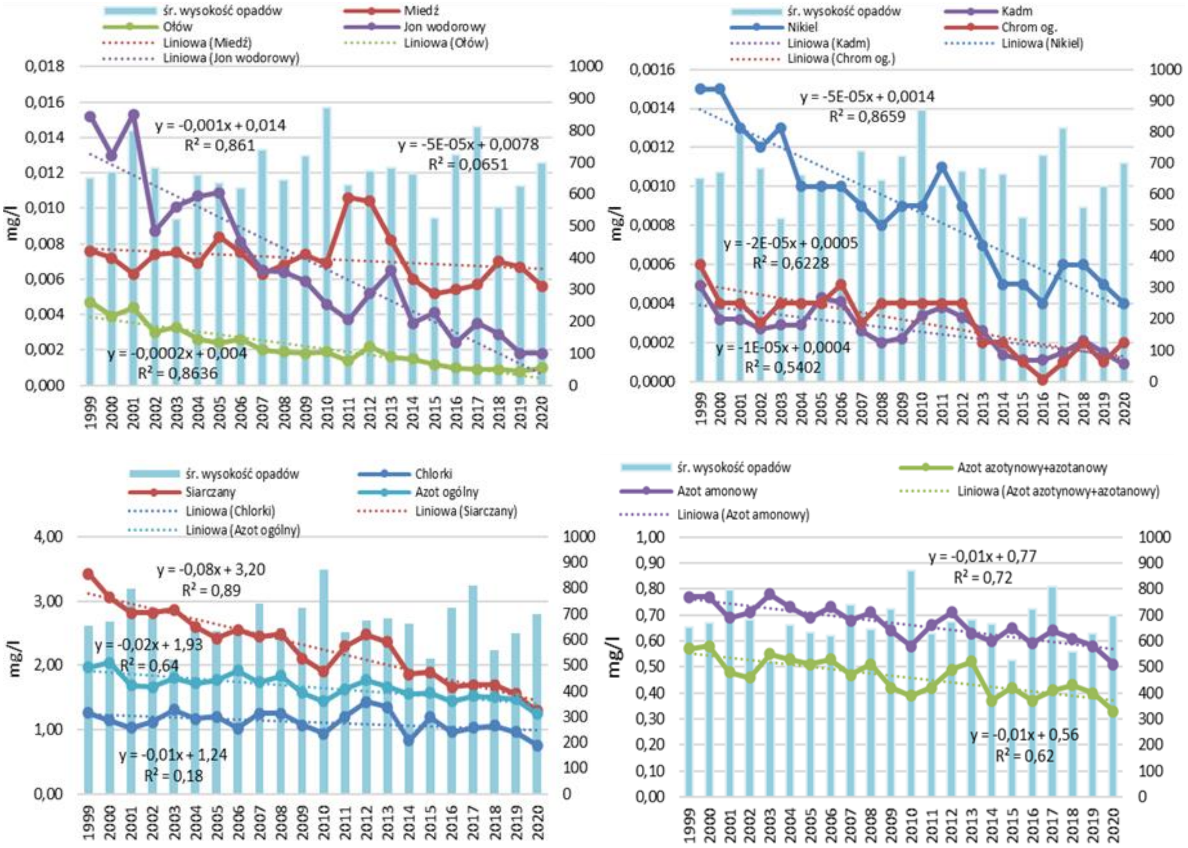
Ci' – concentration of the ith substance in the precipitation sample collected over the measurement period [mg/l].

h – sum of precipitation amounts in the given measurement period for which the load is calculated [mm]; precipitation amount in [mm] corresponds to the number of litres of water per $1m^2$ of surface.

The amount of deposition of a pollutant with precipitation, determined over a period of a year, is calculated as the sum of monthly depositions. Where deposition is missing for a particular constituent month (e.g. due to insufficient precipitation sample volume to allow analysis of all tested components – force majeure – there was a lack of data on concentrations of test substances), the missing concentration is replaced by a weighted average concentration calculated for the expected period using data from the remaining months to obtain an approximate total annual deposition, resulting in a better estimate of deposition for the period.

The monitoring results for a given year shall be presented against the background of the data for the preceding years in order to show the trends in pollutant concentrations in wet precipitation and deposition with precipitation to the ground in successive years. The results of the precipitation chemistry studies are available on the CIEP website at the Air Quality Portal: http://powietrze.gios.gov.pl/pjp/content/chemistry_of_atmospheric_precipitation.

Examples of the study results included in the 2020 Annual Report are presented in Figure 4.5 and Figure 4.6.



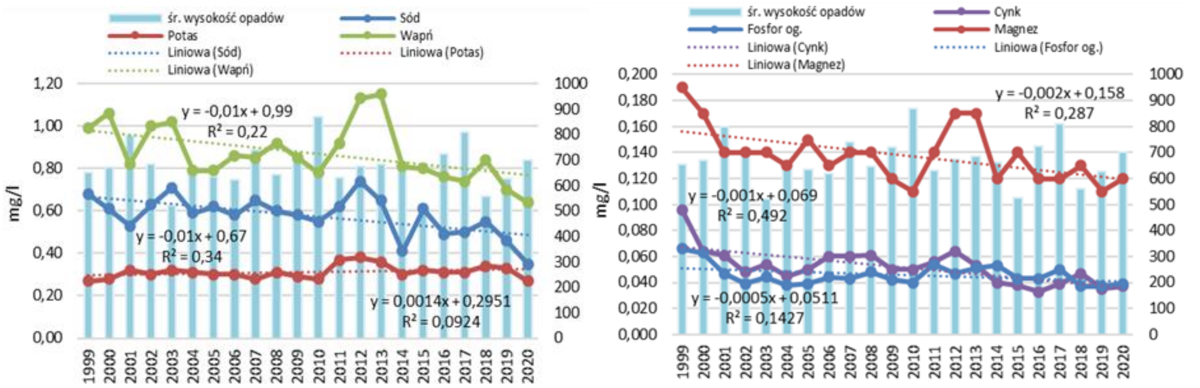
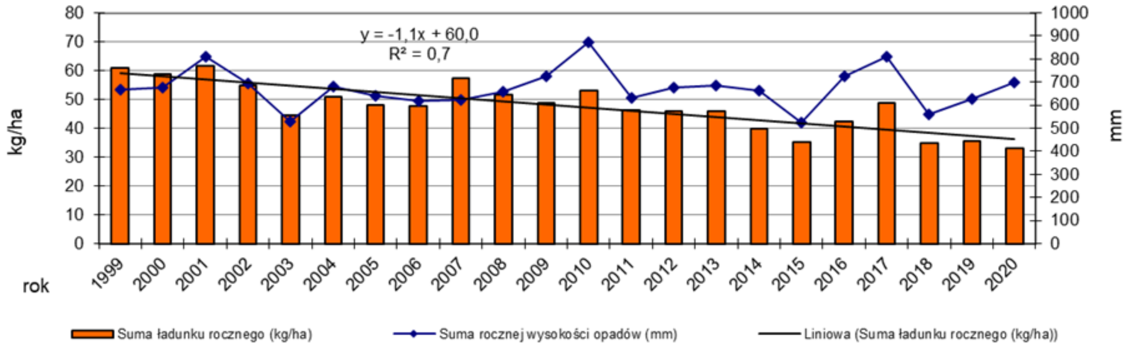


Figure 4.5 Weighted average concentrations (weight – precipitation amount) of selected pollutant indicators in precipitation collected during the study years 1999-2020 against average annual precipitation amounts [mm] [Annual report Monitoring of precipitation chemistry and assessment of pollutant deposition to the ground in 2021-2022*, 2021]*



Total annual load (kg/ha) / Total annual precipitation (mm) / Linear (Total annual load (kg/ha))

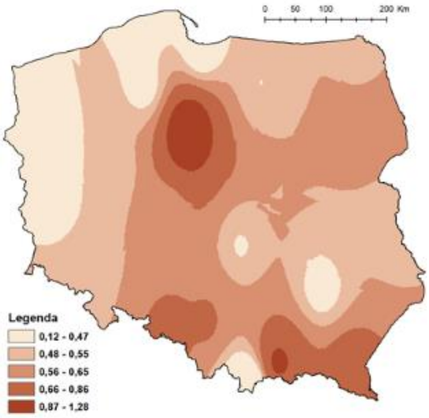
Figure 4.6 Mean annual deposition in precipitation and mean annual totals of precipitation amounts at 22 monitoring stations during the study years 1999-2020 [Annual report Monitoring of precipitation chemistry and assessment of pollutant deposition to the ground in 2021-2022*, 2021]*

In order to be able to assess the impact of wet deposition on other regions of the country, not only at the monitoring sites, it has become necessary to interpolate and calculate deposition with a high resolution of 2.5 x 2.5 km^2 (4 x 4 km^2 – data for websites' purposes). To achieve this, IMWM-NRI performs the IDW interpolation with application of ArcGIS software. The interpolation requires meteorological data from IMWM-NRI, i.e. data on monthly precipitation from the national meteorological observation network consisting of 162 stations selected to represent the field of average precipitation totals in Poland (Figure 4.2).

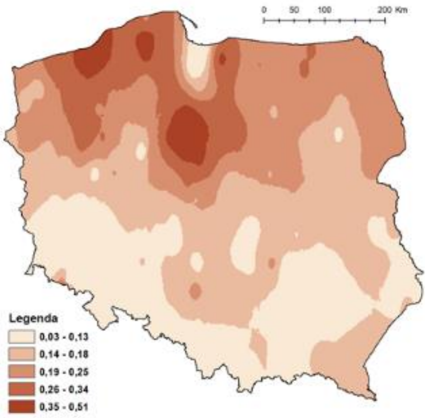
The computational method involves taking the concentration data at the measurement points and interpolating the data from these points to a regular 2.5 x 2.5 km^2 grid called rasters. The same holds for precipitation data from 162 precipitation stations, which are taken from their locations and interpolated to a regular 2.5 x 2.5 km^2 grid. The two data sets obtained in this way are used to calculate wet deposition by multiplying the data from each grid cell (raster), i.e. the interpolated amount of precipitation with the interpolated concentration corresponding to each subsequent grid cell for each indicator studied separately. Such a calculation method allows visualising the deposition distribution throughout the country for each month and the total annual deposition. It also makes it possible to calculate the deposition per unit area of administrative division: voivodship, district or commune as well as hydrographic division: basins of selected rivers or larger water bodies. Figures 4.7, 4.8 and 4.9 illustrate the computational possibilities and graphical presentation of the data.

NITROGEN (NITRITE AND NITRATE)

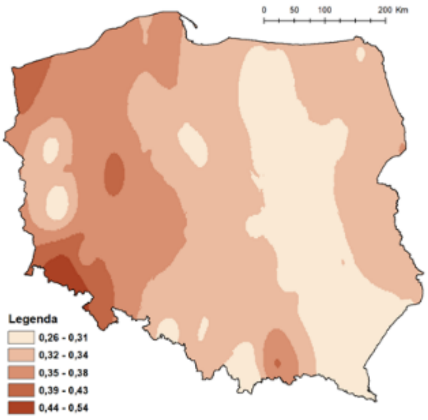
CONCENTRATION [mg/l N] – Jan. 2020



DEPOSITION [kg/ha N] – Jan. 2020

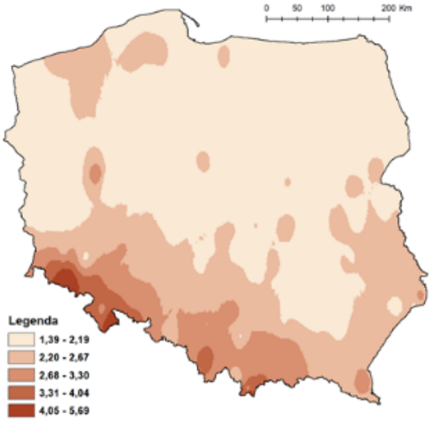


CONCENTRATION [mg/l N] – year 2020



DEPOSITION [kg/ha N] – 2020

DEPOSITION [kg/ha N] - YEAR 2020



DEPOSITION [kg/ha N] – 2020

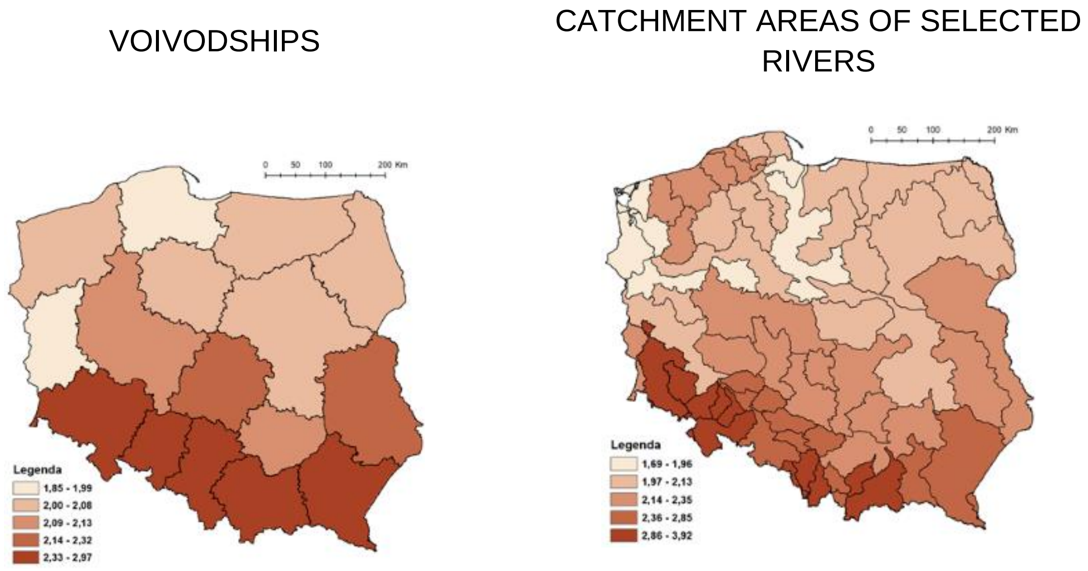


Figure 4.7 Spatial distribution of nitrite and nitrate nitrogen concentrations [mg/l N] in atmospheric precipitation and surface load on the area of Poland by deposition of nitrite and nitrate nitrogen [kg/ha N] contributed by precipitation in I 2020 and in the whole year 2020 (upper part). Deposition of nitrite nitrogen and nitrate nitrogen [kg/ha N] on the voivodship areas and on the surface of selected Polish rivers [own work based on 2020 Annual Report, Monitoring of Precipitation Chemistry*..., 2021].*

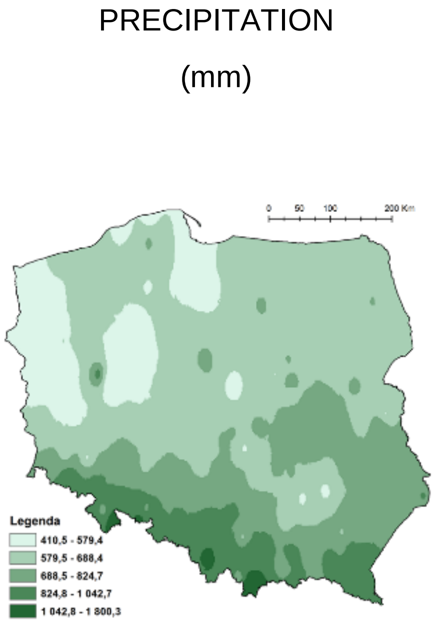
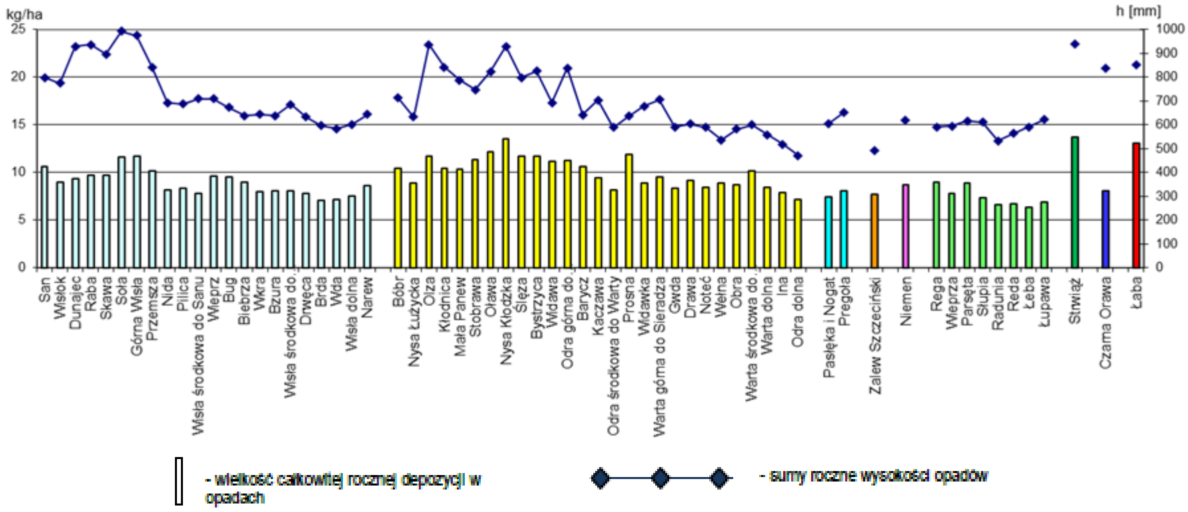


Figure 4.8 Spatial distribution of annual precipitation amounts [mm] [own work based on 2020 Annual Report, Monitoring of Precipitation Chemistry..., 2021].



value of total annual deposition in precipitation / annual precipitation totals

Figure 4.9 *Rates of annual deposition of biogenic compounds in precipitation on the surface of the catchments of selected Polish rivers and precipitation totals for 2020 [own work based on* 2020 Annual Report, Monitoring of Precipitation Chemistry..., *2021].*

Atmospheric pollution background monitoring in Poland under EMEP, GAW/WMO, HELCOM and European Commission programmes

The programme for monitoring background air pollution in Poland is carried out in order to fulfil one of Poland's obligations under the Convention on Long-range Transboundary Air Pollution, referred to as the Geneva Convention, and the Protocol to that Convention on the financing of EMEP (Co-operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe, working name European Monitoring and Evaluation Programme), which is to provide information on concentrations and fluxes of selected pollutants reaching the ground. These include primarily pollutants that cause acidification and eutrophication of the environment, but also other substances the need to investigate which under the programme has emerged over time due to their increasing role in impacts on humans and ecosystems.

The results of the research are used to assess the transboundary flow of pollutants across the continent and to study the distribution of concentrations and deposition in Europe. Due to the fact that the scope of conducted studies allows for simultaneous participation in works carried out within the GAW/WMO system (Global Atmosphere Watch/World Meteorological Organization), the obtained data may be used for the analysis of pollutant concentrations on a global scale. Obtained results allow also to fulfil obligations towards the Helsinki Commission (HELCOM) in the field of air quality and precipitation studies in the Baltic coastal zone (relevant for Łeba only).

GAW/WMO Programme

The World Meteorological Organization (WMO) began its programme to study the chemistry of the atmosphere in the 1950s. The immediate reason for such studies was the significant increase in atmospheric pollution observed after World War II due to the rapid development of industry. Acidification of lakes and forest areas in some parts of North America and Europe, there appeared problems related to depletion of ozone in the atmosphere, and additionally, the presence of more and more greenhouse gases in the atmosphere meant that the possibility of global warming and climate change had to be taken into account. Already in the 1950s the Global Ozone Observing System (GO3OS) was established and the Background Air Pollution Monitoring Network (BAPMoN) was created in the 1960s. It carried out an extensive measurement programme and was aimed at tracking long-term changes in the chemical composition of the atmosphere and to study their impact on the climate and the environment. The first station in Poland within the BAPMoN was in Suwałki, which was put into operation on 1 November 1975 and closed in March 1994. Subsequent stations were those at Śnieżka (1981), in Jarczew (1984) and in Łeba (1989). In 1989, the World Meteorological Organisation consolidated both systems to form the Global Atmosphere Watch (GAW), which included GO3OS and BAPMoN. The mission of the GAW programme has been, and continues to be, to monitor multi-year changes in the chemistry and properties of the atmosphere at global and regional scales to assess its impact on climate change and other environmental issues, taking into account long-range transport of pollutants and conditions in urban areas.

Currently, the GAW programme is carried out on 30 global stations (8 in Europe), more than 400 regional stations and about 100 cooperating stations.

In Poland, there are 6 regional stations implementing, to varying degrees, the GAW programme[1]:

- Jarczew, Legionowo, Łeba, Śnieżka – managed by IMWM-NRI,
- Diabla Góra / Borecka Forest – managed by the Institute of Environmental Protection – National Research Institute (IEP-NRI),
- Belsk – managed by the Institute of Geophysics of the Polish Academy of Sciences.

Four of them, namely Jarczew, Łeba, Puszcza Borecka and Śnieżka, carry out background monitoring of atmospheric pollution.

EMEP programme

The historical background of EMEP also dates back to the middle of the last century. Here, at the root were the problems of the Scandinavian countries, where Swedish and Norwegian scientists observed the phenomenon of acidic precipitation leading to the acidification of surface waters. They noted serious damage to fish stocks and suggested that sulphur dioxide pollution from distant countries – Britain, Germany and Eastern Europe – was to blame. In 1976, the Scandinavian environment ministers proposed a European convention on transboundary air pollution, especially sulphur compounds. The Convention on Long-Range Transboundary Air Pollution (LRTAP), signed in November 1979 by 32 European countries plus the United States and Canada, is one of the main measures to protect our environment. It establishes a broad framework for cooperation in reducing the impact of air pollution and establishes a process for negotiating specific

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[1] More information about the regional stations in Poland and the measurement programme carried out there can be found at: www.empa.ch/gaw/gawsis.

measures to control air pollution emissions through legally binding protocols. In this process, EMEP's main objective is to regularly provide governments and subsidiary bodies under the LRTAP Convention with sound scientific information to support the development and further evaluation of the effects of international emission reduction protocols negotiated under the Convention.

Initially, EMEP focused on the assessment of transboundary transport of sulphur compounds and subsequently, as a result of the signing of seven more protocols to the Convention, the scope of substances was extended to include nitrogen compounds, ground-level ozone formation, volatile organic compounds, heavy metals, persistent organic pollutants and particulate matter.

The EMEP programme is based on three main elements:

- the collection of emissions data,
- measurements of air quality and precipitation,
- modelling of atmospheric transport and deposition of pollutants to the ground.

By combining these three elements, EMEP performs the required assessment and regularly reports on emissions, concentrations and deposition of air pollutants, the amount and significance of transboundary pollutant fluxes and associated exceedances of critical loads and threshold levels. A combination of these elements also provides a good basis for evaluating and qualifying EMEP's estimates.

A total of nearly 200 stations were active within the network in 2019[2]. In 2019, 33 countries submitted their measurement data to the EBAS database at NILU (Norwegian Institute for Air Research), where EMEP data are collected, a total of from 168 stations. Of these, 120 stations reported data on inorganic ions in precipitation and/or major components in air; 73 stations measured both air and precipitation (EMEP Status Report 1/2021). Ozone data network at the ground level of the atmosphere consisted of 138 stations, data on particulate matter were provided by 78 stations. In addition, 56 stations from 21 countries provided data on at least one of the mandatory components in the EMEP advanced programme (level 2). Few stations fulfilled the full measurement scope of level 2, i.e. only 12 stations carried out measurements for all mandatory aerosol parameters.

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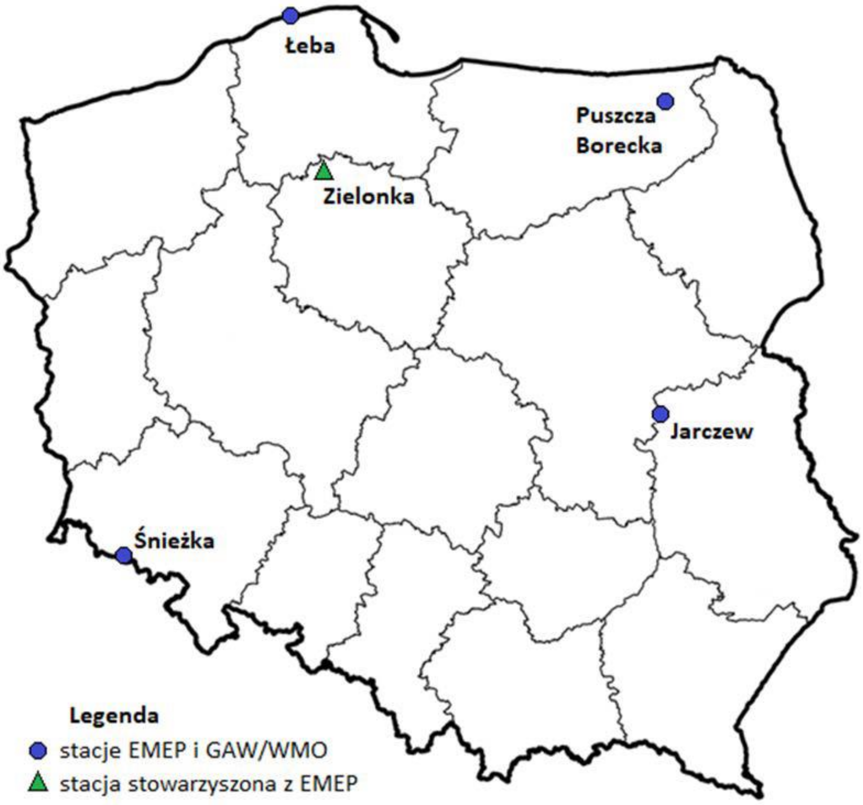
[2] The reports with the measurement data collected in EMEP are published with a delay of almost two years, because this is how long the process of verification, processing and elaboration of the data submitted to EBAS takes.

Polish network of EMEP and GAW/WMO stations

The EMEP and GAW/WMO network in Poland currently includes four regional background stations (Figure 4.10):

1. the station in Łeba (IMWM-NRI), located in the coastal region (Pomeranian Voivodeship),
2. the station in Jarczew (IMWM-NRI – representing the lowland agricultural region of central-eastern Poland (the Lubelskie Voivodeship),
3. the station on Śnieżka (IMWM-NRI) – the highest peak of Karkonosze, representing the high-mountain region (the Dolnośląskie Voivodship),
4. the Puszcza Borecka station (IEP-NRI) – measurement point located in Diabla Góra, which represents the lake district of north-eastern Poland (the Warmińsko-Mazurskie Voivodship).



Key / EMEP and GAW/WMO stations / EMEP associated station

Figure 4.10 Location of background atmospheric pollution monitoring stations in Poland [2020 Synthesis Report].

The station in Suwałki was the first one to be included in the network in 1978, operated by IMWM-NRI but no longer functioning, followed by successive stations: Jarczew (since 1985), Śnieżka (since 1992), Puszcza Borecka (since 1992) and Łeba (since 1993). In 2015, they were joined – as associated with EMEP – by the regional background station Zielonka – Bory Tucholskie, located in the lakeland forest region of northern Poland (Kujawsko-Pomorskie Voivodeship), belonging to the Chief Inspectorate of Environmental Protection (GIOŚ).

The coastal station in Łeba, apart from the EMEP and GAW/WMO programmes, implements BMP/HELCOM programme – the International Baltic Monitoring Programme for the Helsinki Commission. Data from EMEP station are also used for European Commission purposes.

All sites perform tasks indicated in the State Environmental Monitoring Programme, on the basis of contracts with the Chief Inspectorate of Environmental Protection, financed by the National Fund for Environmental Protection and Water Management.

Basic information on background air pollution monitoring stations in Poland is presented in Table 4.4 and their location is shown on the attached map (Fig. 4.10).

Table 4.4 Information on background monitoring stations for atmospheric pollution in Poland [source: 2020 Synthesis Report].

Station	**Jarczew**	**Śnieżka**	**Łeba**	**Puszcza Borecka**	**Zielonka***
φ	51°48'51,87" N	50°44'11,07 "N	54°45'14,02 "N	54°07'29,52" N	53°39'00,00 "N
λ	21°58'20,71" E	15°44'23,70 "E	17°32'03,35 "E	22°02 '17,08" E	17°55'59,90" E
Altitude [m]	180	1603	2	153	121
Station location	eastern central region; lowland, agricultural	south-western region; high mountains (national park)	coastal region (national park)	north-eastern region; lakeland	northern region; lakeland; forest
Institution carrying out measurements	IMWM-NRI	IMWM-NRI	IMWM-NRI	IEP-NRI	RDEM CIEP Bydgoszcz
Start of implementation of BAPMON/ GAW	01.01.1984	01.01.1981	01.01.1993	01.01.1993	-
Start of implementation of EMEP	01.10.1985	01.01.1991	01.01.1993	01.07.1992	01.01.2010 /01.01.2015*
Precipitation station code GAW/WMO	PL4500101 Q08	PL5000101 Q08	PL4000101 Q08	PL5500101 Q08	-
WDCGG index	JCZ651N00	SNZ650N00	LEB654N00	DIG654N00	-

Station	**Jarczew**	**Śnieżka**	**Łeba**	**Puszcza Borecka**	**Zielonka***
EMEP symbol	PL02	PL03	PL04	PL05	PL09

*station affiliated with EMEP since 2015

The atmospheric pollution data collected each year are transferred to the EMEP database, through which they are fed into the GAW/WMO and HELCOM programmes. In addition, the data are used to support air quality assessment for activities carried out by the Chief Inspectorate of Environmental Protection and for the European Commission.

EMEP research programme in Poland

The research programme in the field of background air pollution at the Łeba, Jarczew, Śnieżka and Puszcza Borecka sites includes the measurement of air pollution and precipitation. Within the monitoring of precipitation chemistry, all four stations carry out basic studies on the chemical composition of precipitation. In Łeba and Puszcza Borecka, the content of heavy metals in precipitation water is also measured – in Łeba in wet precipitation, at the Puszcza Borecka station – in total precipitation. At the Puszcza Borecka station the content of polycyclic aromatic hydrocarbons in total precipitation is measured, and recently also the content of mercury in total precipitation. At four stations the programme of measurements of atmospheric pollution complies with the EMEP level 1. At the Puszcza Borecka station some elements of level 2 have been additionally implemented.

Measurements of precipitation in the field of macroelements and precipitation indicators at the existing stations started in 1984 at Sniezka and Jarczew, although until 1988 monthly samples were collected. Daily sampling started in £eba and in Jarczew since 1988, at Śnieżka since 1991 and at the Puszcza Borecka station in 1993.

Measurements of heavy metals in wet precipitation were first initiated at the Łeba station – since 1991 four metals (lead, cadmium, zinc and copper) have been measured, Since 1999, two additional metals (chromium and nickel) have been measured. Measurements of heavy metals in wet precipitation: arsenic, cadmium, chromium, copper, nickel, lead and zinc at the Puszcza Borecka station were entered into the study programme in 2003.

Measurements of polycyclic aromatic hydrocarbons and heavy metals in total precipitation, including mercury, in accordance with requirements of the *Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air* (2004/107/EC), were introduced to the background monitoring programme only at the Puszcza Borecka station. Since 2004 the content of mercury has been determined in total precipitation, and since 2008 also the concentrations of benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, and since 2010 also the concentrations of other heavy metals have been measured in total precipitation in order to determine their total deposition.

Table 4.5 presents detailed information on the measurement programme implemented at the background monitoring stations of atmospheric pollution in Poland in the field of precipitation chemistry studies, including the collection methods and techniques applied for measurement of substances in precipitation water.

Table 4.5 Measurement methods used at background air pollution monitoring stations in Poland to study precipitation chemistry in 2020 [source: 2020 Synthesis Report].

Component/ Indicator	***Institute of Meteorology and Water Management – NRI***		***Institute of Environmental Protection – NRI***	
	Method of collection	Method of measurement	Method of collection	Method of measurement
Precipitation	Hellmann rain gauge*	volumetric	Hellmann rain gauge	volumetric
pH	bulk** type precipitation collector, daily sample	electrometry	wet-only collector, daily test	electrometry
conductivity		electrometry		electrometry
SO_4^{2-}		ion chromatography***		ion chromatography
NO_3^-		ion chromatography***		ion chromatography
NH_4^+		spectrophotometry		spectrophotometry
Cl^-		ion chromatography**		ion chromatography
Na^+		FAAS		ICP-AES
Mg^{2+}		FAAS		ICP-AES
Ca^{2+}		FAAS		ICP-AES
K^+		FAAS		ICP-AES
Pb	precipitation collector (wet only), two-weekly samples (Łeba)	GF-AAS	total precipitation collector, monthly samples collected from	GF-AAS
Cd		GF-AAS		GF-AAS
Cu		GF-AAS		GF-AAS
Zn		FAAS		FAAS

Component/ Indicator	***Institute of Meteorology and Water Management – NRI***		***Institute of Environmental Protection – NRI***	
	Method of collection	Method of measurement	Method of collection	Method of measurement
Cr		GF-AAS	weekly samples	GF-AAS
Ni		GF-AAS		GF-AAS
As				GF-AAS
Hg			total precipitation collector, weekly samples	CV-AFS
benzo(a)pyrene			total precipitation collector, monthly sample collected from weekly samples	HPLC
benzo(a)anthracene				HPLC
benzo(b)fluoranthene				HPLC
benzo(j)fluoranthene				HPLC
benzo(k)fluoranthene				HPLC
dibenzo(a,h)anthracene				HPLC
indeno(1,2,3-cd)pyrene				HPLC

*) Łeba – only during the period of precipitation (e.g. snow, hail); here the instrument in operation since 01.01.2014 has been the SEBA automatic rain gauge,

**) Precipitation, although collected in an open container, is to be treated as wet precipitation; see the description below,

***) Śnieżka: spectrophotometry,

FAAS – flame atomic absorption spectrometry,

ICP-AES – Inductively coupled plasma atomic emission spectroscopy, GF-AAS – graphite furnace atomic absorption spectrometry,

CV-AFS – cold vapour atomic fluorescence spectroscopy,

HPLC – high performance liquid chromatography.

Sampling in EMEP

Samples of precipitation for macronutrient determination are collected in a precipitation day cycle. A precipitation day runs from 6:00 UTC on a given day until 6:00 UTC of the following day, that is 8:00 during summer time and 7:00 during winter time. Sampling are collected daily, including on public holidays.

At the IMWM-NRI stations precipitation samples are collected by means of the bulk method. The bulk method consists in collecting precipitation samples to an open container. Every day at 6:00 UTC the observer changes the container for precipitation collection, irrespective of the fact whether precipitation has occurred or not. They carry the container with the sample from the previous day, covering it tightly with a lid, to the laboratory. The contents of the container, after weighing the container according to the procedures, is then poured into bottles in a thin stream, with as little contact between the sample and the walls of the container as possible, so that as little of the dry deposit as possible enters the sample. After pouring the precipitation water, the precipitation container is washed very thoroughly with deionised water. The procedure is diligently followed and the precipitation water, although collected in an open container, is treated as wet precipitation.

At the Puszcza Borecka station, samples for macronutrient determination are taken into the wet precipitation collector.

Mercury content in precipitation, which is determined in monthly samples of precipitation at the Puszcza Borecka station was collected in a separate collector according to the IVL formula (exposure time – 1 week). The total precipitation samples for determination of the remaining heavy metals and PAHs at the Puszcza Borecka station were collected in two separate collectors in weekly cycles and added to the monthly samples.

Heavy metals in precipitation at the Łeba station collected by the wet-only method were determined in monthly samples collected from bi-weekly samples.

Determination of substances in rainwater with EMEP

Chemical analyses of precipitation samples from EMEP stations are carried out by several laboratories. Samples taken at the IMWM-NRI stations are examined in:

- the laboratory of the Air Quality Monitoring Department of IMWM-NRI in Warsaw,
- the laboratory of High-Mountain Meteorological Observatory IMWM-NRI on Śnieżka,
- the laboratory of the Department of Oceanography and Baltic Monitoring IMWM-NRI in Gdynia.

Analyses of precipitation samples from the Puszcza Borecka site are performed in:

- the laboratory of the Comprehensive Environmental Monitoring Station Puszcza Borecka of the Institute of Environmental Protection-NRI in Diabla Góra,
- the Environmental Monitoring Laboratory of IEP-NRI,

- the Central Laboratory of Environmental Analysis CentLab IEP-NRI in Warsaw,
- the laboratory of the Institute of Oceanology of the Polish Academy of Sciences in Sopot.

The quality of the laboratories' work is subject to constant control under international programmes. The laboratories of IMWM-NRI in Warsaw and Gdynia as well as the laboratories of IEP-NRI participate in inter-laboratory comparative tests on measurement of pollutants in air and precipitation, organised once a year by EMEP Chemical Coordination Centre (EMEP/CCC/NILU). Moreover, twice a year IMWM-NRI laboratories in Warsaw and Śnieżka as well as IEP-NRI laboratories take part in inter-laboratory comparison studies on determination of precipitation components, carried out by the American Centre for Quality Assurance (WMO/QA/SAC).

It should be emphasised that both the Puszcza Borecka Comprehensive Environmental Monitoring Station and the Central Laboratory of Environmental Analyses CentLab of the Institute of Environmental Protection and Water Management performed in 2020 the majority of tests for the needs of EMEP, GAW/WMO and the European Commission with the application of methods accredited by the Polish Centre for Accreditation (PCA). Since 2001, the Comprehensive Environmental Monitoring Station Puszcza Borecka has been accredited by the Polish Centre for Accreditation PCA (Certificate AB 337) for precipitation sampling (standard PN-ISO-5667-8:2003) and determination of pH (standard PN-EN ISO 10523:2012) and conductivity (standard PN-EN 27888:1999) of water bodies. A similar situation is in the case of Central Laboratory of Environmental Analyses CentLab of the Institute of Environmental Protection – National Research Institute in Warsaw, which is accredited by the PCA i.a. to perform measurements of SO_4^{2-} , NO_3^- , Cl^- (standard PN-EN ISO 10304-1:2009), NH_4^+ (procedure BL-PB-21), Na, K, Mg, Ca, Fe, Al, Mn, P (procedure BL-PB-10) in precipitation samples.

It is worth pointing out that sampling of precipitation at the Łeba and Śnieżka stations for monitoring of background air pollution is carried out with methods other than those used in the precipitation chemistry monitoring programme and assessment of deposition to the ground. Chemical analyses are also performed in other laboratories. Therefore, they constitute separate studies and generate quite different sets of data. This leads to differences in results between the programmes. It should be emphasized that the data transferred to the EMEP database, and through EMEP to GAW/WMO database and HELCOM collections, are data obtained within the atmospheric pollution background monitoring measurements rather than results obtained from measurements of the system named Monitoring of precipitation chemistry and assessment of deposition to the ground.

Meteorological data for analysis in EMEP

Atmospheric pollution background stations, on which research is conducted by IMWM-NRI, are located within meteorological stations belonging to IMWM-NRI, the stations in Łeba and Śnieżka, on synoptic stations where meteorological measurements are conducted 24-hourly, and on the climatological station in Jarczew – measurements at 6, 12 and 18 UTC. The Puszcza Borecka station conducts its own meteorological measurements at the station located in Diabla Góra, which it uses for data interpretation purposes and, occasionally and for some of the analyses, it uses meteorological data from the IMWM-NRI meteorological station in Suwałki.

Meteorological data, which are used to interpret the results, apart from precipitation, include mainly such parameters as air temperature, wind speed and direction or sunshine. Moreover, information on the direction of air masses inflow over Poland and daily type of circulation is used according to Lityński, prepared by IMWM-NRI, along with other data, e.g. the data on 48-hourly trajectories of air particles at 850 hPa level from 00:00, 06:00, 12:00 and 18:00 UTC for each of four measurement points are also used. Flextra trajectories – Air mass trajectories, https://projects.nilu.no/ccc/trajectories/, or HYSPLIT trajectories https://www.ready.noaa.gov/HYSPLIT.php are also very helpful in data verification.

Production of data and calculations for EMEP data

Daily data sets, and for some elements weekly and bi-weekly, form the basis for analysis. For longer periods, average values are determined.

The monthly average values of concentrations of precipitation water components are given as **weighted arithmetic averages**, $\hat{c}$, where the weight is the daily precipitation total.

They are calculated with the formula:

$$\hat{c} = \frac{1}{\sum_i p_i} \cdot \sum_i c_i \cdot p_i$$

where:

p_i is the precipitation total measured on day i,

c_i - the concentration of a given rainwater component.

In the case of weekly sampling at the Puszcza Borecka station, monthly average concentrations were calculated on the basis of the samples. Weeks are included in the months, to which most their days belong.

When sampling on a bi-weekly basis for the station in Łeba, it was assumed that the first two weeks cover the period from the 1st to the 15th day of a given month, while the next two weeks last from the 16th day to the end of the month, regardless of whether it is a month lasting 28 or 31 days. This difference was taken into account in the calculation of the monthly average, owing to the use of a weighted average, where the weight is the total precipitation, calculated according to the formula presented above.

The pH, which measures the acidity of a solution, is defined as the negative logarithm of the concentration of free hydrogen ions (in moles per litre):

$pH = -\log_{10} [H^+]$.

The average pH, for periods other than 24 hours, is determined based on the hydrogen ion concentration. First, the pH is converted to hydrogen ion concentration, with the use of the formula:

$[H^+] = 10^{-pH}$

where:

$[H^+]$ – hydrogen ion concentration [g/dm^3]

or

$[H^+] = 10^{(6,0 - pH)}$

where:

$[H^+]$ – hydrogen ion concentration [µg/dm^3]

The weighted average concentration of hydrogen ions in the precipitation for the entire averaging period is then calculated:

$$\overline{[\mathrm{H}^+]} = \frac{1}{\sum_i p_i} \cdot \sum_i [\mathrm{H}^+]_i \cdot p_i$$

The final step is to convert the averaged hydrogen ion concentration back into pH:

$\mathrm{pH} = -\log_{10}\overline{[\mathrm{H}^+]}$

Wet deposition is calculated as the product of the weighted average concentration of a substance and the total precipitation over the period analysed:

$$\mathrm{WD} = \hat{c} \cdot \sum_i p_i$$

where:

WD – wet deposition for the period, [mg/m^2].

$\hat{c}$ – weighted average (weight – total precipitation) concentration of the substance in rainwater for this period [mg/dm^3],

$\sum_i p_i$ – the total amount of precipitation measured during the period [mm]; the amount of precipitation in [mm] corresponds to the volume of precipitation in dm^3 falling on 1 m^2 of ground surface.

To calculate the average deposition over a longer observation period, the average concentration of a substance in the precipitation for the whole period was used, taking into account also the days on which precipitation occurred, but for various reasons the data were not included in the analysis (e.g. samples disqualified – invalid*,* or too small volume or loss of precipitation – missing samples).

When all data were available, the total deposition from individual samples was equal to the deposition calculated from the average concentration multiplied by the total precipitation over the whole period. In the event that, for example, a component was not determined in all samples collected in a given period (for various reasons, e.g. because the sample volume was too small), the average concentration for that period was used. This way of calculation made it possible to assign the value of the average concentration to the missing values in a given period and to obtain a better approximation of the total deposition. When all results were available, the total load calculated by this method was equal to the sum of the loads calculated for individual samples in a given period.

The calculation of deposition was based on the precipitation amount measured with a Hellmann rain gauge.

On the basis of obtained data, annual reports are prepared every year in IMWM-NRI and IEP-NRI, which contain discussion of results of background air pollution studies along with data summaries for a given year and tables containing annual data since 1994 (the year when all four stations were in operation) to the last year inclusive. In addition to the annual reports, both institutions, alternately, prepare the “Background monitoring of atmospheric pollution in Poland for EMEP, GAW/WMO and European Commission purposes – Synthesis Report”, which contains a discussion of the previous year's research results from all EMEP stations in Poland, including changes in the state of atmospheric pollution against the background of many years and showing the situation of Poland in comparison with Europe. These reports are presented on the CIEP website: *http://powietrze.gios.gov.pl/pjp/maps/measuringstation/E*

Examples of study results from the 2020 Synthesis Report are presented in Figures 4.11, 4.12 and 4.13.

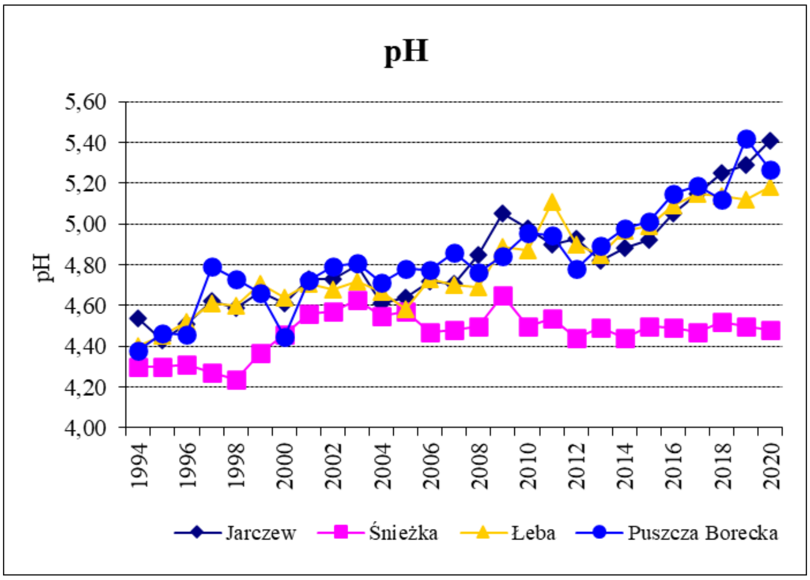


Figure 4.11 Precipitation pH index at atmospheric pollution background stations in Poland between 1994 and 2020 [source: 2020 Synthesis Report].

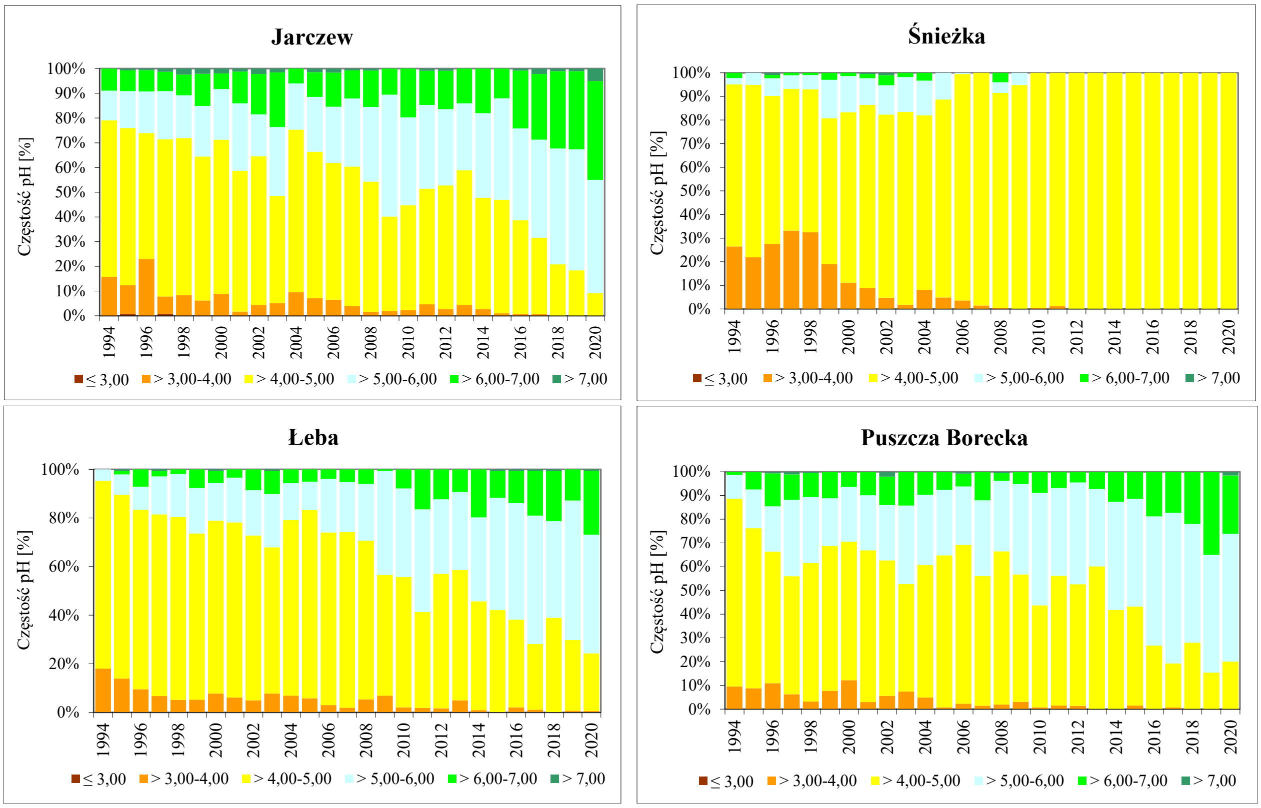


Figure 4.12 Precipitation water pH incidence at atmospheric pollution background stations in Poland between 1994 and 2020 (source: 2020 Synthesis Report)

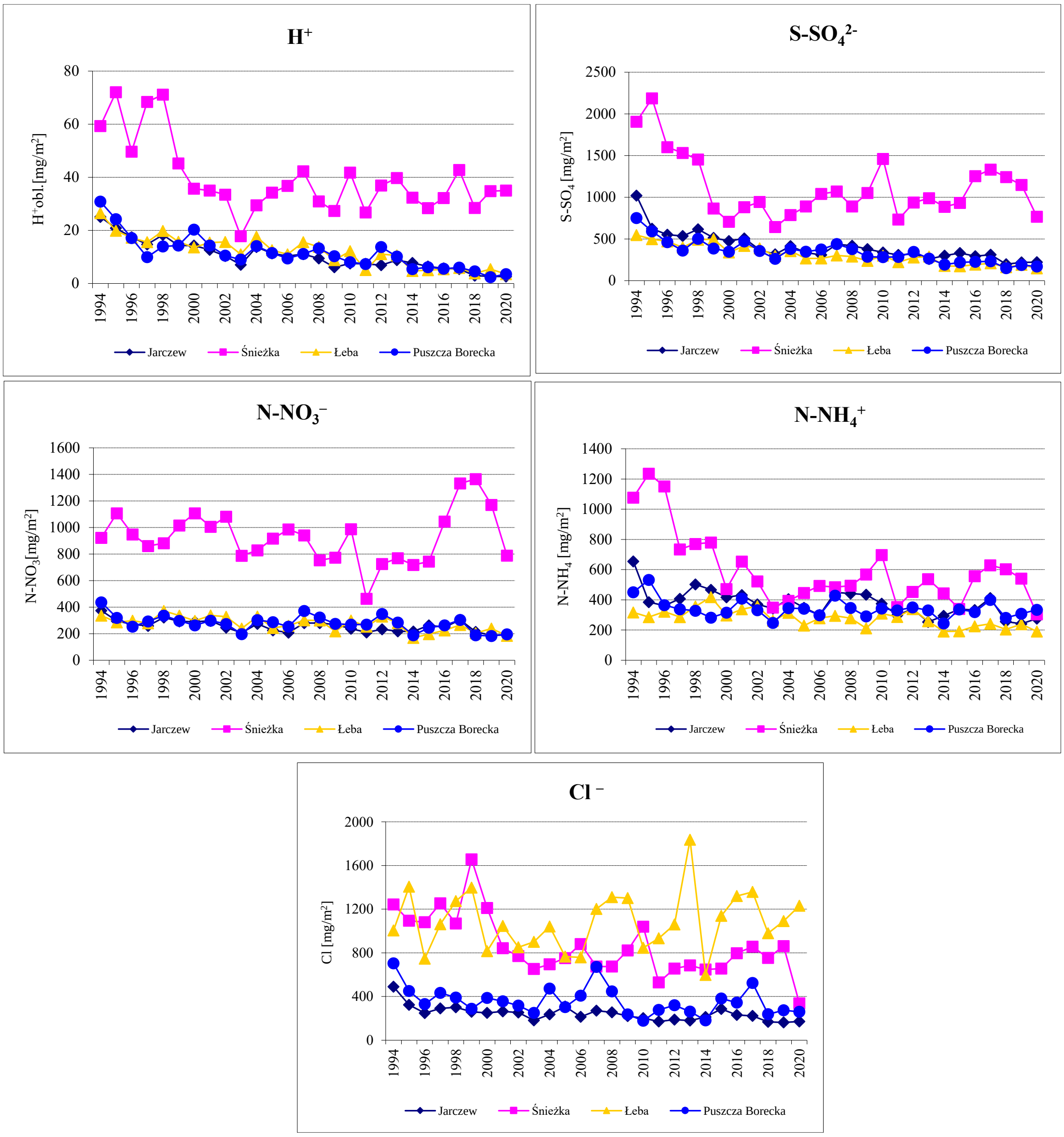


Figure 4.13 Wet deposition of hydrogen ions, sulphate sulphur, nitrogen compounds and chloride ions at background stations of atmospheric pollution in Poland between 1994 and 2020 (source: 2020 Synthesis Report)

Regional background stations measuring total deposition of heavy metals, including mercury and polycyclic aromatic hydrocarbons

At selected stations of the regional background, functioning within the framework of the State Environmental Monitoring, measurements of pollutant loads from the air deposited with precipitation to the ground are carried out. The tasks are connected with research and assessment of the state of air pollution, performed in accordance with the provisions of the Environmental Protection Act[3] transposing the requirements of the Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on air quality and cleaner air for Europe (Official Journal of the EU L 152 of 11.06.2008, p.1),

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[3] Act of 27 April 2001 – Environmental Protection Act (Journal of Laws 2019, item 1396, as amended)

2008/50/EC[4] and Directive 2004/107/EC of the European Parliament and the Council of 15 December 2004 on arsenic, cadmium, nickel, mercury and polycyclic aromatic hydrocarbons in ambient air (Official Journal of the EU L 23 of 26.01.2005, p.3), 2004/107/EC[5]. Directive 2004/107/EC covers, inter alia, monitoring of deposition of heavy metals and polycyclic aromatic hydrocarbons at regional background monitoring stations in Poland.

The Regulation of the Minister of Climate and Environment of 11 December 2020 on the assessment of levels of substances in ambient air (Journal of Laws 2020, item 2279) within the scope of its regulation implements: Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe (2008/50/EC), Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 on arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air (2004/107/EC) and Commission Directive (EU) 2015/1480 of 28 August 2015 amending certain Annexes to Directives 2004/107/EC and 2008/50/EC of the European Parliament and of the Council laying down rules on reference methods, validation of data and location of measuring points for air quality assessment (2015/1480/EC). According to the requirements set out in the Regulation of the Minister of Climate and Environment of 11 December 2020 on the assessment of the levels of substances in ambient air, as a result of the provisions of Directive 2008/50/EC and Directive 2004/107/EC, measurements of the total deposition of heavy metals and PAHs shall be carried out in at least three measuring points of the regional background of the country.

The purpose of these measurements is to fulfil the obligations arising from the requirements of the Directive, as well as to support the assessment of air quality in the country.

Annex 6 to the Regulation of the Minister of Climate and Environment of 11 December 2020 on the assessment of levels of substances in ambient air defines the scope of measurements of pollutants at regional background measurement points in terms of total deposition of pollutants in these areas. These are measurements of total deposition of heavy metals listed in the title of Directive 2004/107/EC, i.e. cadmium, arsenic, nickel and mercury, as well as total deposition of polycyclic aromatic hydrocarbons (PAH): benzo(a)pyrene, benzo(b)anthracene, benzo(a)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene.

The Chief Inspectorate of Environmental Protection selected three stations with a full measurement programme, including analysis of total deposition of heavy metals, including mercury and PAHs, to perform tasks in this respect: Osieczów, Puszcza Borecka and Zielonka (Figure 4.14).

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[4] Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe (Official Journal of the European Union L 152 of 11.06.2008, p.1)

[5] Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, nickel, mercury and polycyclic aromatic hydrocarbons in ambient air (OJ L 23 of 26.01.2005, p.3)

Figure 4.14 Location of regional background stations performing studies on PAHs and heavy metals in total precipitation in Poland [data source: SEM/IMWM-NRI/IEP-NRI].

All three stations are located outside of urban areas, in natural, forested land. The station in Osieczów is situated in the agricultural part of the Lower Silesian Voivodeship. Measurements at the station in Osieczów and chemical analyses for this station are carried out by the CTL of the CIEP Branch Office in Wrocław. The Zielonka station is situated within the Bory Tucholskie forest complex, in the Kujawsko-Pomorskie Voivodeship. Measurements and determinations at the Zielonka station are performed by the CTL of the CIEP Branch in Bydgoszcz. The Puszcza Borecka station is situated in a forested area, next to a small lake and located on the western edge of the Borecka Forest, in the Warmińsko-Mazurskie Voivodeship. Measurements at the Puszcza Borecka station are conducted by the IEP-NRI and the analyses are conducted in the laboratories of the Comprehensive Environmental Monitoring Station Puszcza Borecka and the Environmental Monitoring Laboratory of the IEP-NRI in Warsaw.

Basic data on the stations are presented in Table 4.6., including their location, the unit they belong to, codes in the State Environmental Monitoring and European AirBase database and the list of substances measured in total precipitation. Information was also provided on which synoptic station of IMWM-NRI was selected as a cover station for each of the regional background stations. Data from those stations were used in interpretation of measurement results of heavy metals, including mercury and PAHs.

Table 4.6 Basic information on regional background stations in Poland, performing measurements of PAHs and heavy metals in total precipitation (data source: SEM/IMWM-NRI/IEP-NRI)

	Osieczów	**Puszcza Borecka**	**Zielonka**
Voivodeship	Dolnośląskie	Warminsko-mazurskie	Kujawsko-pomorskie
Coordinates	15°25'54" E	22°02'17" E	17°56'00" E
	51°09'04" N	54°07'30" N	53°39'00" N
Station owner	CIEP CTL Branch in Wrocław	IEP-NRI in Warsaw	CIEP CTL Branch in Bydgoszcz
Code in SI Ekoinfonet (from 2015)	DsOsieczow21	WmPuszczaBor	KpZielBoryTu
Name in SI Ekoinfonet	Osieczów	KMŚ Puszcza Borecka	Bory Tucholskie
Code in EIONET	PL0505A	PL0005R	PL0077A
Cover station	Legnica	Suwałki	Chojnice
Ni	+	+	+
As	+	+	+
Cd	+	+	+
Hg	+	+	+
B(a)P	+	+	+
B(a)A	+	+	+
B(b)F	+	+	+
B(j)F	+	+	+
B(k)F	+	+	+
I(1,2,3-cd)P	+	+	+
D(a,h)A	+	+	+

At the mentioned stations, in accordance with the programme, measurements are made of heavy metals: cadmium, nickel and arsenic as well as polycyclic aromatic hydrocarbons PAH in total precipitation: benzo(a)pyrene – B(a)P, benzo(b)anthracene – B(a)A, benzo(a)fluoranthene – B(a)F, benzo(j)fluoranthene – B(j)F, benzo(k)fluoranthene – B(k)F, indeno(1,2,3-cd)pyrene – I(1,2,3-cd)P and dibenzo(a,h)anthracene – D(a,h)A. Collaborative research has been ongoing since 2010.

Sampling of PAHs and heavy metals

At the Zielonka station, sampling for metals was conducted for 2 weeks per month from May 2015 and for PAHs for the remaining two weeks. The indicators for this station were determined on the basis of data from those periods when samples were taken for the determination of each group of pollutants.

At the Osieczów station in 2015 during three months – February, August and December – such small precipitation samples were collected that it was not possible to perform PAH determinations. The indicators for PAHs were therefore calculated on the basis of the results from 9 months. In Osieczów, the last sample in 2018 was collected over 2 months and pollutant deposition rates were calculated on that basis. The amount of precipitation was arbitrarily divided into two equal parts and one of them was counted as falling in 2018. In Osieczów, until June 2019, samples for heavy metals and PAHs were collected into one cylinder, and then separated, and from July onwards samples were taken into separate cylinders.

At the Puszcza Borecka station, two collectors were used, to which samples for heavy metals and PAH were taken separately.

In 2020, samples for heavy metals and PAHs were collected into two separate collectors at all stations. Precipitation measurements were an integral part of the programme.

Meteorological information

The assessment of meteorological conditions in Poland is based on the results of observations of temperature, precipitation, relative air humidity as well as wind speed and direction. Meteorological cover for the study is provided by the IMWM-NRI synoptic stations in Chojnice, Legnica and Suwałki, located in the regions where the discussed SEM stations are operating and for that reason they were recognised as representative for regions of monitoring stations. Meteorological data from these stations are used to interpret results throughout the study period, except for 2015, when, due to incomplete measurement series (daily) from the cover station in Legnica (representative for Osieczów station), data from meteorological station of IMWM-NRI in Jelenia Góra were taken for the study. The assessment took into account changes in temperature, total precipitation and directions of air masses inflow over Poland (based on daily circulation directions for Poland according to Lityński classification, calculated at IMWM-NRI) as well as the share of days with strong wind (≥10 m/s).

It was noted (Skotak K. i in. 2021) that while the spatial representativeness of the selected cover stations in terms of temperature is very good, as the differences from the results of measurements carried out at the SEM stations usually do not exceed the level of measurement errors, whereas the representativeness of precipitation amount is much lower, as precipitation is one of the most variable meteorological elements in space and time. Therefore, precipitation amounts at the cover stations and at background stations may differ from each other. These differences can be exacerbated by using a different measurement method. At IMWM-NRI meteorological stations rain gauges of Hellmann type are used, placed at the height of 1 m above the ground, whereas at background stations – only Puszcza Borecka station has a standard Hellmann rain gauge, at the remaining two stations there are only precipitation collectors with a larger diameter of the precipitation inlet chamber, placed at the height of 1.5 m above the ground. Therefore, when analysing the results obtained, the data on precipitation from the meteorological cover stations are only used to assess the scale and trends of changes in precipitation conditions in the regions of the regional background stations. The volume of deposition of pollutants to the ground is calculated based on precipitation measurements from collectors located at individual regional background stations.

Compilation of results

The deposition value is estimated from the concentrations of the components under study and the amount of precipitation (calculated from the mass/volume of precipitation collected).

In the reports covering the period until 2014 the following analyses were made for the annual deposition values obtained at the stations mentioned and deposition rates of heavy metals and PAHs expressed in µg/m^2 /day were presented. Since 2015, the analysis has been carried out using the indicators.

On the basis of the measurement results, since 2012 the Institute of Environmental Protection – National Research Institute has been preparing annual research reports covering the period from 2010 to the year preceding the current year. These are cyclical studies containing analysis of results of measurements carried out stations operating within the framework of the State Monitoring of Environment. The scope of the studies includes all studies carried out at the station, i.e. the evaluation for particulate matter and determined pollutants (components), together with references to valid air quality standards, as well as – which is most interesting from the point of view of this report – assessment of air pollutant loads deposited with precipitation to the ground.

The main objective of the study is to present the results of air pollution and precipitation assessment at selected regional background stations in Poland in a given long-term period. The results are presented, where possible, against the background of observed concentrations and deposition rates obtained at non-urban background stations in Europe. The studies are presented on the website: https://powietrze.gios.gov.pl/pjp/maps/measuringstation/U

Exemplary results of the study are presented below: deposition rates of heavy metals and PAHs at regional background stations in 2020 (Figures 4.15, 4.16).

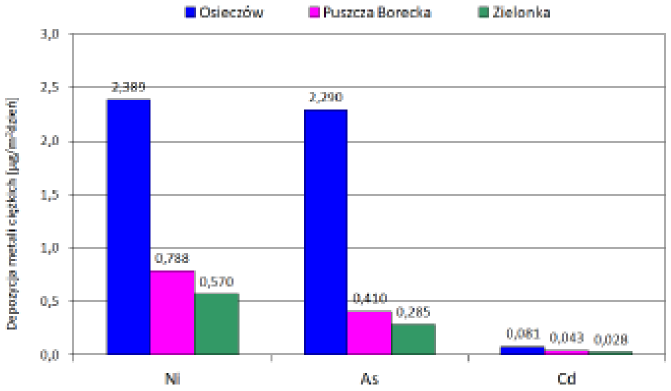


Figure 4.15 Deposition rates of heavy metals at regional background stations in 2020; source: SEM

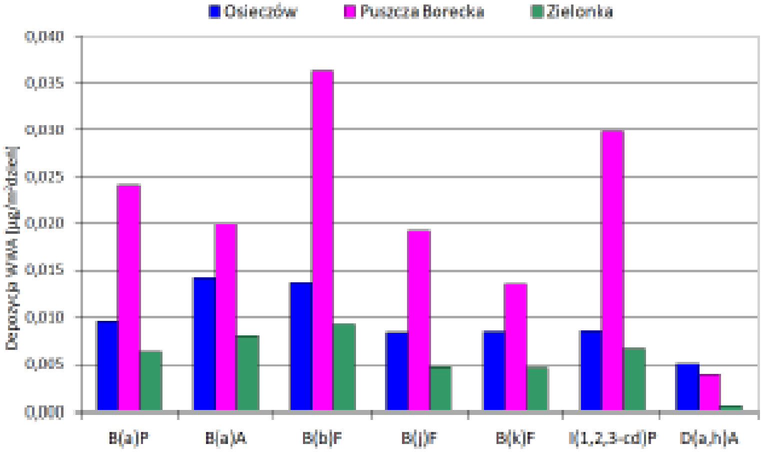


Figure 4.16 Deposition rates of PAHs at regional background stations in 2020; source: SEM

Measurement of mercury in total precipitation

In accordance with the requirements set out in the Regulation of the Minister of Climate and Environment of 11 December 2020 on assessing levels of substances in the air, transposing the provisions of Directive 2008/50/EC of the European Parliament and of the Council on ambient air quality and cleaner air for Europe and Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 on arsenic, cadmium, nickel, mercury and polycyclic aromatic hydrocarbons in ambient air, as well as Commission Directive (EU) 2015/1480 of 28 August 2015 amending certain annexes to Directives 2004/107/EC and 2008/50/EC of the European Parliament and of the Council laying down rules on reference methods, validation of data and location of measurement points for the assessment of air quality, measurements of total mercury deposition (as well as heavy metals and PAHs) are carried out in Poland at selected regional background measurement stations.

Measurements of mercury deposition within the SEM programme are conducted in Poland at three locations, at the same stations where monitoring of other heavy metals and PAHs in total precipitation is conducted: Osieczów, Zielonka and Puszcza Borecka. The measurement programme has been implemented since the beginning of 2010.

In its present form it meets the requirements of the above mentioned Regulation, both in relation to the number of launched stations and the implemented scope of measurements, as well as the applied measurement methodologies, as to their principle.

Sampling and chemical analysis

Two types of open collectors are used for mercury deposition sampling (total deposition) – Eigenbrodt at the station of the Chief Inspectorate of Environmental Protection (exposure time – 1 month), and at the station of the IEP-NRI – IVL type collector (exposure time – 1 week).

Regulation of the Minister of Climate and Environment of 11 December 2020 on the assessment of the levels of substances in the air (RMŚ, 2020), in accordance with the provisions of Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 on arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, indicates reference methodologies for sampling and analysis, for mercury deposition in accordance with PN-EN 15853: Ambient air quality. Standard method for the determination of mercury deposition.

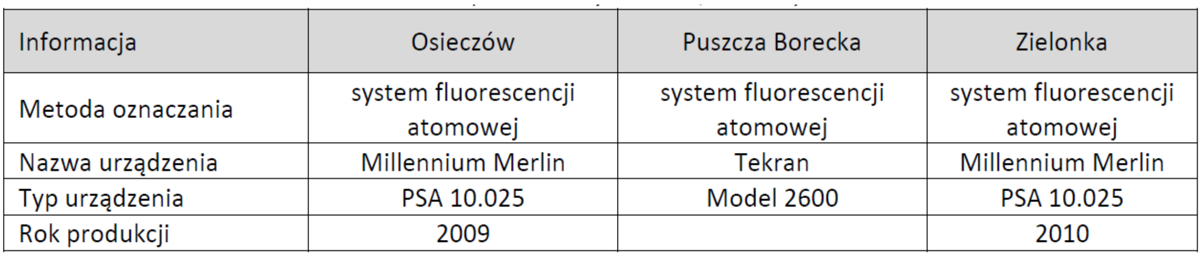
Table 4.7 provides background information on total precipitation sampling methods for measuring mercury deposition rates.

Table 4.7 Information on sampling methods for mercury deposition at regional background stations in Poland (data source: CIEP, IEP-NRI)

Information	Osieczów	Puszcza Borecka	Zielonka
Type of device	total precipitation collector	total precipitation collector	total precipitation collector
Name of device	NSA 181/KD	IVL	NSA 181/KD
Device manufacturer	Eigenbrodt	IVL	Eigenbrodt
Production year	2019	2002	2019
Bottle capacity	5 dm^3	0.5dm^3	5dm^3
Material, from which bottles are made	silica glass	borosilicate glass	silica glass
Temperature of samples in the device	+4 to +6°C	ambient (in winter ca. +5°C)	+4 to +6°C
Possibility to heat the funnel	yes	yes	Yes
Frequency of bottle replacement	every 4-5 weeks	every week	every 2 weeks
Method of determining precipitation amount	calculation based on sample mass	calculation based on sample mass + Hellmann rain gauge	calculation based on sample volume
Method of securing the sample	fixation with HNO_3	fixation with HCl	fixation with HCl + potassium bromate-bromide

Precipitation samples collected at the Chief Inspectorate of Environmental Protection stations are subjected to mineralisation and determined by the CV-AFS method with the use of Millennium Merlin analyser at the Central Research Laboratory of the Chief Inspectorate of Environmental Protection. In the case of the Puszcza Borecka station, determinations are made using the CV-AFS method with the Tekran 2600 analyser at the Institute of Oceanology of the Polish Academy of Sciences in Sopot (Table 4.8).

Table 4.8 Information on methods for measuring mercury deposition at regional background stations in Poland (data source: CIEP, IEP-NRI)



Informacja	Osieczów	Puszcza Borecka	Zielonka
Metoda oznaczania	system fluorescencji atomowej	system fluorescencji atomowej	system fluorescencji atomowej
Nazwa urządzenia	Millennium Merlin	Tekran	Millennium Merlin
Typ urządzenia	PSA 10.025	Model 2600	PSA 10.025
Rok produkcji	2009		2010

Information	Osieczów	Puszcza Borecka	Zielonka
Determination method	atomic fluorescence system	atomic fluorescence system	atomic fluorescence system
Name of device	Millennium Merlin	Tekran	Millenium Merlin
Type of device	PSA 10.025	Model 2600	PSA 10.025
Production year	2009		2010

Compilation of results and reports

Deposition values are calculated from mercury concentrations and precipitation amounts (calculated from the mass/volume of precipitation collected). Variability of mercury deposition at individual monitoring stations measuring this of this pollutant in Poland is analysed on the basis of monthly results.

Compiled reports with research results are presented on the website: https://powietrze.gios.gov.pl/pjp/maps/measuringstation/U

4.2 Information on precipitation chemistry monitoring conducted in European countries based on information and foreign research obtained by the conducting entity and information on Norwegian experience in this field prepared by the Norwegian Institute of Air Research (NILU).

Monitoring of precipitation chemistry is carried out in many European countries. Similarly to Poland, other European countries participate in international programmes such as: EMEP, GAW/WMO and HELCOM, besides running national programmes. The analysis of atmospheric precipitation chemistry monitoring in selected European countries focused on the multi-program experience of Norway, analysis of the Baltic Sea countries to determine the optimum atmospheric chemistry monitoring programme for assessments of atmospheric inflow of substances to the Baltic Sea, and analysis of monitoring programmes of selected countries neighbouring Poland, due to similarities in geographical conditions.

Information on Norwegian experience in this field from the Norwegian Institute of Air Research (NILU)

The Norwegian air quality and deposition monitoring programme offers an example of multi-parameter monitoring that ensures that national and international arrangements and measurement data needs are met, taking into account long-term commitments.

Long-range atmospheric transport contributes significantly to the deposition of air pollutants in Norway. Sulfur emissions on the European continent and in UK caused acid deposition in Norway with large consequences on the aquatic and terrestrial environment. To document the link between long range transport of air pollution, deposition and effect, NILU started routine sampling of precipitation and air in background areas on a daily basis in 1971, with sites located in the southernmost parts of Norway. These observations were coordinated through a project funded by the Organisation for Economic Cooperation and Development (OECD, 1977), a coordinated research effort during the period 1972–1977 to study long range transport of air pollutants.

A national monitoring programme organized by the Norwegian Environment Agency was initiated in 1980, and the national programme become also part of the Monitoring and Evaluation Programme EMEP, following the previous OECD project. EMEP observations include measurements of substances linked to acidification, eutrophication, photochemical oxidants, heavy metals, persistent organic pollutants (POPs) and particulate matter. Most of the substances included in the EMEP monitoring program are also fundamental for improving the knowledge of climate change and both local and urban air quality. Several changes in the content of the measurement programme, as well as in the number and distribution of monitoring sites, has taken place during the 40 years life-time of this monitoring programme. Since around 2010 the has been relatively small changes. The present monitoring programme is presented in Table 4.9 reported to the Norwegian Environmental Agency annually.

The research results obtained are an important database for monitoring compliance with the requirements of the various programmes, as well as providing input data for studies of the impact of air quality on health, the terrestrial environment, the aquatic environment, climate and the ozone layer. The research conducted is also widely used by the scientific community, national environmental authorities and can provide the basis for determining legal aspects in environmental policy.

In Norway, regional and global monitoring of atmospheric composition and deposition is organised as required under national programmes, mainly funded by the Norwegian Environmental Agency and supported by the Ministry of Climate and Environment. The Norwegian Institute for Air Research, NILU, is responsible for the daily operation and reporting of the results of this monitoring.

The monitoring aims to meet several interrelated objectives and is divided into four main programmes: transboundary flows, pollution (including new compounds of concern), climate change and the ozone layer. In addition, there is a monitoring programme designed to assess pollution near the Norwegian-Russian border. Monitoring results also provide data for effects studies (i.e. LRTAP ICP) and assessment of atmospheric processes.

The Norwegian monitoring programmes are built upon international obligations given by several conventions, protocols, frameworks, and directives in addition to national priorities with special focus on the sensitive Arctic environment, and implement the following programmes:

- Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) under the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP),

- International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) and integrated monitoring (ICP-IM) under UNECE-LRTAP,
- Comprehensive Atmospheric Monitoring Programme (CAMP) under OSPAR (the Convention for the Protection of the marine Environment of the North-East Atlantic,
- Arctic Monitoring and Assessment Programme (AMAP),
- The World Meteorological Organization (WMO) Global Atmosphere Watch programme (GAW),
- European Environment Agency (EEA) and different EU air quality directives,
- The Aerosol, Clouds and Trace Gases Research Infrastructure (ACTRIS),
- Integrated Carbon Observation System (ICOS),
- Advanced Global Atmospheric Gas Experiment (AGAGE),
- The Minamata Convention on Mercury under UNEP,
- The Global Monitoring Programme (GMP) of the Stockholm Convention on Persistent Organic Pollutants (POP) under UNEP,
- Montreal Protocol on Substances that Deplete the Ozone Layer under UNEP.

In addition to continuous monitoring, there are also regular campaigns and projects in Norway, with two programmes in particular being important in the deposition:

- Moss survey on trace elements and organic pollutants;
- Total sulfur and nitrogen deposition to be used for 5-year average critical load assessments.

The objectives of the various monitoring programmes are based on adequate spatial and temporal resolution, appropriate survey parameters and complexity of monitoring techniques. The overall strategy is to co-locate measurements with many different components at a few sites for in-depth understanding of atmospheric processes. This is supported by several sites with only basic monitoring of some substances to gather information of regional differences, especially important in Norway with quite large meteorological variations across the country. An overview of the regional sites and their measurement programme is found in Figure 4.17.

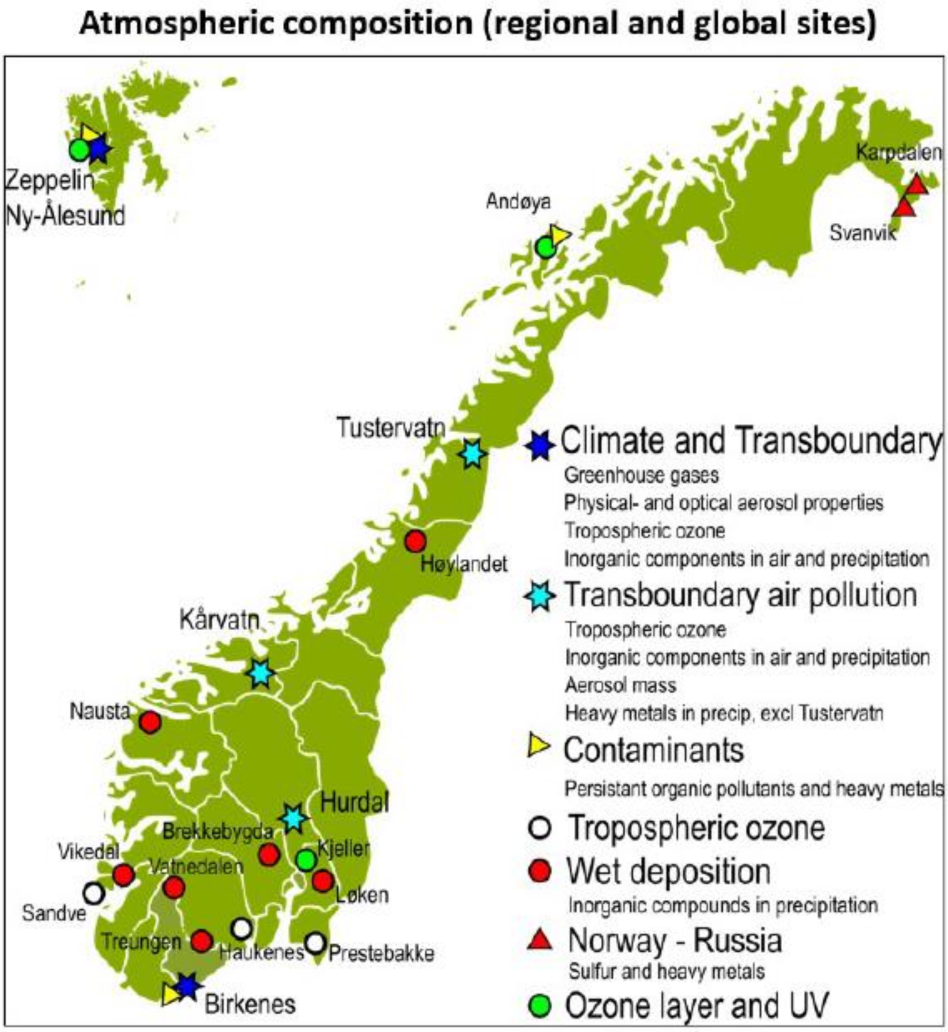

Atmospheric composition (regional and global sites)

Figure 4.17 Overview of Norwegian atmospheric deposition monitoring sites [Monitoring (...) , NILU 2021].

All the sites with atmospheric chemical composition measurements are located in rural areas and are believed to generally give good estimates of long range transported pollutants (Figure 4.17). In regions with local sources such as emissions from industry, traffic or agriculture, pollutant levels may be significantly higher. There is a tendency to monitor air quality in urban and industrial areas in Norway, where there is highest pollution. These sites mainly include observations of particulate matter (PM) and NO, which in Norway are those of highest concern regarding health effects. The monitoring of air quality is conducted by the different municipalities, reported to a national data repository and quality controlled by the national reference laboratory (hosted at NILU).

All Norwegian regional data are publicly available at http://ebas.nilu.no. This is a properly developed database infrastructure for several networks: EMEP, ACTRIS, WMO GAW, AMAP, HELCOM, OSPAR and others. Urban observations, together with tropospheric ozone data, are available at http://www.luftkvalitet.info, these data are also reported and made available by the EEA.

Table 4.9 Measurement programme at Norwegian base stations in 2020, excluding climate gas and ozone layer measurements. Stations in italics are not regionally representative stations [Monitoring..., NILU 2021].

Measure-ment / Position	Air							Precipitation				Data reported to international program-mes
	hourly		daily		weekly		2d per week / month	daily	weekly			
	meteo.	O_3	p. main	NO_2	$PM_{2,5+10}$ + EC/OC	MC	POPs	p. main	P. main	MC	POPs	
Birkenes	X	X	X	X	X	$X^{b,c}$	X^d	X		X^b	X^e	EMEP, ICPs, CAMPs
Vatnedalen									X			
Treungen									X			
Haukenes		X										
Prestebakke		X										EMEP
Løken									X			
Hurdal	X	X	X	X	X			X		X^a		EMEP, ICP-Forest
Brekkebygda									X			ICP-IM
Vikedal									X			CAMP
Sandve		X										EMEP
Nausta									X			CAMP
Kårvatn		X	X	X	X			X		X^a		EMEP, ICP-IM, CAMP
Høylandet									X			
Tustervatn		X	X	X				X				EMEP
Andøya*						$X^{b,c}$	X^f					EMEP, AMAP, CAMP
Karpbukt						$X^{b,c}$			X	X^b		
Svanvik						$X^{b,c}$				X^b		
Zeppelin	X	X	X			$X^{b,c}$	X^g					EMEP, AMAP, GAW
Ny-Ålesund									X			CAMP
Total number	**3^+**	**7+1**	**5**	**4**	**3**	**3+2**	**3**	**4**	**9**	**3+2**	**1**	

Key:
* the station will be closed in 2022.
$^+$ The Norwegian Meteorological Service is closely monitoring several locations
Measurements:
meteo. – meteorological measurements (wind direction, pressure and temperature);

p. main – precipitation: main measurements in precipitation: amount (mm), pH, conductivity, SO_4 , NO_3 , Cl, NH_4 , Ca, K, Mg;
p. main – air: main measurements in air: SO_2, SO_4, HNO_3 + NO_3, NH_4 + NH_3, Ca, K, Mg, Na, Cl;
$PM_{2,5+10}$ +EC/OC – measurement of $PM_{2,5}$ and PM_{10} as well as elemental carbon (EC) and organic carbon (OC);
MC – heavy metals, groups:

- a – Pb, Cd and Zn (Hg tested from 2021),
- b – As, Cd, Cr, Co, Cu, Pb, Mn, Ni, V, Zn and Hg (no Hg at Karpukt and Svanvik),
- c – Al, Fe, Ti.

POPs – persistent organic pollutants, groups:

- d – α– og γ–HXH, HCB, DDT, PCB, PBDE, HBCD, PAHs, PFAS, Siloxanes, SCCP, MCCP,
- e – α– og γ–HXH, HCB, PCB,
- f – HCB, PFAS,
- g – α– og γ–HXH, HCB, DDT, chlordane, PCB, BDE, HBCD, PAHs, PFAS, siloxanes, SCCP.

There are thirteen monitoring sites in Norway where precipitation chemistry is studied. At five of them, measurements of major ions are made not only in the precipitation, but also in the air. Four sites are located on the mainland (Table 4.9, Figures 4.18, 4.19). At these four monitoring stations sampling is conducted on a daily basis as recommended by EMEP. Measurements at the remaining stations are conducted measurements at the remaining stations are conducted on a weekly basis and data from these stations are not reported to EMEP. Two gauging stations are part of the CAMP programme, where measurements on weekly cycles are sufficient. Some stations are also part of the GAW/WMO, AMAP and two ICP programmes (Table 4.9). However, all sites are part of the national programme for atmospheric deposition of sulphur and nitrogen compounds, and data are submitted and available in the same database (EBAS).

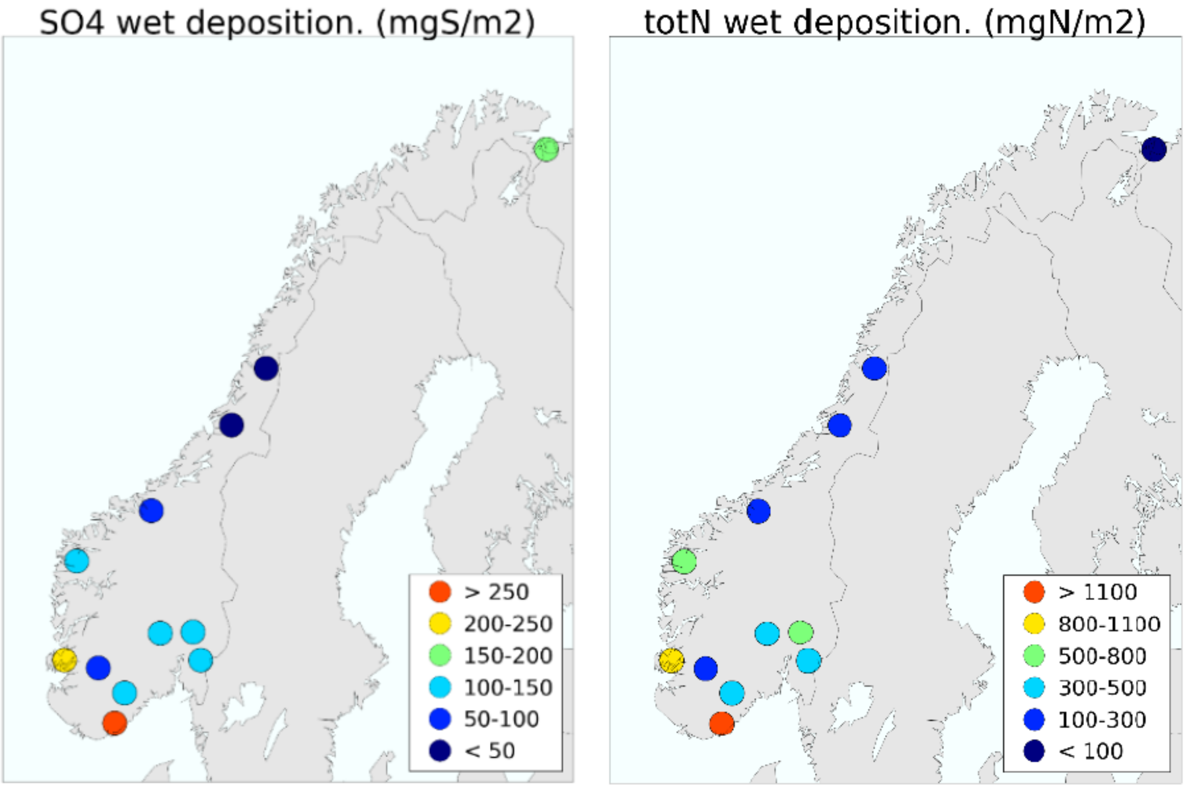


Figure 4.18 Wet deposition of sulphate (left), total nitrate and ammonium (right) at Norwegian base stations in 2020 without observations on Spitsbergen [Monitoring..., NILU 2021].

The observations used to estimate the total dry deposition of sulphur and nitrogen compounds and the measured wet deposition at the sites with both precipitation and air measurements, as shown in Figure 4.19.

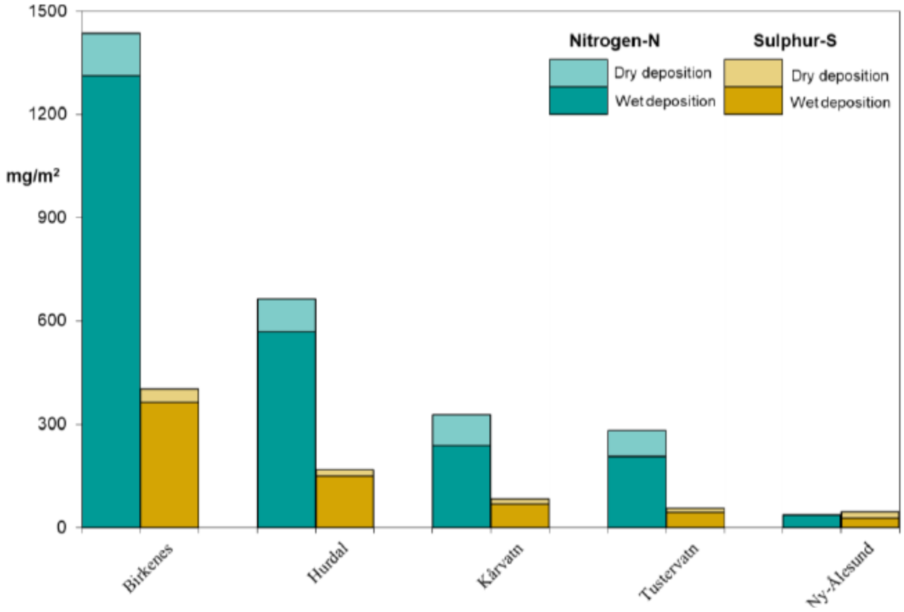


Figure 4.19 Total depositions (wet + dry) of sulphur-S (SO_2 , SO_4^{2-}) and nitrogen-N (NO_2, NH_4^+, NH_3, NO_3^-, HNO_3) at Norwegian base stations 2020 [Monitoring..., NILU 2021].

In order to evaluate the exceedance of critical loads to the ecosystems, these site-specific depositions are not sufficient. It is necessary to interpolate and estimate the deposition with a high spatial resolution to reflect on the available information on spatial variation of the land surface (vegetation, soil and aquatic environment). In Norway we are using two different approaches:

1) from measurements of air and precipitation chemistry combined with statistical interpolation,
2) combine observations and atmospheric model calculations, often called data assimilation or data-model fusion.

These depositions are combined to five-year average to get less affected by annual variations.

For both methods, data from the regular Norwegian monitoring network (Table 4.9) are combined with concentrations in precipitation and air from the Swedish, Danish, Finnish and Russian EMEP stations to get better information of deposition along the border. The precipitation amount data used for the calculations of the wet deposition is taken from the national meteorological observation network (MET) in addition to the NILU sites. Data from in total 300 automatic meteorological sites. Figure 4.20 gives and overview of the sites used in this assessment done on a five-year interval.

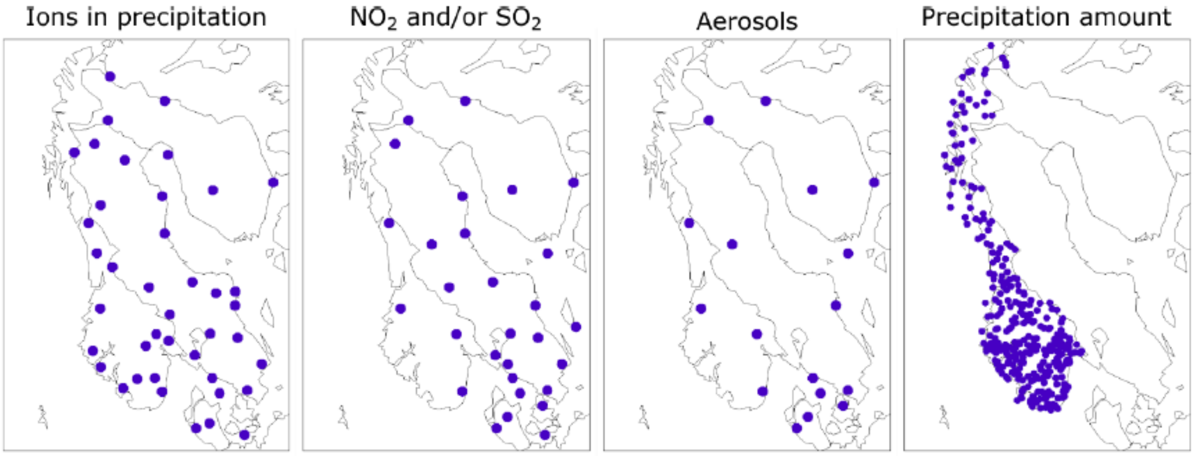


Figure 4.20 Overview of sites used to estimate sulphur and nitrogen deposition between 2012 and 2016 [Monitoring..., NILU 2021].

In method one, the concentrations in precipitation and air are interpolated from fixed sites to a regular grid of 50×50 km2 using linear "kriging". Annual wet deposition was calculated at each site with precipitation amount multiplied with the interpolated concentration in the respective grid cell. And dry deposition was calculated on a 50x50 grid with estimated dry deposition velocity for each grid depending on surface type multiplied with the interpolated concentration in the grid. The total deposition estimated at each meteorological sites are visualized using standard interpolation routines, illustrated with sulfur deposition in Figure 4.21.

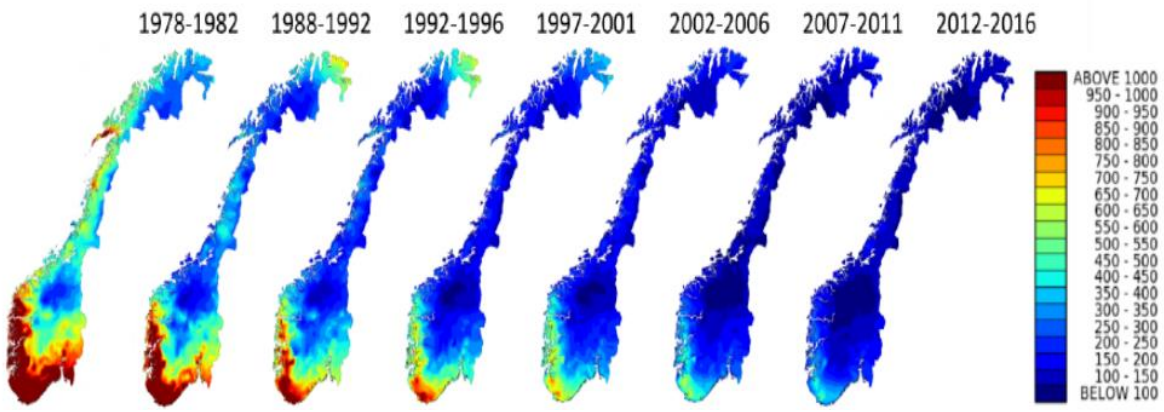


Figure 4.21 Trend of sulphur deposition from non-marine salts in Norway (mgS/m^2 year), calculated using an observation-based method [Monitoring..., NILU 2021].

There are two main limitations of this method. Firstly, at the Norwegian mainland, there are currently only 12 regional sites with precipitation chemistry and 4 with gas and aerosols measurements. Thus, there are large areas of Norway where these sites not necessarily are representative, and the uncertainty in the interpolation between these sites is large. Secondly, the dry deposition is not measured directly, and it is necessary to estimate the deposition velocities based on literature values combined with information on climatic conditions and ground cover. These are very crude estimates, both spatially and temporally and do not take into account the interaction between species, i.e., co-deposition.

The atmospheric chemical transport models usually have a much higher spatial and temporal coverage and can potentially fill the gaps and limitations of the observational based method. In Norway we have used the dispersion model developed by the Norwegian Meteorological Institute (MET) under the Co-operative programme for monitoring and evaluation of long-range transmissions of air pollutants in Europe (EMEP). These model calculations have been combined with observations for the period 2012-2017.

In the second method, the model results are adjusted by the observations giving large weight to the observed values close to stations and using the modelled values in areas with no observations. The dry deposition rates are taken from the EMEP model using the monthly averages for each species specified for each grid cell.

Another way of measuring deposition is by using the throughfall method as done by ICP Forest. In Norway, there are three ICP Forest sites: Birkenes, Hurdal and Osen. The sulfur deposition from throughfall is quite comparable with what is estimated using wet+dry deposition at the Norwegian sites. For nitrogen deposition it is larger deviation probably due to the difficulties estimating the interaction between nitrogen and the canopy, i.e uptake and leaking from the canopy, i.e. absorption and transpiration, as shown in Figure 4.22.

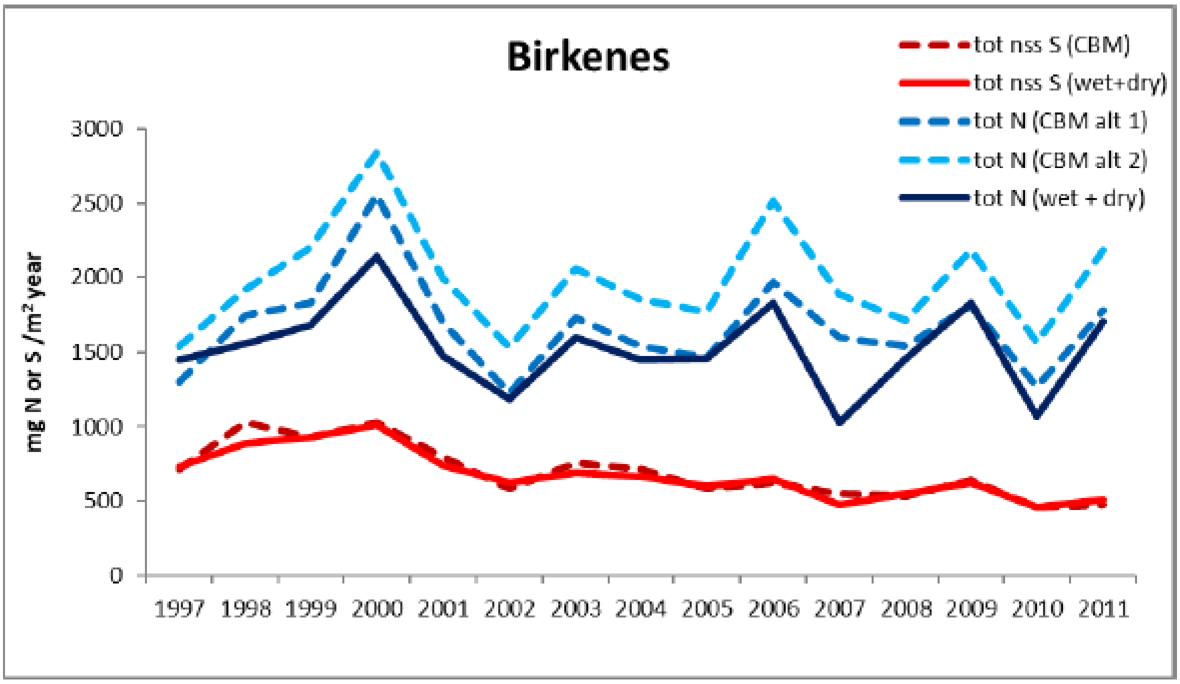


Figure 4.22 Comparison of total deposition of sulfur (red) and nitrogen (blue) using the observations of precipitation and air concentration (wet + dry) with the throughfall measurement combined with canopy budget model (CBM) at Birkenes [Monitoring..., NILU 2021] .

As outlined in the report [Monitoring..., NILU 2021], Norwegian monitoring programmes have had a long-term perspective, which makes the observations made valuable well beyond national interests. Involvement in international programmes has been crucial in order to develop a standardised methodology and share knowledge on atmospheric composition and deposition. An open data sharing policy was a prerequisite.

In addition to long-term perspectives, the close cooperation between the research and regulatory sectors in Norway allows for continuous renewal of the monitoring programme, i.e. moving the measurement of pollution data from the screening/innovation level to the monitoring level allows for rapid development of standardised methods, and the data provide important input for regulators.

Different monitoring programmes benefit from sharing infrastructure (observatories, laboratories and databases). This is cost-effective and creates synergies between different environmental issues.

To understand the effects and sources of air pollution and deposition, many different components need to be measured and confronted. For atmospheric deposition, the challenge is to have a sufficiently representative number of stations, which is especially difficult in Norway where there are large geographical differences. To get a deeper analysis and better estimation of deposition, there has been an interesting development of different measurement model fusion tools that may become part of more routine monitoring products in the future.

Monitoring of precipitation chemistry in selected Baltic countries

In order to determine the optimum atmospheric chemistry monitoring programme for the assessment of atmospheric inflow of substances to the Baltic Sea, an analysis of the scope of research carried out in individual Baltic Sea states was conducted. The analysis included 13 measurement sites located in Finland, Sweden and Germany (Table 4.10, Figure 4.23). At the same time, because some of the monitored parameters can be used both for HELCOM and EMEP purposes, analysis of EMEP data use for HELCOM purposes at individual stations was conducted and common stations were indicated on the map (Figure 4.24). The analysis also considered the parameters studied in the air under both programmes.

Table 4.10 List of HELCOM stations in the Baltic States [own work based on EBAS database]

No.	**Country**	**Station code**	**Station name**	**Geographical coordinates**		**Programme**
				Longitude E	**Latitude N**	
1	Finland	FI0053R	Hailuoto II	24.69417	65.00000	HELCOM, EMEP
2	Finland	FI0050R	Hyytiälä	24.28333	61.85000	HELCOM, EMEP
3	Finland	FI0009R	Utö	21.37722	59.77917	HELCOM, EMEP
4	Finland	FI0018R	Virolahti III	27.66754	60.53002	HELCOM, EMEP
5	Germany	DE0007R	Neuglobsow	13.03333	53.16667	HELCOM, EMEP
6	Germany	DE0003R	Schauinsland	7.90861	47.91472	HELCOM, EMEP
7	Germany	DE0008R	Schmücke	10.76667	50.65000	HELCOM, EMEP
8	Germany	DE0002R	Waldhof	10.75944	52.80222	HELCOM, EMEP
9	Germany	DE0009R	Zingst	12.72490	54.43680	HELCOM, EMEP
10	Sweden	SE0020R	Hallahus	13.14800	56.04290	HELCOM, EMEP
11	Sweden	SE0022R	Norunda Stenen	17.50528	60.08580	HELCOM, EMEP
12	Sweden	SE0014R	Råö	11.91400	57.39400	HELCOM, EMEP
13	Sweden	SE0053R	Rickleå	20.93333	64.16667	HELCOM

Figure 4.23 Location of EMEP and HELCOM stations in the Baltic States [own work based on EBAS database].

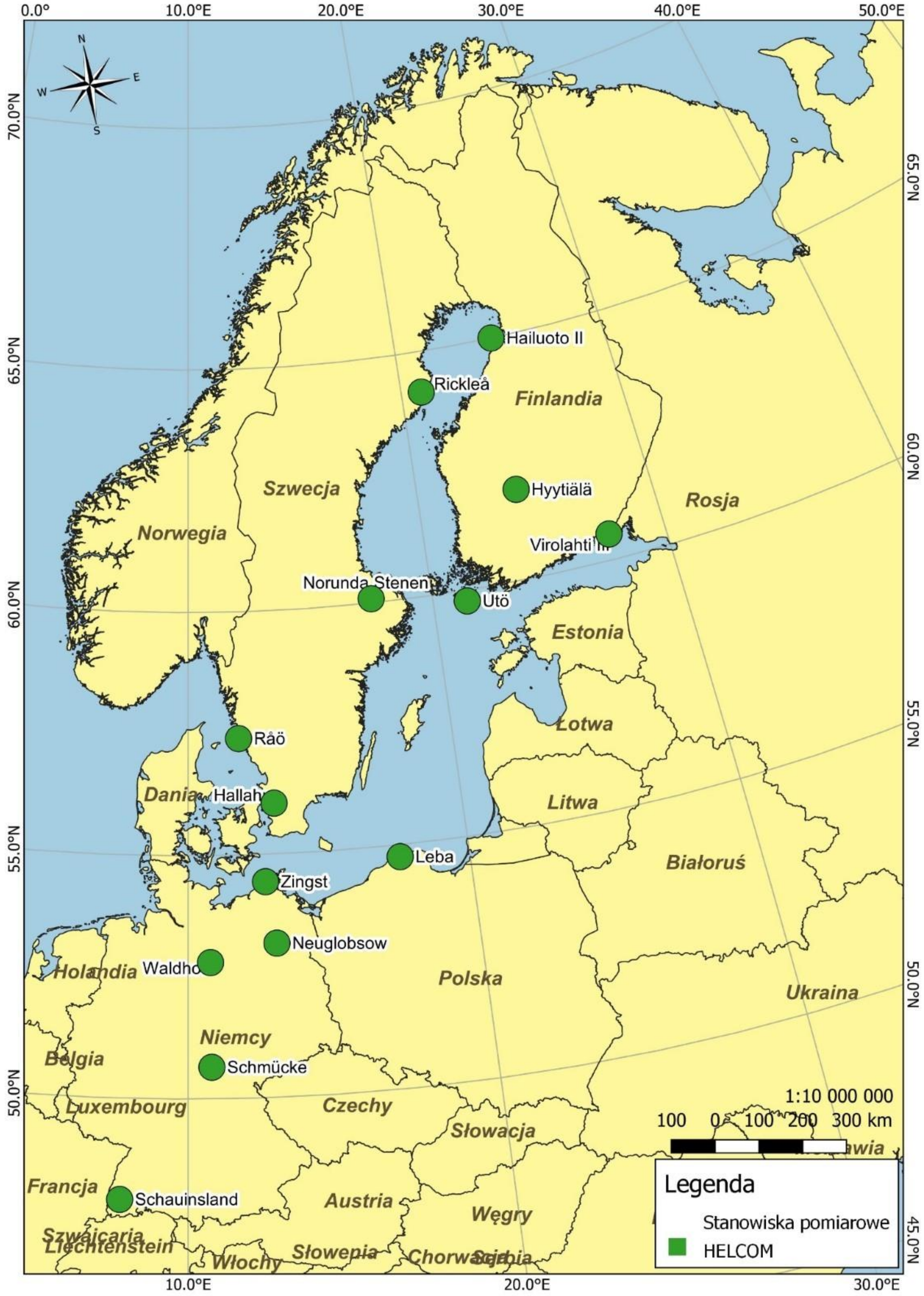


Figure 4.24 Location of HELCOM stations in Finland, Sweden, Germany and Poland [own work based on EBAS database].

Finland

In Finland, atmospheric chemistry measurements for assessing atmospheric inputs of substances to the Baltic Sea within HELCOM are conducted at 4 stations.

The Hailuoto II station under HELCOM conducts research on pollutants in precipitation (Table 4.11). Of the 5 mandatory parameters, cadmium, lead, nitrate and precipitation amount are measured at the station. Apart from the mentioned mandatory parameters, voluntary parameters such as copper, iron, nickel, arsenic, zinc, calcium ion, chlorine ion, potassium ion, magnesium ion, sodium ion, sulphate ion, conductivity and pH are also analysed at the station. Testing of the parameters is carried out using a bulk precipitation collector with a frequency between 1 week and 1 month.

Measurements at the Hyytiälä station are conducted under HELCOM and EMEP (Table 4.12). Under HELCOM, research is conducted only in atmospheric precipitation. Of the 5 mandatory parameters, cadmium and lead, as well as precipitation amount. Apart from the mentioned obligatory parameters, voluntary parameters such as chromium, copper, iron, nickel, arsenic and zinc are analysed at the site. These tests are performed using a bulk type collector with a frequency of 1 month. In addition, as part of the EMEP programme, mercury, nitrate, ammonium cation, calcium ion, chlorine ion, potassium ion, magnesium ion, sodium ion, sulphate ion, conductivity, pH and benzo(a)pyrene are measured in precipitation.

Air pollutants are measured within EMEP and include all biogenic pollutants required by HELCOM, such as nitric acid, ammonia, ammonium cation, nitrate and nitrite, the sum of nitric acid and nitrates and the sum of ammonia and ammonium cation. In addition, at the station within the EMEP programme, parameters such as cadmium, lead, chromium, copper, iron, nickel, arsenic, mercury and benzo(a)pyrene are analysed in the air.

The Utö station of the HELCOM programme only conducts research on mandatory parameters in the air such as nitric acid, ammonia, ammonium cation , nitrates and nitrites, sum of nitric acid and nitrates and ammonia and ammonium cation (Table 4.13). Parameter tests are performed in samples collected on filters at a frequency between 1 hour and 1 day.

At the Virolahti III station, research is conducted within the HELCOM and EMEP, both in atmospheric precipitation and in air (Table 4.14). In atmospheric precipitation, 3 parameters such as ammonium cation and nitrate, as well as precipitation amount are studied under HELCOM out of 5 mandatory parameters. In addition to the listed mandatory parameters, the following voluntary components are also measured in precipitation at the station: calcium ion, chlorine ion, potassium ion, magnesium ion, sodium ion, sulphate ion, conductivity and pH. These are performed using a bulk type collector with a frequency of 1 week. As part of the EMEP programme, there are performed tests for cadmium and lead are performed in precipitation, which are mandatory parameters required by HELCOM, and additionally tests for mercury, chromium, copper, iron, nickel, arsenic and zinc, as well as benzo(a)pyrene.

The following mandatory parameters are measured in the air under HELCOM: nitric acid, ammonia, ammonium cation, nitrates and nitrites, sum of nitric acid and nitrates and ammonia and ammonium cation. Samples are collected on filters at a frequency of 1 day. Under EMEP, metals such as cadmium, lead, chromium, copper, iron nickel, arsenic and zinc are tested in the air.

Table 4.11 Scope of HELCOM monitoring carried out at the Hailuoto II station (Finland).

Hailuoto II (Finland)							
HELCOM Recommendation 37-38/2 for Air Monitoring Programme for monitoring of the pollution of air and precipitation				**HELCOM PROGRAMME**			**NOTES**
Matrix	Type of pollutant	Parameter Mandatory Voluntary	**Maximum collection time**	**Method of measurement/ collection**	**Matrix type**	**Collection frequency**	
Pollutants in precipitation	Metals	Cd	1 month	bulk	precipitation	1 month	
		Pb		bulk	precipitation	1 month	
		Hg					
		Cr					
		Cu		bulk	precipitation	1 month	
		Fe		bulk	precipitation	1 month	
		Ni		bulk	precipitation	1 month	
		As		bulk	precipitation	1 month	
		Zn		bulk	precipitation	1 month	
	Biogenes	NH_4^+		🟩	🟩	🟩	
		NO_3^-		bulk	precipitation	1 week	
		total phosphorus					
	Ions	Ca^{2+}		bulk	precipitation	1 week	
		Cl^-		bulk	precipitation	1 week	
		pH		bulk	precipitation	1 week	
		conductivity		bulk	precipitation	1 week	
		SO_4^{2-} (total)		bulk	precipitation	1 week	
		K^+		bulk	precipitation	1 week	
		Mg^{2+}		bulk	precipitation	1 week	
		Na^+		bulk	precipitation	1 week	
	Precipitation	precipitation		bulk	precipitation	1 week/1 month	
	POPs	γ-HCH (lindane)					
	PCB	Congeners 28,52,101,118, 138,153,180					
	PAHs	BaP					
Air pollutants	Metals	Cd	1 week				
		Pb					
		Hg					
		Cr					
		Cu					
		Fe					
		Ni					
		As					
		Zn					
	Biogenes	HNO_3	24 hours	🟩	🟩	🟩	
		NH_3		🟩	🟩	🟩	
		NH_4^+		🟩	🟩	🟩	
		NO_2		🟩	🟩	🟩	
		NO_3^-		🟩	🟩	🟩	
		sum of HNO_3 and NO_3^-		🟩	🟩	🟩	
		sum of NH_3 and NH_4^+		🟩	🟩	🟩	
		total phosphorus	1 week				
	POPs	γ-HCH (lindane)	1 week				
	PCB	Congeners 28,52,101,118,138,153,180	1 week				
	PAHs	BaP	1 week				

Table 4.12 Scope of HELCOM monitoring carried out at the Hyytiälä station (Finland).

Hyytiälä (Finland)							
HELCOM Recommendation 37-38/2 for Air Monitoring Programme for monitoring of the pollution of air and precipitation				**HELCOM PROGRAMME**			**NOTES**
Matrix	**Type of pollutant**	**Parameter** **Mandatory** **Voluntary**	**Maximum collection time**	**Method of measurement/ collection**	**Matrix type**	**Collection frequency**	
Pollutants in precipitation	Metals	Cd	1 month	bulk	precipitation	1 month	
		Pb		bulk	precipitation	1 month	
		Hg					EMEP
		Cr		bulk	precipitation	1 month	
		Cu		bulk	precipitation	1 month	
		Fe		bulk	precipitation	1 month	
		Ni		bulk	precipitation	1 month	
		As		bulk	precipitation	1 month	
		Zn		bulk	precipitation	1 month	
	Biogenes	NH_4^+					EMEP
		NO_3^-					EMEP
		total phosphorus					
	Ions	Ca^{2+}					EMEP
		Cl^-					EMEP
		pH					EMEP
		conductivity					EMEP
		SO_4^{2-} (total)					EMEP
		K^+					EMEP
		Mg^{2+}					EMEP
		Na^+					EMEP
	Precipitation	precipitation		bulk	precipitation	1 month	
	POPs	γ-HCH (lindane)					
	PCB	Congeners 28,52,101,118, 138,153,180					
	PAHs	BaP					EMEP
Air pollutants	Metals	Cd	1 week				EMEP
		Pb					EMEP
		Hg					
		Cr					EMEP
		Cu					EMEP
		Fe					EMEP
		Ni					EMEP
		As					EMEP
		Zn					EMEP
	Biogenes	HNO_3	24 hours				EMEP
		NH_3					EMEP
		NH_4^+					EMEP
		NO_2					EMEP
		NO_3^-					EMEP
		sum of HNO_3 and NO_3^-					EMEP
		sum of NH_3 and NH_4^+					EMEP
		total phosphorus	1 week				
	POPs	γ-HCH (lindane)	1 week				
	PCB	Congeners 28,52,101,118, 138,153,180	1 week				
	PAHs	BaP	1 week				EMEP

Table 4.13 Scope of HELCOM monitoring carried out at the Utö station (Finland)

Utö (Finland)							
HELCOM Recommendation 37-38/2 for Air Monitoring Programme for monitoring of the pollution of air and precipitation				HELCOM PROGRAMME			NOTES
Matrix	Type of pollutant	Parameter Mandatory Voluntary	Maximum collection time	Method of measurement/ collection	Matrix type	Collection frequency	
Pollutants in precipitation	Metals	Cd	1 month	🟩	🟩	🟩	
		Pb		🟩	🟩	🟩	
		Hg					
		Cr					
		Cu					
		Fe					
		Ni					
		As					
		Zn					
	Biogenes	NH_4^+		🟩	🟩	🟩	
		NO_3^-		🟩	🟩	🟩	
		total phosphorus					
	Ions	Ca^{2+}					
		Cl^-					
		pH					
		conductivity					
		SO_4^{2-} (total)					
		K^+					
		Mg^{2+}					
		Na^+					
	Precipitation	precipitation		🟩	🟩	🟩	
	POPs	γ-HCH (lindane)					
	PCB	Congeners 28,52,101,118, 138,153,180					
	PAHs	BaP					
Air pollutants	Metals	Cd	1 week				
		Pb					
		Hg					
		Cr					
		Cu					
		Fe					
		Ni					
		As					
		Zn					
	Biogenes	HNO_3	24 hours	filters	air	1 day	
		NH_3		filters	air	1 day	
		NH_4^+		filters	aerosol	1 day	
		NO_2		photolytic chemiluminescence	air	1 hour	
		NO_3^-		filters	aerosol	1 day	
		sum of HNO_3 and NO_3^-		filters	air+ aerosol	1 day	
		sum of NH_3 and NH_4^+		filters	air+ aerosol	1 day	
		total phosphorus	1 week				
	POPs	γ-HCH (lindane)	1 week				
	PCB	Congeners 28,52,101,118, 138,153,180	1 week				
	PAHs	BaP	1 week				

Table 4.14 Scope of HELCOM monitoring carried out at Virolahti III station (Finland)

Virolahti III (Finland)							
HELCOM Recommendation 37-38/2 for Air Monitoring Programme for monitoring of the pollution of air and precipitation				**HELCOM PROGRAMME**			**NOTES**
Matrix	**Type of pollutant**	**Parameter** 🟩 **Mandatory** **Voluntary**	**Maximum collection time**	**Method of measurement/ collection**	**Matrix type**	**Collection frequency**	
Pollutants in precipitation	Metals	🟩 Cd	1 month	🟩	🟩	🟩	EMEP
		🟩 Pb		🟩	🟩	🟩	EMEP
		Hg					EMEP
		Cr					EMEP
		Cu					EMEP
		Fe					EMEP
		Ni					EMEP
		As					EMEP
		Zn					EMEP
	Biogenes	🟩 NH_4^+		bulk	precipitation	1 week	
		🟩 NO_3^-		bulk	precipitation	1 week	
		total phosphorus					
	Ions	Ca^{2+}		bulk	precipitation	1 week	
		Cl^-		bulk	precipitation	1 week	
		pH		bulk	precipitation	1 week	
		conductivity		bulk	precipitation	1 week	
		SO_4^{2-} (total)		bulk	precipitation	1 week	
		K^+		bulk	precipitation	1 week	
		Mg^{2+}		bulk	precipitation	1 week	
		Na^+		bulk	precipitation	1 week	
	Precipitation	🟩 precipitation		bulk	precipitation	1 week	
	POPs	γ-HCH (lindane)					
	PCB	Congeners 28,52,101,118, 138,153,180					
	PAHs	BaP					EMEP
Air pollutants	Metals	Cd	1 week				EMEP
		Pb					EMEP
		Hg					
		Cr					EMEP
		Cu					EMEP
		Fe					EMEP
		Ni					EMEP
		As					EMEP
		Zn					EMEP
	Biogenes	🟩 HNO_3	24 hours	filters	air	1 day	
		🟩 NH_3		filters	air	1 day	
		🟩 NH_4^+		filters	aerosol	1 day	
		🟩 NO_2		🟩	🟩	🟩	EMEP
		🟩 NO_3^-		filters	aerosol	1 day	
		🟩 sum of HNO_3 and NO_3^-		filters	air+ aerosol	1 day	
		🟩 sum of NH_3 and NH_4^+		filters	air+ aerosol	1 day	
		total phosphorus	1 week				
	POPs	γ-HCH (lindane)	1 week				
	PCB	Congeners 28,52,101,118, 138,153,180	1 week				
	PAHs	BaP	1 week				

Sweden

In Sweden, atmospheric chemistry measurements for assessing atmospheric inputs of substances to the Baltic Sea within HELCOM are carried out at 4 stations.

At the Hallahus station, research is conducted under HELCOM and EMEP in both precipitation and air (Table 4.15). Under HELCOM, out of 5 mandatory parameters, ammonium cation, nitrate and precipitation amount are tested in precipitation. As voluntary parameters, mercury, calcium ion, chlorine ion, potassium ion, magnesium ion, sodium ion, sulphate ion, conductivity and pH are tested. These tests are performed using a wet only collector and a bulk collector at a frequency between 2 weeks and 1 month. In addition, metals such as lead, chromium, copper, nickel and zinc are analysed in precipitation as part of the EMEP programme.

All mandatory parameters shall be analysed in the air under HELCOM: nitric acid, ammonia, ammonium cation, nitrates and nitrites, the sum of nitric acid and nitrates and the sum of ammonia and ammonium cation. Samples are collected on filters and using an absorption tube at a frequency of 1 day. As part of EMEP, metals such as cadmium, lead, mercury, chromium, copper, nickel, arsenic and zinc are measured in the air.

At the Norunda Stenen station, research is conducted under HELCOM and EMEP in both precipitation and air (Table 4.16). Under HELCOM, ammonium cation, nitrate and precipitation amount are tested in precipitation out of 5 mandatory parameters. As voluntary parameters the following are measured: calcium ion, chlorine ion, potassium ion, magnesium ion, sodium ion, sulphate ion, conductivity and pH. These tests are performed using a wet only collector with a frequency of 1 month. In addition, as part of the EMEP programme, parameters such as cadmium and lead, which are among the mandatory parameters under HELCOM, and chromium, copper, nickel, zinc, γ-HCH (lindane), congeners 28, 52, 101, 118, 138, 153, 180 and benzo(a)pyrene are measured in precipitation.

All mandatory parameters shall be analysed in the air under HELCOM: nitric acid, ammonia, ammonium cation, nitrates and nitrites, the sum of nitric acid and nitrates and the sum of ammonia and ammonium cation. Samples shall be collected on filters and using an absorption tube with a frequency of 1 day. Within the EMEP programme, metals such as cadmium, lead, chromium, copper, nickel, arsenic and zinc are measured in the air, as well as γ-HCH (lindane), congeners 28, 52, 101, 118, 138, 153, 180 and benzo(a)pyrene.

At the Råö station, research is conducted under HELCOM and EMEP in both precipitation and air (Table 4.17). Under HELCOM, ammonium cation, nitrate and precipitation amount are measured in precipitation out of 5 mandatory parameters. As voluntary parameters, calcium ion, chlorine ion, potassium ion, magnesium ion, sodium ion, sulphate ion, conductivity, pH and mercury are tested. These tests are performed using a wet only collector and a bulk collector with a frequency between 1 day and 2 weeks. In addition, parameters such as lead, which is a mandatory parameter group according to HELCOM, and chromium, copper, nickel, zinc, γ-HCH (lindane), congeners 28, 52, 101, 118, 138, 153, 180 are tested in the precipitation within EMEP.

All mandatory parameters are measured in the air under HELCOM: nitric acid, ammonia, ammonium cation, nitrates and nitrites, the sum of nitric acid and nitrates and the sum of ammonia and ammonium cation. Mercury is tested as a voluntary parameter.

Samples are collected on filters and using an absorption tube with a frequency of 1 day. Within the EMEP programme, metals such as cadmium, lead, chromium, copper, nickel, arsenic and zinc as well as γ-HCH (lindane), congeners 28, 52, 101, 118, 138, 153, 180 and benzo(a)pyrene are measured in the air.

At Rickleå station, research is only conducted as part of the HELCOM programme and concerns pollutants in atmospheric precipitation (Table 4.18). Of the 5 mandatory parameters, ammonium cation, nitrate, calcium ion, chlorine ion, potassium ion, magnesium ion, sodium ion, sulphate ion, conductivity and pH are tested. These tests are performed using a bulk collector with a frequency of 1 month.

Table 4.15 Scope of HELCOM monitoring carried out at the Hallahus station (Sweden)

Hallahus (Sweden)							
HELCOM Recommendation 37-38/2 for Air Monitoring Programme for monitoring of the pollution of air and precipitation				**HELCOM PROGRAMME**			**NOTES**
Matrix	**Type of pollutant**	**Parameter** **Mandatory** **Voluntary**	**Maximum collection time**	**Method of measurement/ collection**	**Matrix type**	**Collection frequency**	
Pollutants in precipitation	Metals	Cd	1 month				
		Pb					EMEP
		Hg		bulk	precipitation	2 weeks	
		Cr					EMEP
		Cu					EMEP
		Fe					
		Ni					EMEP
		As					
		Zn					EMEP
	Biogenes	NH_4^+		wet only	precipitation	1 month	
		NO_3^-		wet only	precipitation	1 month	
		total phosphorus					
	Ions	Ca^{2+}		wet only	precipitation	1 month	
		Cl^-		wet only	precipitation	1 month	
		pH		wet only	precipitation	1 month	
		conductivity		wet only	precipitation	1 month	
		SO_4^{2-} (total)		wet only	precipitation	1 month	
		K^+		wet only	precipitation	1 month	
		Mg^{2+}		wet only	precipitation	1 month	
		Na^+		wet only	precipitation	1 month	
	Precipitation	precipitation		bulk / wet only	precipitation	2 weeks/ 1 month	
	POPs	γ-HCH (lindane)					
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180					
	PAHs	BaP					
Air pollutants	Metals	Cd	1 week				EMEP
		Pb					EMEP
		Hg					EMEP
		Cr					EMEP
		Cu					EMEP
		Fe					
		Ni					EMEP
		As					EMEP
		Zn					EMEP
	Biogenes	HNO_3	24 hours	filters	air	1 day	
		NH_3		filters	air	1 day	
		NH_4^+		filters	aerosol	1 day	
		NO_2		absorption tube	air	1 day	
		NO_3^-		filters	aerosol	1 day	
		sum of HNO_3 and NO_3^-		filters	air+ aerosol	1 day	
		sum of NH_3 and NH_4^+		filters	air+ aerosol	1 day	
		total phosphorus	1 week				
	POPs	γ-HCH (lindane)	1 week				
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180	1 week				
	PAHs	BaP	1 week				EMEP

Table 4.16 Scope of HELCOM monitoring carried out at the Norunda Stenen station (Sweden)

Norunda Stenen (Sweden)							
HELCOM Recommendation 37-38/2 for Air Monitoring Programme for monitoring of the pollution of air and precipitation				**HELCOM PROGRAMME**			**NOTES**
Matrix	**Type of pollutant**	**Parameter** **Mandatory** **Voluntary**	**Maximum collection time**	**Method of measurement/ collection**	**Matrix type**	**Collection frequency**	
Pollutants in precipitation	Metals	Cd	1 month				EMEP
		Pb					EMEP
		Hg					
		Cr					
		Cu					
		Fe					
		Ni					EMEP
		As					EMEP
		Zn					EMEP
	Biogenes	NH_4^+		wet only	precipitation	1 month	
		NO_3^-		wet only	precipitation	1 month	
		total phosphorus					
	Ions	Ca^{2+}		wet only	precipitation	1 month	
		Cl^-		wet only	precipitation	1 month	
		pH		wet only	precipitation	1 month	
		conductivity		wet only	precipitation	1 month	
		SO_4^{2-} (total)		wet only	precipitation	1 month	
		K^+		wet only	precipitation	1 month	
		Mg^{2+}		wet only	precipitation	1 month	
		Na^+		wet only	precipitation	1 month	
	Precipitation	precipitation		wet only	precipitation	1 month	
	POPs	γ-HCH (lindane)					EMEP
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180					EMEP
	PAHs	BaP					EMEP
Air pollutants	Metals	Cd	1 week				EMEP
		Pb					EMEP
		Hg					
		Cr					EMEP
		Cu					EMEP
		Fe					
		Ni					EMEP
		As					EMEP
		Zn					EMEP
	Biogenes	HNO_3	24 hours	filters	air	1 day	
		NH_3		filters	air	1 day	
		NH_4^+		filters	aerosol	1 day	
		NO_2		absorption tube	air	1 day	
		NO_3^-		filters	aerosol	1 day	
		sum of HNO_3 and NO_3^-		filters	air+ aerosol	1 day	
		sum of NH_3 and NH_4^+		filters	air+ aerosol	1 day	
		total phosphorus	1 week				
	POPs	γ-HCH (lindane)	1 week				EMEP
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180	1 week				EMEP
	PAHs	BaP	1 week				EMEP

Table 4.17 Scope of HELCOM monitoring at the Råö station (Sweden)

Råö (Sweden)							
HELCOM Recommendation 37-38/2 for Air Monitoring Programme for monitoring of the pollution of air and precipitation				**HELCOM PROGRAMME**			**NOTES**
Matrix	**Type of pollutant**	**Parameter** **Mandatory** **Voluntary**	**Maximum collection time**	**Method of measurement/ collection**	**Matrix type**	**Collection frequency**	
Pollutants in precipitation	Metals	Cd	1 month				
		Pb					EMEP
		Hg		bulk	precipitation	2 weeks	
		Cr					EMEP
		Cu					EMEP
		Fe					
		Ni					EMEP
		As					
		Zn					EMEP
	Biogenes	NH_4^+		wet only	precipitation	1 day	
		NO_3^-		wet only	precipitation	1 day	
		total phosphorus					
	Ions	Ca^{2+}		wet only	precipitation	1 day	
		Cl^-		wet only	precipitation	1 day	
		pH		wet only	precipitation	1 day	
		conductivity		wet only	precipitation	1 day	
		SO_4^{2-} (total)		wet only	precipitation	1 day	
		K^+		wet only	precipitation	1 day	
		Mg^{2+}		wet only	precipitation	1 day	
		Na^+		wet only	precipitation	1 day	
	Precipitation	precipitation		bulk/ wet only	precipitation	2 weeks/ 1 day	
	POPs	γ-HCH (lindane)					EMEP
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180					EMEP
	PAHs	BaP					
Air pollutants	Metals	Cd	1 week				EMEP
		Pb					EMEP
		Hg		denuder tube / amalgam tube	air+ aerosol	4 days	
		Cr					EMEP
		Cu					EMEP
		Fe					
		Ni					EMEP
		As					EMEP
		Zn					EMEP
	Biogenes	HNO_3	24 hours	filters	air	1 day	
		NH_3		filters	air	1 day	
		NH_4^+		filters	aerosol	1 day	
		NO_2		absorption tube	air	1 day	
		NO_3^-		filters	aerosol	1 day	
		sum of HNO_3 and NO_3^-		filters	coating + aerosol.	1 day	
		sum of NH_3 and NH_4^+		filters	coating + aerosol.	1 day	
		total phosphorus	1 week				
	POPs	γ-HCH (lindane)	1 week				EMEP
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180	1 week				EMEP
	PAHs	BaP	1 week				EMEP

Table 4.18 Scope of HELCOM monitoring at the Rickleå station (Sweden)

Rickleå (Sweden)							
HELCOM Recommendation 37-38/2 for Air Monitoring Programme for monitoring of the pollution of air and precipitation				**HELCOM PROGRAMME**			**NOTES**
Matrix	**Type of pollutant**	**Parameter** **Mandatory** **Voluntary**	**Maximum collection time**	**Method of measurement/ collection**	**Matrix type**	**Collection frequency**	
Pollutants in precipitation	Metals	Cd	1 month	🟩	🟩	🟩	
		Pb		🟩	🟩	🟩	
		Hg					
		Cr					
		Cu					
		Fe					
		Ni					
		As					
		Zn					
	Biogenes	NH_4^+		bulk	precipitation	1 month	
		NO_3^-		bulk	precipitation	1 month	
		total phosphorus					
	Ions	Ca^{2+}		bulk	precipitation	1 month	
		Cl^-		bulk	precipitation	1 month	
		pH		bulk	precipitation	1 month	
		conductivity		bulk	precipitation	1 month	
		SO_4^{2-} (total)		bulk	precipitation	1 month	
		K^+		bulk	precipitation	1 month	
		Mg^{2+}		bulk	precipitation	1 month	
		Na^+		bulk	precipitation	1 month	
	Precipitation	precipitation		bulk	precipitation	1 month	
	POPs	γ-HCH (lindane)					
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180					
	PAHs	BaP					
Air pollutants	Metals	Cd	1 week				
		Pb					
		Hg					
		Cr					
		Cu					
		Fe					
		Ni					
		As					
		Zn					
	Biogenes	HNO_3	24 hours	🟩	🟩	🟩	
		NH_3		🟩	🟩	🟩	
		NH_4^+		🟩	🟩	🟩	
		NO_2		🟩	🟩	🟩	
		NO_3^-		🟩	🟩	🟩	
		sum of HNO_3 and NO_3^-		🟩	🟩	🟩	
		sum of NH_3 and NH_4^+		🟩	🟩	🟩	
		total phosphorus	1 week				
	POPs	γ-HCH (lindane)	1 week				
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180	1 week				
	PAHs	BaP	1 week				

Germany

In Germany, atmospheric chemistry measurements for assessing atmospheric inputs of substances to the Baltic Sea within HELCOM are carried out at 5 stations.

At the Neuglobsow station, under the HELCOM programme, measurements are conducted in precipitation (Table 4.19). In addition, measurements of pollutants in air are conducted at this station within the EMEP programme. Within the HELCOM programme, all mandatory parameters such as cadmium, lead, ammonium cation, nitrates and precipitation amount are tested in atmospheric precipitation. In addition, voluntary parameters such as chromium, copper, iron, nickel, arsenic, zinc, calcium ion, chlorine ion, potassium ion, magnesium ion, sodium ion, sulphate ion, conductivity and pH are also tested. These tests are carried out using a wet-only collector with a frequency between 1 day and 1 week. In addition, as part of the EMEP programme, mercury analyses are carried out in the precipitation.

Research in the air is performed within the EMEP programme and also includes parameters required by HELCOM, such as: nitric acid, ammonium cation, nitrates and nitrites. In the air, metals such as cadmium, lead, copper, iron, nickel, arsenic and zinc are also identified within the EMEP programme.

At the Schauinsland station, under the HELCOM programme, studies are conducted in precipitation (Table 4.20). In addition, measurements of pollutants in precipitation and air are conducted at this station as part of the EMEP programme. In the framework of HELCOM programme, all obligatory parameters are tested in precipitation such as: cadmium, lead, ammonium cation, nitrates and precipitation amount. In addition, voluntary parameters such as chromium, copper, iron, nickel, arsenic, zinc, calcium ion, chlorine ion, potassium ion, magnesium ion, sodium ion, sulphate ion, conductivity and pH are also tested. These tests are carried out using a wet-only collector with a frequency between 1 day and 1 week. Mercury studies in precipitation are carried out as part of the EMEP programme.

Air testing is performed within the EMEP programme and also includes parameters required by HELCOM such as: ammonia, ammonium, nitrates and nitrites. In addition, metals such as cadmium, lead, copper, iron, nickel, arsenic and zinc are tested in the air within the EMEP programme.

At the Schmücke station within the HELCOM programme, tests are performed in precipitation (Table 4.21). In addition, measurements of pollutants in precipitation and air are carried out at this station as part of the EMEP programme. Under HELCOM, all mandatory parameters are tested in precipitation: cadmium, lead, ammonium cation, nitrate and precipitation amount. In addition, the following are carried out voluntary parameters such as chromium, copper, iron, nickel, arsenic, zinc, calcium ion, chlorine ion, potassium ion, magnesium ion, sodium ion, sulphate ion, conductivity and pH. These tests are performed using a wet-only collector with a frequency of 1 week. Mercury studies in precipitation are carried out as part of the EMEP programme.

Airborne surveys are conducted as part of the EMEP programme and include parameters required by HELCOM, such as: ammonia, ammonium, nitrates and nitrites. In addition, metals: cadmium, lead, copper, iron, nickel, arsenic and zinc are tested in the air within the EMEP programme.

At the Waldhof station, within the HELCOM programme, tests are performed in precipitation (Table 4.22). At this station measurements of pollutants in precipitation and air are also carried out within the EMEP programme. Under HELCOM, all mandatory parameters are measured in precipitation: cadmium, lead, ammonium cation, nitrate and precipitation amount. In addition, the following voluntary parameters are subject to measurements: chromium, copper, iron, nickel, arsenic, zinc, calcium ion, chlorine ion, potassium ion, magnesium ion, sodium ion, sulphate ion, conductivity and pH. These tests are performed using a wet-only collector with a frequency between 1 day and 1 week. Testing of parameters such as: mercury, γ-HCH (lindane) and congeners 28, 52, 101, 118, 138, 153, 180 in precipitation are performed within the framework of the EMEP programme.

In air, research is conducted as part of the EMEP programme and also include parameters required by HELCOM, such as ammonia, ammonium cation, nitrate and nitrites. In addition, metals such as cadmium, lead, copper, iron, nickel, arsenic and zinc are also tested in the air within the EMEP programme.

At the Zingst station, within the HELCOM programme, studies are performed in precipitation and in air (Table 4.23). In addition, EMEP surveys are also conducted at the station in precipitation. Research within HELCOM, in atmospheric precipitation include all obligatory parameters: cadmium, lead, ammonium cation, nitrates and precipitation amount. In addition, tests are also carried out for voluntary parameters such as mercury, chromium, copper, iron, nickel, arsenic, zinc, calcium ion, chlorine ion, potassium ion, magnesium ion, sodium ion, sulphate ion, conductivity and pH. These tests are performed using a wet-only collector with a frequency between 1 week and 1 month. Testing of parameters such as mercury, γ-HCH (lindane) and congeners 28, 52, 101, 118, 138, 153, 180 in precipitation is conducted within the framework of the EMEP programme.

The following mandatory parameters are measured in the air under HELCOM: ammonia, ammonium cation, nitrates and nitrites, and the sum of nitric acid and nitrates as well as ammonia and ammonium. Among the voluntary parameters in the air, the following metals are also studied: cadmium, lead, copper, iron, nickel, arsenic and zinc and benzo(a)pyrene. Testing of parameters in the air is performed using a low volume sampler (LVS), denuder and photolytic chemiluminescence with frequencies ranging from 1 hour to 1 month.

Table 4.19 Scope of HELCOM monitoring carried out at the Neuglobsow station (Germany)

Neuglobsow (Germany)							
HELCOM Recommendation 37-38/2 for Air Monitoring Programme for monitoring of the pollution of air and precipitation				**HELCOM PROGRAMME**			**NOTES**
Matrix	**Type of pollutant**	**Parameter** **Mandatory** **Voluntary**	**Maximum collection time**	**Method of measurement/ collection**	**Matrix type**	**Collection frequency**	
Pollutants in precipitation	Metals	Cd	1 month	wet only	precipitation	1 week	
		Pb		wet only	precipitation	1 week	

		Hg					
		Cr		wet only	precipitation	1 week	
		Cu		wet only	precipitation	1 week	
		Fe		wet only	precipitation	1 week	
		Ni		wet only	precipitation	1 week	
		As		wet only	precipitation	1 week	
		Zn		wet only	precipitation	1 week	
	Biogenes	NH_4^+		wet only	precipitation	1 day	
		NO_3^-		wet only	precipitation	1 day	
		total phosphorus					
	Ions	Ca^{2+}		wet only	precipitation	1 day	
		Cl^-		wet only	precipitation	1 day	
		pH		wet only	precipitation	1 day	
		conductivity		wet only	precipitation	1 day	
		SO_4^{2-} (total)		wet only	precipitation	1 day	
		K^+		wet only	precipitation	1 day	
		Mg^{2+}		wet only	precipitation	1 day	
		Na^+		wet only	precipitation	1 day	
	Precipitation	precipitation		wet only	precipitation	1 week/1 day	
	POPs	γ-HCH (lindane)					
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180					
	PAHs	BaP					
Air pollutants	Metals	Cd	1 week				EMEP
		Pb					EMEP
		Hg					
		Cr					
		Cu					EMEP
		Fe					EMEP
		Ni					EMEP
		As					EMEP
		Zn					EMEP
	Biogenes	HNO_3	24 hours				EMEP
		NH_3					
		NH_4^+					EMEP
		NO_2					EMEP
		NO_3^-					EMEP
		sum of HNO_3 and NO_3^-					
		sum of NH_3 and NH_4^+					
		total phosphorus	1 week				
	POPs	γ-HCH (lindane)	1 week				
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180	1 week				
	PAHs	BaP	1 week				

Table 4.20 Scope of HELCOM monitoring carried out at the Schauinsland station (Germany)

Schauinsland (Germany)							
HELCOM Recommendation 37-38/2 for Air Monitoring Programme for monitoring of the pollution of air and precipitation				**HELCOM PROGRAMME**			**NOTES**
Matrix	**Type of pollutant**	**Parameter** **Mandatory** **Voluntary**	**Maximum collection time**	**Method of measurement/ collection**	**Matrix type**	**Collection frequency**	
Pollutants in precipitation	Metals	Cd	1 month	wet only	precipitation	1 week	
		Pb		wet only	precipitation	1 week	
		Hg					EMEP
		Cr		wet only	precipitation	1 week	
		Cu		wet only	precipitation	1 week	
		Fe		wet only	precipitation	1 week	
		Ni		wet only	precipitation	1 week	
		As		wet only	precipitation	1 week	
		Zn		wet only	precipitation	1 week	
	Biogenes	NH_4^+		wet only	precipitation	1 day	
		NO_3^-		wet only	precipitation	1 day	
		total phosphorus					
	Ions	Ca^{2+}		wet only	precipitation	1 day	
		Cl^-		wet only	precipitation	1 day	
		pH		wet only	precipitation	1 day	
		conductivity		wet only	precipitation	1 day	
		SO_4^{2-} (total)		wet only	precipitation	1 day	
		K^+		wet only	precipitation	1 day	
		Mg^{2+}		wet only	precipitation	1 day	
		Na^+		wet only	precipitation	1 day	
	Precipitation	precipitation		wet only	precipitation	1 day/1 week	
	POPs	γ-HCH (lindane)					
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180					
	PAHs	BaP					
Air pollutants	Metals	Cd	1 week				EMEP
		Pb					EMEP
		Hg					
		Cr					
		Cu					EMEP
		Fe					EMEP
		Ni					EMEP
		As					EMEP
		Zn					EMEP
	Biogenes	HNO_3	24 hours				
		NH_3					EMEP
		NH_4^+					EMEP
		NO_2					EMEP
		NO_3^-					EMEP
		sum of HNO_3 and NO_3^-					
		sum of NH_3 and NH_4^+					
		total phosphorus	1 week				
	POPs	γ-HCH (lindane)	1 week				
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180	1 week				
	PAHs	BaP	1 week				EMEP

Table 4.21 Scope of HELCOM monitoring carried out at the Schmücke station (Germany)

Schmücke (Germany)							
HELCOM Recommendation 37-38/2 for Air Monitoring Programme for monitoring of the pollution of air and precipitation				**HELCOM PROGRAMME**			**NOTES**
Matrix	**Type of pollutant**	**Parameter** **Mandatory** **Voluntary**	**Maximum collection time**	**Method of measurement/ collection**	**Matrix type**	**Collection frequency**	
Pollutants in precipitation	Metals	Cd	1 month	wet only	precipitation	1 week	
		Pb		wet only	precipitation	1 week	
		Hg					EMEP
		Cr		wet only	precipitation	1 week	
		Cu		wet only	precipitation	1 week	
		Fe		wet only	precipitation	1 week	
		Ni		wet only	precipitation	1 week	
		As		wet only	precipitation	1 week	
		Zn		wet only	precipitation	1 week	
	Biogenes	NH_4^+		wet only	precipitation	1 week	
		NO_3^-		wet only	precipitation	1 week	
		total phosphorus					
	Ions	Ca^{2+}		wet only	precipitation	1 week	
		Cl^-		wet only	precipitation	1 week	
		pH		wet only	precipitation	1 week	
		conductivity		wet only	precipitation	1 week	
		SO_4^{2-} (total)		wet only	precipitation	1 week	
		K^+		wet only	precipitation	1 week	
		Mg^{2+}		wet only	precipitation	1 week	
		Na^+		wet only	precipitation	1 week	
	Precipitation	precipitation		wet only	precipitation	1 week	
	POPs	γ-HCH (lindane)					
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180					
	PAHs	BaP					
Air pollutants	Metals	Cd	1 week				EMEP
		Pb					EMEP
		Hg					
		Cr					
		Cu					EMEP
		Fe					EMEP
		Ni					EMEP
		As					EMEP
		Zn					EMEP
	Biogenes	HNO_3	24 hours				
		NH_3					EMEP
		NH_4^+					EMEP
		NO_2					EMEP
		NO_3^-					EMEP
		sum of HNO_3 and NO_3^-					
		sum of NH_3 and NH_4^+					
		total phosphorus	1 week				
	POPs	γ-HCH (lindane)	1 week				
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180	1 week				
	PAHs	BaP	1 week				EMEP

Table 4.22 Scope of HELCOM monitoring carried out at the Waldhof station (Germany)

Waldhof (Germany)							
HELCOM Recommendation 37-38/2 for Air Monitoring Programme for monitoring of the pollution of air and precipitation				**HELCOM PROGRAMME**			**NOTES**
Matrix	**Type of pollutant**	**Parameter** 🟩 **Mandatory** **Voluntary**	**Maximum collection time**	**Method of measurement/ collection**	**Matrix type**	**Collection frequency**	
Pollutants in precipitation	Metals	Cd	1 month	wet only	precipitation	1 week	
		Pb		wet only	precipitation	1 week	
		Hg					EMEP
		Cr		wet only	precipitation	1 week	
		Cu		wet only	precipitation	1 week	
		Fe		wet only	precipitation	1 week	
		Ni		wet only	precipitation	1 week	
		As		wet only	precipitation	1 week	
		Zn		wet only	precipitation	1 week	
	Biogenes	NH_4^+		wet only	precipitation	1 day	
		NO_3^-		wet only	precipitation	1 day	
		total phosphorus					
	Ions	Ca^{2+}		wet only	precipitation	1 day	
		Cl^-		wet only	precipitation	1 day	
		pH		wet only	precipitation	1 day	
		conductivity		wet only	precipitation	1 day	
		SO_4^{2-} (total)		wet only	precipitation	1 day	
		K^+		wet only	precipitation	1 day	
		Mg^{2+}		wet only	precipitation	1 day	
		Na^+		wet only	precipitation	1 day	
	Precipitation	precipitation		wet only	precipitation	1 day/1 week	
	POPs	γ-HCH (lindane)					EMEP
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180					EMEP
	PAHs	BaP					EMEP
Air pollutants	Metals	Cd	1 week				EMEP
		Pb					EMEP
		Hg					
		Cr					
		Cu					EMEP
		Fe					EMEP
		Ni					EMEP
		As					EMEP
		Zn					EMEP
	Biogenes	HNO_3	24 hours	🟩	🟩	🟩	
		NH_3		🟩	🟩	🟩	EMEP
		NH_4^+		🟩	🟩	🟩	EMEP
		NO_2		🟩	🟩	🟩	EMEP
		NO_3^-		🟩	🟩	🟩	EMEP
		sum of HNO_3 and NO_3^-		🟩	🟩	🟩	
		sum of NH_3 and NH_4^+		🟩	🟩	🟩	
		total phosphorus	1 week				
	POPs	γ-HCH (lindane)	1 week				
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180	1 week				
	PAHs	BaP	1 week				EMEP

Table 4.23 Scope of HELCOM monitoring carried out at Zingst station (Germany)

Zingst (Germany)							
HELCOM Recommendation 37-38/2 for Air Monitoring Programme for monitoring of the pollution of air and precipitation				**HELCOM PROGRAMME**			**NOTES**
Matrix	**Type of pollutant**	**Parameter** **Mandatory** **Voluntary**	**Maximum collection time**	**Method of measurement/ collection**	**Matrix type**	**Collection frequency**	
Pollutants in precipitation	Metals	Cd	1 month	wet only	precipitation	1 week	
		Pb		wet only	precipitation	1 week	
		Hg		wet only	precipitation	1 month	
		Cr		wet only	precipitation	1 week	
		Cu		wet only	precipitation	1 week	
		Fe		wet only	precipitation	1 week	
		Ni		wet only	precipitation	1 week	
		As		wet only	precipitation	1 week	
		Zn		wet only	precipitation	1 week	
	Biogenes	NH_4^+		wet only	precipitation	1 week	
		NO_3^-		wet only	precipitation	1 week	
		total phosphorus					
	Ions	Ca^{2+}		wet only	precipitation	1 week	
		Cl^-		wet only	precipitation	1 week	
		pH		wet only	precipitation	1 week	
		conductivity		wet only	precipitation	1 week	
		SO_4^{2-} (total)		wet only	precipitation	1 week	
		K^+		wet only	precipitation	1 week	
		Mg^{2+}		wet only	precipitation	1 week	
		Na^+		wet only	precipitation	1 week	
	Precipitation	precipitation		wet only	precipitation/ total precipitation	1 week/	
	POPs	γ-HCH (lindane)					EMEP
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180					EMEP
	PAHs	BaP		wet only	total precipitation	1 month	
Air pollutants	Metals	Cd	1 week	low volume sampler	pm10	1 week	
		Pb		low volume sampler	pm10	1 week	
		Hg					
		Cr					
		Cu		low volume sampler	pm10	1 week	
		Fe		low volume sampler	pm10	1 week	
		Ni		low volume sampler	pm10	1 week	
		As		low volume sampler	pm10	1 week	
		Zn		low volume sampler	pm10	1 week	
	Biogenes	HNO_3	24 hours				
		NH_3		denuder	air	1 week	
		NH_4^+		low volume sampler	pm25	6 days	
		NO_2		photolytic chemiluminescence	air	1 hour	
		NO_3^-		low volume sampler	pm25	6 days	
		sum of HNO_3 and NO_3^-					
		sum of NH_3 and NH_4^+					
		total phosphorus	1 week				
	POPs	γ-HCH (lindane)	1 week				
	PCB	Congeners 28, 52, 101, 118, 138, 153, 180	1 week				
	PAHs	BaP	1 week	high volume sampler	air +pm10	1 month	

Monitoring of precipitation chemistry in selected countries neighbouring Poland

Slovakia

In Slovakia, air quality monitoring, including precipitation chemistry monitoring, is carried out by the Slovak Hydrometeorological Institute – SHMI.

Precipitation quality is monitored at four EMEP stations: Chopok, Starina, Topoľníky, Stará Lesná and at the Bratislava, Jeséniova station, which is an urban background station used for comparison with values measured at regional stations.

Precipitation quality (pH, conductivity, sulphates, nitrates, chlorides, ammonia and alkaline ions) is analysed from samples taken at EMEP stations operating in the daily (Chopok, Starina) and weekly (Topoľníky, Stará Lesná) sampling modes. At the station in Bratislava, Jeséniova precipitation samples are collected monthly. The results of analyses are daily or weekly average values, depending on the sampling interval. Sampling for determination of heavy metals is performed on a monthly basis, except at the EMEP Starina station, where the sampling interval is one week. For precipitation sampling, precipitation collectors of two types are used: “wet only” for collecting wet precipitation only and “bulk” for collecting dry and wet precipitation. Wet-only sampling is the basis for calculating and assessing wet deposition. Sampling with the “bulk” method is carried out at the Chopok station, where precipitation sampling is carried out into an open bucket due to the location of the station and unfavourable weather conditions occurring at this location.

The results of precipitation chemistry measurements, together with the results of air quality monitoring, are published in annual reports, available at: https://www.shmu.sk/en/?page=997

Table 4.24 provides information on the stations, indicators and parameters studied and the frequency of sampling and measurements.

Table 4.24 List of precipitation chemistry monitoring measurement stations in Slovakia [Own work based on Appendix A of SHMU Report, 2021]

Station name	**Stara Lesna**	**Starina**	**Chopak**	**Topolniki**	**Bratislava, Jeseniova**
Longitude	20°17’22’’E	22°15’36’’E	19°35’21’’E	17°51’37’’E	17°06’22’’E
Latitude	49°09’05’’N	49°02’34’’N	48°56’37’’N	47°57’34’’N	48°10’05’’N
Altitude	808 m	345 m	2008 m	113 m	287 m
Method of collection	wet only	wet only	bulk	wet only	wet only bulk
Programme	EMEP, GAW/WMO	EMEP, GAW/WMO	EMEP, GAW/WMO	EMEP, GAW/WMO	ŠÚ SR Urban background
Component/ parameter	Intake frequency	Intake frequency	Intake frequency	Intake frequency	Intake frequency
NH_4^+					monthly
NO_3^-					

Station name	Stara Lesna	Starina	Chopak	Topolniki	Bratislava, Jeseniova
SO_4^{2-}	weekly	daily	daily	weekly	
Cl^-					
Na^+					
K^+					
Ca^{2+}					
Mg^{2+}					
conductivity					
pH					
Cu	monthly	weekly	monthly	monthly	monthly
Cr					
Pb					
Ni					
Cd					
As					
Zn					

Czech Republic

In the Czech Republic, the measurement of the chemical composition of precipitation is carried out by several institutions: Czech Hydrometeorological Institute (CHMU), Czech Geological Survey (CGS), Forestry and Hunting Research Institute (VULHM), Institute of Hydrobiology of the Academy of Sciences of the Czech Republic (HBÚ AV CR), Institute of Hydrobiology (UH AV CR), Institute for Global Change Research – CzechGlobe (UVGZ AV CR) and Institute of Geology (GLÚ AS CR). In total, the precipitation chemistry monitoring system consists of dozens of stations. In 2020, data were collected from 39 locations: CHMU – 14 stations; CGS – 10 stations; VULHM – 10 stations; HBU AV CR – 2 stations; UH AV CR, UVGZ AV CR and GLU AV CR – 1 station each. 3 stations belonging to CHMU are EMEP sites: Kosetice, Churanov and Svratouch, the others are part of international programmes: GAW/WMO, ICP Forests and national programmes for atmospheric deposition monitoring and geochemical monitoring.

At CHMU stations, precipitation measurements are made using the “wet only” method (wet precipitation) and are collected on a weekly basis. The exception is the National Atmospheric Observatory in Kosetice, where precipitation is collected by the “wet only”, “bulk” (dry and wet precipitation) and “throughfall” methods daily, weekly and monthly. At the stations belonging to other Institutions, measurements are made on a monthly basis or irregularly with the “bulk” and “throughfall” methods. Heavy metal analyses are performed at all stations. The map below (Figure 4.25) shows the network of precipitation chemistry monitoring stations in the Czech Republic. Table 4.25 shows the measurement range of the 3 EMEP stations. Table 4.26 shows the measurement range of the other stations studying precipitation quality in the Czech Republic.

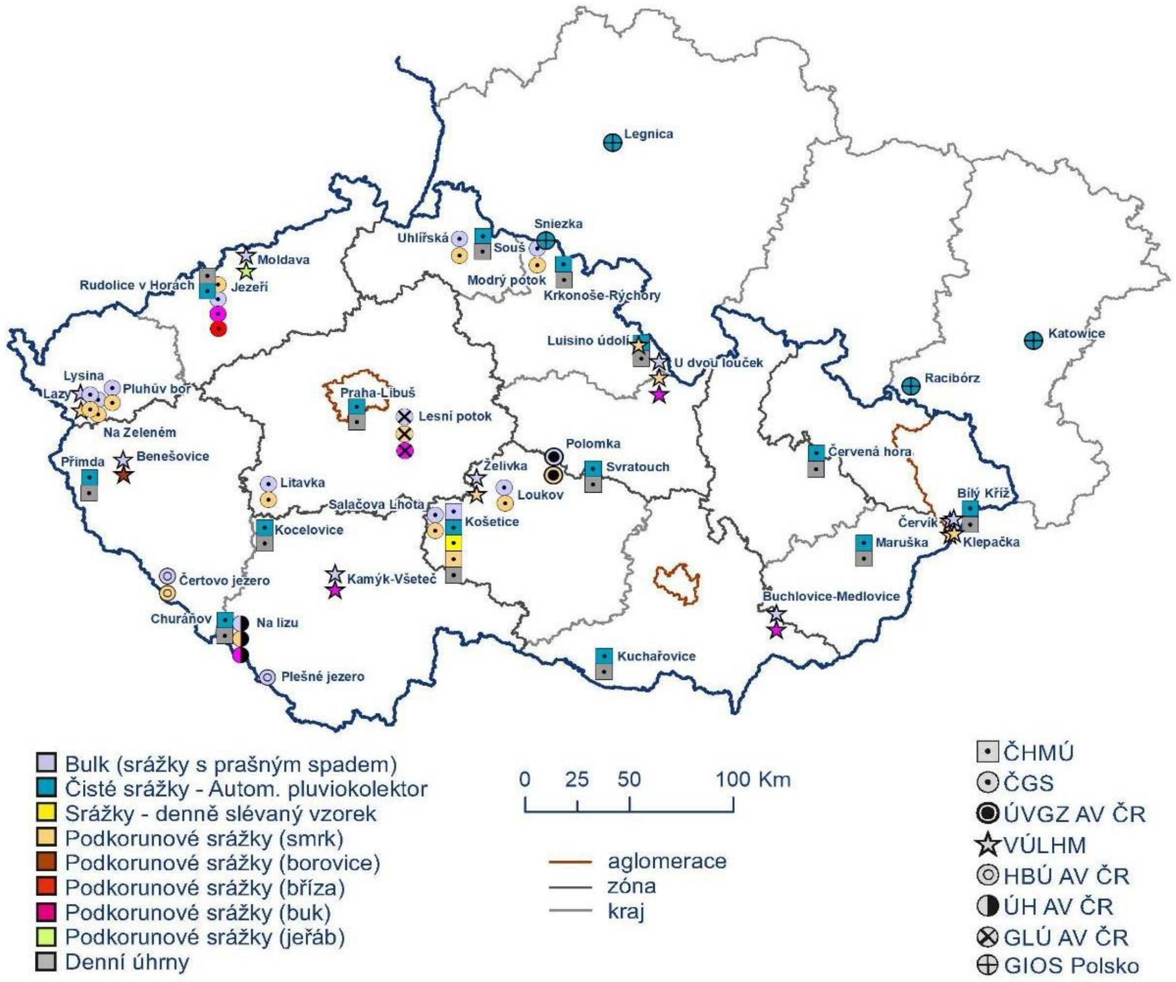


Figure 4.25 Networks of precipitation quality and atmospheric deposition monitoring stations in the Czech Republic, 2020

Table 4.25 Precipitation research stations in the Czech Republic participating in EMEP [own work based on CHMU data: https://www.chmi.cz/files/portal/docs/uoco/web_generator/locality/precipitation_locality/index_GB.html

Station name	**Kosetice (NOAK)**			**Churanov**	**Svratouch**
Longitude	15° 4’ 49.782’’E			13° 36’ 53.285’’E	16° 2’ 3.109’’E
Latitude	49° 34’ 24.825’’N			49° 4’ 6.368’’N	49° 44’ 6.304’’N
Altitude	535 m			1118 m	735 m
Method of collection	wet only	bulk	throughfall	wet only	wet only
Programme	EMEP, GAW/WMO, ICP IM			EMEP	EMEP, GAW/WMO
Component/ parameter	Collection frequency			Collection frequency	Collection frequency

Station name	**Kosetice (NOAK)**			**Churanov**	**Svratouch**
pH	day	month	month	7 days	7 days
Conductivity					
Na^+					
K^+					
NH_4^+					
Mg^{2+}					
Ca^{2+}					
Fe		-	-		
Zn		month	month		
Mn					
Pb					
Cd					
Ni					
As					
Cu		-	-		
Co		-	-		
Cr		-	-		
V		-	-		
Se		-	-		
F^-		month	month		
Cl^-					
NO_3^-					
SO_4^{2-}					
Hg	-	7 days	-	-	-
Sr	-	month	month	-	-
DOC	-			-	-
P-sum	-			-	-
DN	-			-	-

Explanations:

DOC – dissolved organic carbon,
DN – dissolved nitrogen.

Table 4.26 Precipitation research stations in the Czech Republic participating in the ICP Forests, GAW/WMO and national programmes [own work based on CHMU data:

https://www.chmi.cz/files/portal/docs/uoco/web_generator/locality/precipitation_locality/index_GB.html

Station name	Praha – Libus	Lesni Potok		Litavka 1	Litavka 2	Kamyk-Vsetec	
Longitude	14° 26’ 49.401’’E	14° 46’ 40’’E		13° 52’ 7.990’’E	13° 52’ 10.201’’E	14° 18´ 0.001’’E	
Latitude	50° 0’ 28.400’’N	49° 58’ 35.007’’N		49° 39’ 29.476’’N	49° 39’	49° 13’ 47.998’’N	
Altitude.	301 m	400 m		700 m	710 m	593 m	
Station owner	CHMU	AV CR		CGS	CGS	VULHM	
Measurement programme	monitoring of atmospheric deposition	geochemical monitoring			geochemical monitoring	ICP Forests	
Method of collection	wet only	bulk	through-fall	bulk	throughfall	bulk	through-fall
Component/	Collection frequency						
pH	weekly	monthly	monthly	monthly	monthly	monthly	monthly
Conductivity							
Na^+							
K^+							
NH_4^+							
Mg^{2+}							
Ca^{2+}							
Fe							
Zn							
Mn							
Pb						-	-
Cd						-	-
Ni						-	-
As						-	-
Cu		-	-	-		monthly	monthly
Co		-	-	-		-	-
Cr		-	-	-		-	-
V		-	-	-		-	-
Se		-	-	-		-	-
F^-		monthly	monthly	monthly	monthly	monthly	monthly
Cl^-							
NO_3^-							
SO_4^{2-}						monthly	monthly
Hg	-	-	-	-	-	-	-
Sr	-		monthly			-	-
DOC	-					monthly	monthly

P-sum	-	monthly		monthly	monthly	-	-
DN	-					-	-
Al.	-	-	-	-	-	monthly	monthly
N-sum	-	-	-	-	-		
P_PO4	-	-	-	-	-		
alkalinity	-	-	-	-	-		
Cox	-	-	-	-	-	-	-

Station name	On a lick		Plesne Jezero 1	Plesne Jezero 2	Plesne Jezero 3	Kocelovice
Longitude	13° 41’ 3.001’’E		13° 52’ 15.000’’E	13° 52’ 4.800’’E	13° 51’ 16.999’’E	13° 50’ 17.642’’E
Latitude	49° 4’ 0.999’’N		48° 47’ 34.001’’N	48° 46’ 30.994’’N	48° 46’	49° 28’ 2.076’’N
Altitude	828 m		1087 m	1122 m	1334 m	519 m
Station owner	AV CR		HBU AV CR	HBU AV CR	HBU AV CR	CHMU
Measurement programme	Geochemical monitoring		GAW/WMO	GAW/WMO		Monitoring of atmospheric deposition
Method of collection	bulk	throughfall	bulk	bulk	bulk	wet only
Component/ parameter	Collection frequency					
pH	monthly	monthly	irregular	irregular	Irregular	weekly
Conductivity						
Na$^+$						
K$^+$						
NH$_4^+$						
Mg^{2+}						
Ca^{2+}						
Fe						
Zn			-	-	-	
Mn			irregular	irregular	irregular	
Pb			-	-	-	
Cd			-	-	-	
Ni			-	-	-	
As			-	-	-	
Cu	-	-	-	-	-	
Co	-	-	-	-	-	
Cr	-	-	-	-	-	
V	-	-	-	-	-	
Se	-	-	-	-	-	
F$^-$						

Cl^-	monthly	monthly	irregular		irregular	
NO_3^-				irregular		
SO_4^{2-}						
Hg	-	-	-	-	-	-
Sr	monthly	monthly	-	-	-	-
DOC			irregular	irregular	Irregular	-
P-sum			-	-	-	-
DN			-	-	-	-
Al	-	-	Irregular	irregular	irregular	-
N-sum	-	-	-	-	-	-
P_PO4	-	-	-	-	-	-
alkalinity	-	-	-	-	-	-
Cox	-	-	-	-	-	-

Station name	Certovo jezero 1	Certovo jezero 2	Benesonice		Primda	Lazy	
Longitude	13° 11’ 56.000’’E	13° 11’ 57.002’’E	12° 51’ 41.001’’E		12° 40’ 40.383’’E	12° 37’ 30.000’’E	
Latitude	49° 10’ 31.000’’N	49° 9’ 45.997’’N	49° 44’ 30.996’’N		49° 40’	50° 2’ 35.992’’N	
Altitude	1180 m	1057 m	535 m		740 m	875 m	
Station owner	HBU AV CR	HBU AV CR	VULHM		CHMU	VULHM	
Measurement programme	GAW/WMO	GAW/WMO	ICP Forests		Monitoring of atmospheric deposition	ICP Forests	
Method of collection	bulk	throughfall	bulk	through-fall	wet only	bulk	through-fall
Component/	Collection frequency						
pH	irregular	irregular			weekly		
Conductivity							
Na^+							
K^+			monthly	monthly			
NH_4^+						monthly	monthly
Mg^{2+}							
Ca^{2+}							
Fe							
Zn	-	-					
Mn	irregular	irregular					
Pb	-	-	-	-		-	-
Cd	-	-	-	-		-	-
Ni	-	-	-	-		-	-
As	-	-	-	-		-	-

Cu	-	-	monthly	monthly		monthly	monthly
Co	-	-	-	-		-	-
Cr	-	-	-	-		-	-
V	-	-	-	-		-	-
Se	-	-	-	-		-	-
F^-	irregularly					monthly	monthly
Cl^-							
NO_3^-		irregularly					
SO_4^{2-}			monthly	monthly			
Hg	-	-	-	-	-	-	-
Sr	-	-	-	-	-	-	-
DOC	irregularly	irregularly	monthly	monthly	-	monthly	monthly
P-sum	-	-	-	-	-	-	-
DN	-	-	-	-	-	-	-
Al	irregularly	irregularly	monthly	monthly	-		monthly
N-sum	-	-			-	monthly	
P_PO4	-	-			-		
alkalinity	-	-			-		
Cox	-	-	-	-	-	-	-

Station name	Lysine 1	Lysine 2	Na zelenem 1	Na zelenem 2	Pluhuv boron 1
Longitude	12° 40’ 14.002’’E	12° 40’ 14.002’’E	12° 42’ 32.000’’E	12° 42’ 32.399’’E	12° 47’ 21.998’’E
Latitude	50° 2’ 7.002’’N	50° 2’ 7.002’’N	49° 59’ 46.006’’N	49° 59’	50° 3’ 47.005’’N
Altitude	867 m	836 m	773 m	750 m	753 m
Station owner	CGS	CGS	CGS	CGS	CGS
Measurement programme	geochemical monitoring	geochemical monitoring			geochemical monitoring
Method of collection	bulk	throughfall	bulk	throughfall	bulk
Component/	Collection frequency				
pH	monthly	monthly	monthly	monthly	monthly
Conductivity					
Na^+					
K^+					
NH_4^+					
Mg^{2+}					
Ca^{2+}					
Fe					
Zn					

Mn					
Pb					
Cd					
Ni					
As					
Cu	-		-	-	-
Co	-		-	-	-
Cr	-		-	-	-
V	-		-	-	-
Se	-		-	-	-
F^-	monthly	monthly			
Cl^-			monthly	monthly	monthly
NO_3^-					
SO_4^{2-}					
Hg	-	-	-	-	-
Sr	monthly	monthly	monthly	monthly	monthly
DOC					
P-sum					
DN					
Al.	-	-	-	-	-
N-sum	-	-	-	-	-
P_PO4	-	-	-	-	-
alkalinity	-	-	-	-	-
Cox	-	-	-	-	-

Station name	Pluhuv boron 2	Jezeri		Rudolice v Hor.	Sous	Moldava	
Longitude	12° 47’ 21.998’’E	13° 28’ 42.001’’E		13° 25’ 10.222’’E	15° 19’ 10.859’’E	13° 39’ 23.485’’E	
Latitude	50° 3’ 47.005’’N	50° 32’ 54.998’’N		50° 34’ 47.402’’N	50° 47’	50° 43’ 11.098’’N	
Altitude.	714 m	820 m		840 m	771 m	805 m	
Station owner	CGS	CGS		CHMU	CHMU	VULHM	
Measurement programme	geochemical monitoring	geochemical monitoring		Monitoring of atmospheric deposition	Monitoring of atmospheric deposition		
Method of collection	throughfall	bulk	through-fall	Wet only	Wet only	bulk	through-fall
Component/	Intake frequency						
pH							
Conductivity							
Na^+							

K^+	monthly	monthly	monthly	weekly	weekly	monthly	monthly
NH_4^+							
Mg^{2+}							
Ca^{2+}							
Fe							
Zn							
Mn							
Pb						-	-
Cd						-	-
Ni						-	-
As						-	-
Cu	-	-	-			monthly	monthly
Co	-	-	-			-	-
Cr	-	-	-			-	-
V	-	-	-			-	-
Se	-	-	-			-	-
F^-	monthly	monthly	monthly			monthly	monthly
Cl^-							
NO_3^-							
SO_4^{2-}							
Hg	-	-	-	-	-	-	-
Sr	monthly	monthly	monthly	-	-	-	-
DOC				-	-	monthly	monthly
P-sum				-	-		
DN				-	-		
Al.	-	-	-	-	-		
N-sum	-	-	-	-	-		
P_PO4	-	-	-	-	-		
alkalinity	-	-	-	-	-		
Cox	-	-	-	-	-		
Station name	Uhlirska	Luisino udoli		Luisino udoli	U dvou Loucek	Krkonose-Rychory	
Longitude	15° 8’ 53.997’’E	16° 23’ 18.862’’E		16° 23’ 26.998’’E	16° 29’ 56.004’’E	15° 51’ 0.324’’E	
Latitude	50° 49’ 31.005’’N	50° 17’ 13.292’’N		50° 17’ 36.995’’N	50° 13’	50° 39’ 37.579’’N	
Altitude	780 m	875 m		940 m	880 m	1001 m	
Station owner	CGS	CHMU		VULHM	VULHM	CHMU	
Measurement programme	geochemical monitoring	Monitoring of atmospheric deposition		ICP Forests	Geochemical monitoring	Monitoring of atmospheric deposition	

Method of collection	bulk	through-fall	Wet only	throughfall	bulk	through-fall	Wet only
Component/	Collection frequency						
pH	monthly	monthly	weekly	monthly	month-ly	month-ly	weekly
Conductivity							
Na^+							
K^+							
NH_4^+							
Mg^{2+}							
Ca^{2+}							
Fe					-	-	
Zn					month-ly	month-ly	
Mn							
Pb				-			
Cd				-			
Ni				-			
As				-			
Cu	-	-		monthly	-	-	
Co	-	-		-	-	-	
Cr	-	-		-	-	-	
V	-	-		-	-	-	
Se	-	-		-	-	-	
F^-	monthly	monthly		monthly	month-ly	month-ly	
Cl^-							
NO_3^-							
SO_4^{2-}							
Hg	-	-	-	-	-	-	-
Sr	monthly	monthly	-	-	month-ly	month-ly	-
DOC			-	monthly			-
P-sum			-	-			-
DN			-	-			-
Al	-	-	-	monthly	-	-	-
N-sum	-	-	-		-	-	-
P_PO4	-	-	-		-	-	-
alkalinity	-	-	-	monthly	-	-	-
Cox	-	-	-	-	-	-	-
Station name	Modry potok		Polomka	Salacova Lhota	Loukov		Zelivka
Longitude	15° 42’ 48.998’’E		15° 46’ 10.000’’E	15° 0’ 0.000’’E	15° 20’ 46.001’’E		15° 13’ 46.999’’E

Latitude	50° 42’ 47.999’’N		49° 47’ 29.002’’N		49° 32’ 0.000’’N		49° 38’		49° 40’ 31.000’’N	
Altitude	1010 m		512 m		557 m		500 m		440 m	
Station owner	CGS		CGS		CGS		CGS		VOULHM	
Measurement programme	Geochemical monitoring		Geochemical monitoring		Geochemical monitoring		Geochemical monitoring		ICP Forests	
Method of collection	bulk	through-fall	bulk	through-fall	bulk	through-fall	bulk	through-fall	bulk	through-fall
Component/	Collection frequency									
pH	monthly	monthly	monthly	monthly	monthly	monthly	monthly	monthly	monthly	monthly
Conductivity										
Na^+										
K^+										
NH_4^+										
Mg^{2+}										
Ca^{2+}										
Fe	-	-	-	-	-	-	-	-		
Zn	monthly	monthly	monthly	monthly	monthly	monthly	monthly	monthly		
Mn										
Pb									-	-
Cd									-	-
Ni									-	-
As									-	-
Cu	-	-	-	-	-	-	-	-	monthly	monthly
Co	-	-	-	-	-	-	-	-	-	-
Cr	-	-	-	-	-	-	-	-	-	-
V	-	-	-	-	-	-	-	-	-	-
Se	-	-	-	-	-	-	-	-	-	-
F^-	monthly	monthly	monthly	monthly	monthly	monthly	monthly	monthly	monthly	monthly
Cl^-										
NO_3^-										
SO_4^{2-}										
Hg	-	-	-	-	-	-	-	-	-	-
Sr	monthly	monthly	monthly	monthly	monthly	monthly	monthly	monthly	-	-
DOC									monthly	monthly
P-sum									-	-
DN									-	-
Al	-	-	-	-	-	-	-	-	-	-
N-sum	-	-	-	-	-	-	-	-	monthly	monthly
P_PO4	-	-	-	-	-	-	-	-		

alkalinity	-	-	-	-	-	-	-	-		
Cox	-	-	-	-	-	-	-	-		

Station name	Kucharovice	Buchlovice-Med.		Maruska	Bily Kriz	Cervik	
Longitude	16° 5’ 8.709’’E	17° 16’ 20.997’’E		17° 49’ 39.925’’E	18° 32’ 18.819’’E	18° 23’ 0.000’’E	
Latitude	48° 52’ 52.810’’N	49° 4’ 20.005’’N		49° 21’ 56.629’’N	49° 30’ 9.393’’N	49° 27’ 0.003’’N	
Altitude	334 m	350 m		664 m	890 m	640 m	
Station owner	CHMU	VULHM		CHMU	CHMU	VULHM	
Measurement programme	Monitoring of atmospheric deposition	ICP Forests			Monitoring of atmospheric deposition	Geochemical monitoring	
Method of collection	wet only	bulk	through-fall	wet only	wet only	bulk	through-fall
Component/	Collection frequency						
pH	weekly	monthly	monthly	weekly	weekly	monthly	monthly
Conductivity							
Na^+							
K^+							
NH_4^+							
Mg^{2+}							
Ca^{2+}							
Fe						-	-
Zn						monthly	monthly
Mn							
Pb		-	-				
Cd		-	-				
Ni		-	-				
As		-	-				
Cu		monthly	monthly			-	-
Co		-	-			-	-
Cr		-	-			-	-
V		-	-			-	-
Se		-	-			-	-
F^-		monthly	monthly			monthly	monthly
Cl^-							
NO_3^-							
SO_4^{2-}						monthly	monthly
Hg	-	-	-	-	-	-	-
Sr	-	-	-	-	-		
DOC	-	monthly	monthly	-	-		

P-sum	-	-	-	-	-	monthly	monthly
DN	-	-	-	-	-		
Al	-	monthly	monthly	-	-	-	-
N-sum	-			-	-	-	-
P_PO4	-			-	-	-	-
alkalinity	-			-	-	-	-
Cox	-	-	-	-	-	-	-

Station name	Klepacka		Cervena hora
Longitude	18° 23’ 51.999’’E		17° 32’ 31.007’’E
Latitude	49° 27’ 12.994’’N		49° 46’ 37.710’’N
Altitude	650 m		749 m
Station owner	VULHM		CHMU
Measurement programme	ICP Forests		Monitoring atmospheric deposition
Method of collection	bulk	throughfall	Wet only
Component/	Collection frequency		
pH	monthly	monthly	weekly
Conductivity			
Na^+			
K^+			
NH_4^+			
Mg^{2+}			
Ca^{2+}			
Fe			
Zn			
Mn			
Pb	-	-	
Cd	-	-	
Ni	-	-	
As	-	-	
Cu	monthly	monthly	
Co	-	-	
Cr	-	-	
V	-	-	
Se	-	-	
F^-			
Cl^-			

NO_3^-	monthly	monthly	
SO_4^{2-}			
Hg	-	-	-
Sr	-	-	-
DOC	monthly	monthly	-
P-sum	-	-	-
DN	-	-	-
Al	monthly	monthly	-
N-sum			-
P_PO4			-
alkalinity			-
Cox	-	-	-

Explanations:
DOC – dissolved organic carbon,
DN – dissolved nitrogen,
Cox – oxidising carbon.

The Czech monitoring system of precipitation chemistry is an example of a very extensive system for the study of precipitation quality. Within the monitoring of atmospheric deposition, in addition to the metals recommended in EMEP (Cd, Pb, Cu, Zn, As, Cr, Ni), metals such as Fe, Mn, Co, V and Se are determined. Geochemical monitoring identifies: Zn, Mn, Pb, Cd, Ni, As and Sr. For the ICP Forests programme, Fe, Zn, Mn, Cu are determined.

In addition to wet-only and bulk measurements, Czech stations use the throughfall method. This method collects sub-canopy precipitation. Sub-canopy precipitation is considered to be the best possible estimate of the total atmospheric deposition. Tree crowns effectively “filter” dry pollutants, which then fall along with the wet component into containers. However, this applies only to pollutants that do not interact significantly with the canopy, such as sulphur, but not nitrogen.

The results of measurements of precipitation chemistry together with the results of air quality monitoring are published in annual reports available on the CHMU website. For elaboration of the measurement results, besides the data from Czech stations, there are used data from Polish CIEP monitoring stations and German stations. Report for 2020: https://www.chmi.cz/files/portal/docs/uoco/isko/grafroc/20groc/gr20cz/20_rocenka_UKO_v4_WEB_ISBN.pdf

Germany

In Germany, EMEP measurements are carried out by the German Federal Environmental Agency (UBA) and the Troposphere Research Institute Leipzig (TROPOS) at 7 stations. At 6 of these stations managed by the German Environmental Agency (Westerland, Waldhof, Schauinsland, Neuglobsow, Schmücke, Zingst) precipitation samples are taken to determine their parameters (Table 4.27). At 5 stations: Waldhof, Schauinsland, Neuglobsow, Schmücke, Zingst, as mentioned when analysing the Baltic countries, measurements are carried out within the HELCOM programme.

At all of these stations, the concentrations of inorganic ions (sulphates, nitrates, chlorides, ammonium ions, magnesium, sodium, calcium, potassium), as well as pH, conductivity and precipitation are studied. Wet precipitation samples are taken for this purpose, with daily sampling at the Waldhof, Schauinsland and Neuglobsow stations and weekly sampling at the other stations. The pH is measured with a pH-meter, the conductivity with a conductivity sensor, the amount of precipitation is determined using the gravimetric method and the other components using ion chromatography (IC).

At these stations samples are also taken for determination of heavy metals in atmospheric precipitation. Concentrations of arsenic, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, antimony, selenium, titanium, thallium, vanadium and zinc shall be determined at all stations. Mercury is determined at all stations except the Neuglobsow station. For measurement of the above constituents, weekly wet precipitation samples are collected, in which the content of individual components is determined by means of inductively coupled plasma mass spectrometry (ICP-MS), except for mercury, for which the cold vapour atomic fluorescence spectroscopy (CV-AFS) method is applied.

Additionally, monthly wet precipitation samples are taken at selected stations for determination of persistent organic pollutants (POPs). The samples collected at the Westerland, Waldhof and Zingst stations measure concentrations of PAHs, PCBs, HCB, DDT, HCH, PCOs, whereas at the Schauinsland and Schmücke stations only PAHs are measured. The content of these components is determined in samples by gas chromatography mass spectrometry (GC-MS).

Table 4.27 Precipitation studying stations in Germany participating in the international EMEP and HELCOM programmes [own work based on the EBAS database].

Station	Westerland	Waldhof	Schauinsland	Neuglobsow	Schmücke	Zingst
Longitude	08°18'35’’E	10°45'34’’E	07°54'31’’E	13°02'00’’E	10°46'00’’E	12°44'00’’E
Latitude	54°55'32’’N	52°48'08’’N	47°54'53’’N	53°10'00’’N	50°39'00’’N	54°26'00’’N
Altitude	12 m	74 m	1205 m	62 m	937 m	1 m
Measurement programme	EMEP	EMEP, HELCOM	EMEP, GAW/WMO, HELCOM, ICOS	EMEP, GAW/WMO, HELCOM, ICP-Forest,	EMEP, HELCOM	EMEP, HELCOM
Method of selection	wet precipitation	wet precipitation	wet precipitation	wet precipitation	wet precipitation	wet precipitation
Component/ parameter	Collection frequency					
Amount of precipitation	weekly	daily	daily	daily	weekly	weekly
pH						
Conductivity						

Station	Westerland	Waldhof	Schauinsland	Neuglobsow	Schmücke	Zingst
SO_4^{2-}						
NO_3^-						
NH_4^+						
Cl^-						
Na^+						
Mg^{2+}						
K^+						
Ca^{2+}						
As	weekly	weekly	weekly	weekly	weekly	weekly
Cd						
Cr						
Co						
Cu						
Fe						
Pb						
Mn						
Mo						
Ni						
Sb						
Se						
Ti						
Tl						
V						
Zn						
Hg				-		
PAHs	monthly	monthly	monthly	-	monthly	monthly
PCB			-		-	
HCB						
DDT						
HCH						
PCO						

4.3 Guidelines and requirements for monitoring precipitation chemistry developed under the Convention on Long-range Transboundary Air Pollution, including EMEP and related International Cooperative Programmes (ICP's, i.e. ICP Forest and ICP Integrated Monitoring)

The current guidelines for the EMEP network are contained in the document Monitoring Strategy for the Cooperative Programme for Monitoring and Evaluation of Long-range Transmission of Air Pollutants in Europe 2020-2029 (EMEP, 2019: Decision 2019/1), which replaced the previous document in force in the years 2010-2019.

The work of EMEP is intended to fulfil the provisions of the Protocol to the 1979 Convention on Long-range Transboundary Air Pollution on the long-term financing of the cooperative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (EMEP).

In particular, the tasks of the programme include:

(a) provision of observational and modelling data on concentrations of air pollutants, deposition rates, emissions and transboundary flows on a regional scale and determination of their trends over time;

(b) identification of sources of concentrations and deposition of pollutants and assessment of responses to changes in emissions;

(c) improving the understanding of the chemical and physical processes relevant to the assessment of impacts of air pollutants on ecosystems, human health, materials and climate, in order to support the development of cost-effective emission abatement strategies;

(d) testing of environmental concentrations of new chemical substances that may require the attention of the Convention in the future.

At the European level, EMEP observations are of fundamental importance in relation to the European Union Directive on Air Quality and Cleaner Air for Europe (Directive 2008/50/EC, the so-called CAFE Directive) and the Directive on national emission ceilings (Directive 2016/2284 of the European Parliament and of the Council (EU) of 14 December 2016 on the reduction of national emissions of certain atmospheric pollutants, amending Directive 2003/35/EC and repealing Directive 2001/81/EC, the so-called NEC Directive) and there are close links between EMEP monitoring requirements and these Directives. In addition, EMEP observations are used as part of the assessments of the air quality situation in Europe by the European Environment Agency (EEA) and, in addition, EMEP stations usually contribute some of their data to the European Environment Agency database.

The monitoring strategy for 2020-2029 consolidates the accepted methods and aspirations of monitoring activities to ensure consistent and adequate observational data in support of EMEP's objectives. In addition, it makes some minor changes to the detailed requirements to meet EMEP's needs for the coming decade.

EMEP formulates requirements, consisting of differentiated ranges of the measurement programme, for the different station levels defined in the monitoring strategy.

Level 1. The main purpose of level 1 monitoring stations is to provide long-term measurements of the main physical and chemical EMEP parameters. Level 1 activities should be a priority when extending the monitoring network in areas with a small number of stations, such as Eastern Europe, the Caucasus and Central Asia and south-eastern Europe. Level 1 measurements include parameters required to describe basic aspects of troposphere chemistry and deposition rates of substances involved in atmospheric circulation: particulate matter (PM), photochemical oxidants, acidifying and eutrophying compounds and heavy metals. The requirements shall also include standard meteorological parameters, which can be retrieved from a nearby meteorological station provided they are representative.

Level 2. Level 2 parameters should be measured at stations where Level 1 measurements are made, potential additional parameters include: higher temporal resolution; reliable gas/particle distribution information for semi-volatile compounds; speciation/measurement of photochemical oxidant precursors (nitrogen oxides (NO_x) and volatile organic compounds (VOCs); physical and optical properties of aerosols (including soot, black carbon); optical thickness of aerosols and optical properties of aerosols (including soot, black carbon); aerosol optical thickness; further chemical speciation of particles (elemental and organic carbon in PM10, mineral dust); tracers to determine the origin of the air mass and the role of anthropogenic vs. natural influences, methane (CH_4) and halocarbons. For heavy metals, the level 2 programme includes air concentrations of cadmium (Cd) and lead (Pb) as first priority (and copper (Cu), zinc (Zn), arsenic (As), chromium (Cr) and nickel (Ni) as second priority), and mercury (Hg) in precipitation and air (total gaseous mercury, TGM). Level 2 monitoring of persistent organic pollutants (POPs) should ideally include measurements of congeners or isomers, both in air and in precipitation (polycyclic aromatic hydrocarbons (PAHs) polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), chlordane, hexachlorocyclohexanes (HCH) dichlorodiphenyltrichloroethane and dichlorodiphenyl dichloroethylene (DDT/DDE). However, full implementation of all the above parameters is not required to ensure compliance with the monitoring strategy; it is recommended that the level 1 station programme is progressively updated to include the mandatory variables for level 2.

The aim of the programme is to have at least 30 stations providing level 2 data across the EMEP domain. Level 2 variables are defined according to the issues that the States Parties conducting measurements there may choose to address, while they may focus on considering their own national priorities, bearing in mind that unless it is important to them, not all measurements need to be included in the study programme. A station that extends its programme to include both level 1 and level 2 requirements will be referred to as an “EMEP superstation”.

Level 3. Level 3 measurements are based on short-term research and measurement campaigns and may be carried out at different locations than the measurement stations providing level 1 and level 2 data. Parameters of interest for EMEP level 3 stations are: dry deposition flux measurements (sulphur, nitrogen, ozone, VOCs, Hg, others); vertical profiles of ozone and aerosols (SODAR or LiDAR), observations of POPs and Hg in non-atmosphere media; chemical speciation of organic carbon (OC) in aerosols, measurements of carbon dioxide (CO_2) and nitrous oxide (N_2O) made at EMEP stations in conjunction with other monitoring systems, and information on organic carbon isotopes and VOCs. The list is not complete and other parameters may be added to it when they become relevant to EMEP. Level 3 observations are a voluntary part of the monitoring effort and carried out in collaboration with the wider scientific community.

The following tables (Table 4.28, 4.29) provide a summary of the variables to be measured at the primary EMEP stations as part of the precipitation chemistry study.

Table 4.28 Level 1 – “variables to be measured at all basic EMEP sites” [own work based on Monitoring strategy..., EMEP 2019].

Level 1 “variables to be measured at all basic EMEP sites”		**Recommended time resolution**
Inorganic compounds in precipitation	SO_4^{2-}, NO_3^-, NH_4^+, H^+ (pH), Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, total precipitation	24 hours

Heavy metals in precipitation	Cd, Pb (first priority), Cu, Zn, As, Cr, Ni (second priority)	7 days
Meteorology	Precipitation amount (RR), temperature (T), wind direction (dd), wind speed (ff), relative humidity (rh), atmospheric pressure (pr)	24 hours (RR), other 1 hour

Table 4.29 Level 2 – "additional variables to be measured at a subset of sites - EMEP level 2 sites" [own work based on Monitoring strategy..., EMEP 2019].

Level 2 – "additional variables to be measured at a subset of sites – EMEP level 2 sites"		**Recommended time resolution**
Mercury in precipitation	Hg	7 days
POPs in precipitation	PAHs, PCBs, HCB, chlordane, HCHs, DDT/DDE	7 days

No precipitation chemistry measurements are to be carried out at EMEP level 3 stations.

For information on reference methods for use within the EMEP network, please refer to the EMEP Manual for Sampling and Chemical Analysis (Manual EMEP, 2014) and the Quality Assurance/Quality Control (QA/QC) section, available on the EMEP Chemistry Coordination Centre (CCC/EMEP) website: www.emep.int; https://projects.nilu.no//ccc/index.html

The guidelines are summarised in Table 4.30.

The time resolution of the measurements should generally not exceed 24 hours. If suitable methods exist, a higher temporal resolution is recommended. However, individual countries may commit to monitoring at a lower temporal resolution (maximum 7 days) when the measurement activity is resource-intensive, making continuous time-integrated sampling at 24-hour resolution impracticable.

Similarly, longer sampling times should be considered if concentration levels are so low that problems with detection limits may arise. Please also take special care to avoid sampling at a temporal resolution that affects data quality, for example, if methods are endangered by sampling artefacts. In such cases it is recommended to continue the current practice of limiting the sampling to a few short-term integrated samples per week instead of long sampling periods (for example, weekly and monthly sampling is not recommended for POPs and VOCs).

In terms of spatial resolution, it is recommended for level 1 variables that there should be at least one to two stations per 100 000 km^2 and at least one measuring point in countries with an area greater than 10 000 km^2 . It is recommended that small countries with large geographical and climatic variations further increase the density of the station network, taking into account that monitoring should also be carried out in mountainous regions.

For the level 2 variables, at least one such station shall be operated in countries with more than greater than 50 000 km^2 at least one such station should be in operation. However, Parties are free to choose and focus on variables that reflect their national priorities. If there are obstacles or financial constraints to implementing monitoring programmes, regional cooperation on station operation should be explored. Most of the existing EMEP level 2 stations are currently part of the Aerosol, Clouds and Trace Gases Research Infrastructure (ACTRIS) network, which focuses exclusively on gases and aerosols in its scope of work.

Level 3 measurements are voluntary and no specific requirements for station density are provided.

A key issue for the EMEP network is to ensure that measurements meet the requirements for quality assurance, quality control and data reporting. Reporting formats as well as criteria for instrumentation and analytical methods are also defined and available on the Chemical Coordinating Centre (CCC EMEP) website https://ebas-submit.nilu.no/SOPs.

Other methods of collection and analysis may be used provided that it can be demonstrated that the quality of the data obtained is equivalent.

Table 4.30 Mandatory and voluntary scope of monitoring of pollutants in precipitation according to the EMEP Strategy (matrix: wet precipitation) [own work based on Monitoring strategy..., EMEP 2019].

Level	Parameter group	Parameter	Temporal resolution
Level 1- “variables to be measured at all basic EMEP sites"	Inorganic compounds in the precipitation	SO_4^{2-}	24 hours
		NO_3^-	24 hours
		NH_4^+	24 hours
		H^+ (pH)	24 hours
		Na^+	24 hours
		K+	24 hours
		Ca^{2+}	24 hours
		Mg^{2+}	24 hours
		Cl^-	24 hours
	Heavy metals in precipitation	Cd	7 days
		Pb	7 days
		Cu	7 days
		Zn	7 days
		As	7 days

Level	Parameter group	Parameter	Temporal resolution
		Cr	7 days
		Ni	7 days
	Meteorological	Precipitation amounts	24 hours
		temperature (T)	1 hour
		wind direction (dd)	1 hour
		wind speed (ff)	1 hour
		relative humidity (rh)	1 hour
		atmospheric pressure (pr)	1 hour
Level 2 - “additional variables to be measured at a subset of sites – EMEP level 2 sites”	Mercury in	Hg	7 days
	POPs (POPs) in precipitation	PAHs	7 days
		PCB (polychlorinated biphenyls)	7 days
		HCB (hexachlorobenzene)	7 days
		chlordane	7 days
		HCH (hexachlorocyclohexanes)	7 days
		DDT/DDE (dichlorodiphenyltrichloroethane/dichloro diphenyl dichloroethylene)	7 days

EMEP Manual i.e. Sampling and Chemical Analysis Manual (EMEP Manual, 2014) is a document that describes the standard recommended sampling and chemical analysis methods for the EMEP measurement network. The paper version is not updated, but the online version of the manual, which can be found on the EMEP website www.nilu.no/projects/ccc/manual/, is continuously revised and updated.

Over the years, both sampling methods and methods of substance measurement have changed, many have been replaced by new and better methods, and a number of new compounds not previously covered by the programme are still emerging that require monitoring and for which the methodologies need to be adapted. The Manual has been expanded to include a chapter on quality assurance. Other revisions and extensions to the Manual are also expected in the coming years.

Station representativeness is a very important, if not the most important issue for a measurement network such as EMEP. In the case of EMEP, a station must be located in such a way that air quality and precipitation are representative of a larger area. For the condition to be fulfilled, influences and pollution from local sources must be avoided. Chapter 2 of the Manual (Manual EMEP, 2014) gives distances from potential sources where the station should be located. In practice, sulphur dioxide and nitrogen oxides emission sources should be avoided within the nearest 100 m radius, and emissions within the nearest 2 km radius should be less than 100 kg/year, within the nearest 20 km radius less than 1000 kg/year. What is more, local meteorological conditions such as prevailing winds or formation of stagnant air should be taken into account. In the case of precipitation, local sources of sulphur dioxide or nitrogen oxides emissions are generally less important, while sources of dust and ammonia should be avoided. Guidelines for minimum distances from emission sources are given in the table below.

The location of the collector should be in accordance with WMO location requirements for rain gauges. There should be no obstructions, such as trees, more than 30° from the perimeter of the precipitation collector, and buildings, hedges or topographical features that may cause ascending/descending air movements should be avoided. When locating the sampler, it is advisable to take into account the prevailing winds during precipitation.

Sedimentation of soil dust particles from the immediate vicinity is of particular concern. Dirt roads, backyards and farmland in the immediate area within 100m to 1km should be avoided. Other potential local sources of pollution can be wood-, peat- or coal-fired houses. Potassium is an indicator of such pollution. Local high sources of ammonia from agricultural activities should also be avoided (Table 4.31).

An electricity supply is required to operate the wet precipitation samplers. A small room in the building or a container for storing samples, equipment and documents is needed to operate the sampling site. It is necessary to equip such a mini-workroom with a refrigerator to store the collected precipitation samples.

Table 4.31 EMEP station guidelines for minimum distance from pollution sources (according to EMEP Manual for Sampling and Analysis (EMEP Manual, 2014); current version available at https://projects.nilu.no/ccc/manual/index.html)

Type	Minimum distance	Comment
Large pollution sources (cities, power plants, major motorways)	50 kilometres	Depending on prevailing wind directions
Small scale domestic heating with coal, fuel oil or wood	100 metres	Only one emission source at minimum distance
Minor roads	100 metres	Up to 50 vehicles per day
Main roads	500 metres	Up to 500 vehicles per day
Application of manure, stabling of animals	2 km	Depending on the number of animals and size of fertilized field or pastures

Type	Minimum distance	Comment
Grazing by domestic animals on fertilized pasture	500 metres	Depending on the number of animals and size of fertilized field or pastures

Another important element ensuring correctness of sampling is the location of the sampling station on the area. The site must also be representative in terms of exposure to the air mass. Valleys or areas where stagnant air may form in inversion conditions as well as mountain peaks and passes should be avoided. Well-lit sites in moderately undulating terrain are best or, if valleys cannot be avoided, on the side of the valley above the most pronounced night-time inversion layer. Coastal sites with pronounced diurnal wind variations due to land-sea breeze effects are also not recommended. Vegetation is a sink for many air pollutants, and it is important to avoid situations where sheltering by vegetation, e.g. by a stand of trees, results in lowered concentration when the wind is blowing from a particular direction.

It should also be borne in mind that the spatial correlation between measured concentrations of air pollutants in Europe is highly anisotropic. depends on the position and strength of emission sources, wind directions, topography and the chemical and physical properties of the various pollutants, it is therefore recommended that the distance between sites in central parts of Europe should be 150-200 km.

The purpose of sampling and chemical analysis of precipitation in the EMEP network is generally to give an accurate indication of precipitation chemical composition, which can be used to derive deposition by scaling with precipitation amounts, both on short-term (day-month) and on long-term bases.

For transboundary fluxes and deposition of air pollutants, the concentrations of sulphate, ammonium and nitrate in precipitation are particularly important. However, determination of one or more of the sea-salt constituents (Na, Cl, Mg) is also necessary in order to determine the fraction of sulphate concentration which is due to marine sea-spray aerosols; and determination of the base cations Ca, K, and Mg is desirable in order to give an indication of the large-scale deposition of bases which is needed in connection with the determination of critical loads.

Also, pH and conductivity should be determined in order to give an indication of the overall composition of the samples, and to check the consistency of the chemical analyses.

The sampling vessel must be constructed from a material which does not alter the chemical composition of the sample. Both the sample vessel as well as all material that comes into contact with the sample must be chemically inert. This guideline becomes particularly important when sampling precipitation and measuring heavy metals.

Samples should be taken daily, at the same time as the rain gauge reading in the respective measurement network. This will normally be 08:00 local time. Daily sampling includes activities such as transferring the sample to a sample storage and transport bottle, measuring the sample volume and thorough washing and cleaning of the equipment used. A detailed written standard operating procedure must be developed for each station and should be located at the station in an easily accessible place.

The manual also contains information on EMEP's recommended methods for chemical analysis. Most major ions in precipitation samples can be determined by ion chromatography, which is the generally recommended method for anions such as chlorides, nitrates and sulphates. Table 4.31 below lists the recommended and alternative methods, with reference to Chapter 4 of the manual (EMEP Manual, 2014), where the individual procedures are described in detail.

Table 4.32 below summarises the EMEP measurement programme and recommended methods as described in the *EMEP Manual for sampling and chemical analysis*. (EMEP Manual, 2014) (link: https://projects.nilu.no/ccc/manual/index.html).

Table 4.32 EMEP measurement programme and recommended methods (according to EMEP Manual for Sampling and Analysis. (EMEP Manual, 2014); current version available *at https://projects.nilu.no/ccc/manual/index.html)*

Precipitation				
Component or parameter	**Measure-ment period**	**Frequency of measure-ment**	**On site measure-ment methods**	**Laboratory methods**
Amount of precipitation	24 hours / week	daily / weekly	rain gauge	by weight
SO_4^{2-}	24 hours / week	daily / weekly	wet only	IC
H^+	24 hours / week	daily / weekly	wet only	titration
pH	24 hours / week	daily / weekly	wet only	pH meter
NH_4^+	24 hours / week	daily / weekly	wet only	IC / indophenol
NO_3^-	24 hours / week	daily / weekly	wet only	IC / Griess after reduction
Na^+	24 hours / week	daily / weekly	wet only	IC / AES
Mg^{2+}	24 hours / week	daily / weekly	wet only	IC / AAS
Cl^-	24 hours / week	daily / weekly	wet only	IC / *Thiocyanate*
Ca^{2+}	24 hours / week	daily / weekly	wet only	IC / AAS
K^+	24 hours / week	daily / weekly	wet only	IC / AES
conductivity	24 hours / week	daily / weekly	wet only	conductivity sensor
Cd, Pb (first order)	weekly	weekly	wet only	ICP-MS / GF-AAS
Cu, Zn, As, Cr, Ni (second order)	weekly	weekly		

Precipitation				
Component or parameter	**Measure-ment period**	**Frequency of measure-ment**	**On site measure-ment methods**	**Laboratory methods**
Hg^{2+}	weekly (1 sampler) or monthly (2 samplers)	weekly or monthly	wet only IVL collector	CV-AFS
POPs (PAHs, PCBs, HCB, chlordane, lindane, a-HCH, DDT/DDE)	discretionary	discretionary	wet only	

IC – ion chromatography
(Indophenol) – indophenol method
(Griess after reduction) – Griess spectrophotometric method after reduction
AES – atomic emission spectrometry
AAS – atomic absorption spectrometry
Thiocyanate – Spectrophotometric method with mercuric (II) rhodanate
ICP-MS – inductively coupled plasma – mass spectrometry
GF-AAS – *graphite furnace atomic absorption spectrometry*
CV-AFS – cold vapour atomic fluorescence spectroscopy

The EBAS website, which is the data bank for EMEP, contains many useful tools, e.g. the Standard Operating Procedures (SOPs) for most substances tested in EMEP are described at https://ebas-submit.nilu.no/SOPs.

The EBAS website also contains detailed instructions on how to check and prepare measurement data for submission to EMEP by the required deadline. The EBAS Data Submission Manual contains diagrams and forms as well as detailed information and guidance. For several years reporting has been done online via and tools at https://ebas-submit.nilu.no/.

ICP's international cooperation programmes

ICP's (International Cooperative Programmes) were launched under the Convention on Long Range Transboundary Air Pollution (CLRTAP) in 1985.

ICP IM – Integrated Monitoring

The International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems (ICP IM), like the other ICPs, is a scientific programme that is coordinated by a Task Force (TF). The ICP IM Programme Centre is located in Helsinki at the Finnish Environment Institute. The Task Force (TF) is located in Sweden. It should be added that currently an important task in the functioning of ICP IM is scientific research on the impact of so-called megatrends, above all climate change, on ecosystems and biodiversity. This line of research, and above all its results, are meant to be useful for the United Nations Framework Convention on Climate Change and the Convention on Biological Diversity. This research approach is similar to the assumptions of the ZMŚP programme carried out in Poland, i.e. the Integrated Monitoring of Environment in which, on the basis of detailed studies on particular elements of the natural environment, the condition of geoecosystem environment is determined in relation to climate changes and various directions of anthropopressure, directions of threats are indicated and proposals of protection are presented. The measurement system is usually located within the range of river or lake catchments considered representative for a given physical-geographical region. In accordance with the requirements of ICP IM, in the experimental catchments of the ZMŚP it is possible to determine the energy and material balance. Within the framework of the ZMŚP, systematic observations of land use changes are made. All changes related to catchment area management, as recommended by the ICP IM, are properly documented.

One of the ICP IM sub-programmes (source: ICP IM Manual) is the precipitation chemistry programme (Table 4.33). The purpose of the sub-programme is to quantify the impact of precipitation and ions in precipitation (wet deposition) to the integrated monitoring area. The deposition of pollutants in ecosystems by precipitation is considered to be the primary factor influencing natural environmental processes. The main objective of the precipitation chemistry subprogramme is the sampling and chemical analysis of precipitation, with a focus on acidifying compounds and nutrients.

Table 4.33 ICP IM subprogramme – Precipitation Chemistry Programme [source: ICP IM Manual].

Subprogramme: Precipitation Chemistry	
Mandatory parameter	**Voluntary parameter**
Amount of precipitation	
pH and conductivity at 25°C	
Na, K, Mg, Ca, NH_4^+	Al, Mn, Fe, As, Cd, Cr, Cu, Mo, Ni, Pb, Zn
Cl^-, NO_3^-, SO_4^{2-}	P_sum, PO_4^{3-}
Alkalinity	
	S_sum, N_sum

The frequency of sampling depends on the element under study. Daily, weekly or monthly precipitation samples are taken.

The aim of the study is to obtain normal monthly values. To ensure quality, samples should be taken as often as possible, preferably weekly or, if possible, daily.

It is recommended to check precipitation with a standard rain gauge.

Most of the requirements and recommendations of the programme coincide with EMEP. This applies e.g. to the location criteria, the sampling procedure itself. Many points in the ICP IM Manual are followed by references to the EMEP Manual (Manual EMEP, 2014).

The recommended way of preparing samples for analysis is described. It is noted that weekly samples may be analysed as they are collected or, to save expenditure, aggregated into monthly samples. If samples are combined, they must be mixed in proportion to the total sample volume. Great care must be taken during the pooling procedure to avoid contamination and errors.

The recommended method for measuring major ions is e.g. ion chromatography. Suitable alternative methods are for example atomic absorption spectrometry for Na, K, Ca, Mg and spectrometric methods for ammonium ions. The recommended method for the determination of pH, strong and weak acids is potentiometry, whereas the alternative method for the determination of strong and weak acids is coulometric titration (modified Gran titration). Conductometry is the recommended method for the determination of conductivity. For all recommended analytical methods, reference is made to the methods presented in the EMEP Manual (Manual EMEP, 2014).

ICP Forests – International Cooperative Programme on Assessment and Monitoring of Air Pollution Effects on Forests

The International Cooperative Programme for Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) is one of the largest biomonitoring networks. Its results provide information on forest status, air pollution, climate change and biodiversity.

ICP Forests monitors forest condition at two levels of monitoring intensity (Table 4.34):

- Level I, which aims to provide a periodic overview of spatial and temporal changes in the condition of forests in relation to anthropogenic and natural stress factors (in particular air pollution) by means of pan-European and nationally representative monitoring on a large scale in a systematic network,
- Level II, which aims to better understand causal links between forest ecosystem conditions and anthropogenic and natural stress factors (in particular air pollution) by intensively monitoring a number of selected permanent observation plots distributed across Europe and studying the development of important forest ecosystems in Europe**.**

Deposition monitoring shall be carried out at specific points. Measurements shall be made in such a way that they are spatially well distributed throughout the country, if necessary on all level II plots. Deposition measurements of precipitation on the ground surface shall be carried out on the surface itself. If this is not measurements shall be made close to the site and in the same tree stand. Measurements shall in no way interfere with other measurements of soil and vegetation. Care shall be taken not to cause any damage to the ground.

Table 4.34 Mandatory deposition sampling parameters on standard core plots [ICP Forests, 2020].

Mandatory parameter	Voluntary parameter
Amount of precipitation	

pH and conductivity at 25°C	
Na, K, Mg, Ca, NH_4^+	Al, Mn, Fe and other heavy metals, e.g. Cu, Zn, Hg, Pb, Cd, Co, Ni, Cr
Cl^- , NO_3^- , SO_4^{2-}	P_sum, PO_4^{3-}, NO_2^-
Total alkalinity, mandatory for individual samples if pH>5	
dissolved organic carbon DOC, N_sum (N_sum is not mandatory, but is highly recommended)	S_sum, HCO_3^-, N_org, C_sum The HCO_3^- concentration can be obtained either from calculations (from pH, total alkalinity, temperature and ionic strength) or from direct measurements

4.4. Guidelines and requirements of EU Directives for atmospheric deposition monitoring.

The basic legal act binding for the European Union countries in the scope of air quality is the Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe (Official Journal of the EU L 152 of 11.06.2008, p.1), popularly known as the CAFE Directive (Clean Air for Europe Directive).

The second legal act of equal importance is Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, nickel, mercury and polycyclic aromatic hydrocarbons in ambient air (Official Journal of the EU L 23 of 26.01.2005, p.3).

Furthermore, the Implementing Decision of the Commission of the European Communities of 12 December 2011 laying down rules for Directives 2004/107/EC and 2008/50/EC of the European Parliament and of the Council as regards the reciprocal exchange of information and reporting on ambient air quality (2011/850/EU) is relevant.

It should be mentioned that Directive 2008/50/EC consolidated and replaced the provisions of the earlier Council Directive 96/62/EC of 27 September 1996 on ambient air quality assessment and management of ambient air quality (1996/62/EC), and three of its four daughter directives: the first daughter directive, Council Directive 1999/30/EC of 22 April 1999 relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air (1999/30/EC), the second daughter Directive 2000/69/EC of the European Parliament and of the Council of 16 November 2000 relating to limit values for benzene and carbon monoxide in ambient air (2000/69/EC) and the third daughter Directive 2002/3/EC of the European Parliament and of the Council of 12 February 2002 relating to ozone in ambient air (2002/3/EC), as well as Decision 97/101/EC. The fourth daughter directive, the aforementioned Directive 2004/107/EC, remained in force with the proviso that, once sufficient experience has been accumulated with regard to experience with its implementation, consideration could be given to merging its provisions with those of Directive 2008/50/EC.

In the preamble to the CAFE Directive, the very first paragraph cites, that the Sixth Community Environment Action Programme, adopted under Decision No 1600/2002/EC of the European Parliament and of the Council of 22 July 2002 states that it is necessary to reduce pollution to levels which minimise harmful effects on human health, paying particular attention to sensitive populations, and the environment as a whole, to improve the monitoring and assessment of air quality, including the assessment of the impacts of pollutants on human health and the environment and assessment of air quality, including the deposition of pollutants, and for the provision of information to the public.

The preamble further states that in order to ensure adequate representativeness and comparability of air quality data throughout the Community, standardised measurement techniques and common criteria for both the number and location of measurement sites should be used to assess ambient air quality. Techniques other than measurements can be used to assess ambient air quality and it is therefore necessary to define criteria for the use and required accuracy of such techniques. Detailed measurements of air pollution, especially fine particulate matter, should be made at rural background monitoring stations. Such measurements should be made in a manner consistent with the cooperative programme for monitoring and evaluation of the long range transmission of air pollutants in Europe (EMEP) set up under the 1979 Convention on Long-range Transboundary Air Pollution.

Article 2(3) of the Directive defines “level” as meaning concentration of a pollutant in ambient air or the deposition thereof on surfaces over a given period of time. Thus, in the Directive any use of the word “level” can mean deposition.

Under Directive 2008/50/EC, Member States shall ensure that, throughout their zones and agglomerations, levels of sulphur dioxide, PM 10, lead and carbon monoxide in ambient air do not exceed the values laid down in the Directive; that for nitrogen dioxide and benzene the limit values may not be exceeded from certain dates; similar arrangements apply to PM 2.5 (Articles 13 and 15).

In Article 3, the Directive lays down the obligations of Member States, which include responsibility for the assessment of air quality, approval of measurement systems (including methods, equipment, networks and laboratories), ensuring the accuracy of measurements, analysis of assessment methods, coordination of Community-wide quality assurance programmes within their territory and cooperation with other Member States and with the Commission.

The CAFE Directive attaches particular importance to particulate matter in ambient air. In Article 6(5), in non-urban background locations away from significant sources of pollution, it recommends that measurements be carried out to obtain annual average information at least on the total mass concentration and chemical composition of fine particulate matter (PM2.5), and that these measurements be carried out in accordance with according to the following criteria:

(a) there shall be one measuring point for every 100 000 km^2 ;

(b) each Member State shall set up at least one measuring station or, in order to achieve the necessary spatial resolution, may set up, by agreement with adjoining Member States, one or more jointly operated measuring stations, covering neighbouring zones of adjoining Member States;

(c) where appropriate, the monitoring system should be coordinated with the monitoring strategy and measurement programme of the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP).

Member States are to inform the Commission of the methods adopted and the results of the measurements.

Annex III to Directive 2008/50 lays down the principles for the location of macro- and micro-scale measuring points, in particular for the assessment of air quality with respect to sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter (PM10 and PM2,5), lead, benzene and carbon monoxide. In the case of the assessment of non-urban background levels, and such conditions are assumed to be represented by the stations taken into consideration for the assessment of precipitation chemistry in Poland, the measuring point should not be influenced by agglomerations or industrial facilities located in the vicinity, e.g. facilities at a distance of less than five kilometres. In addition, Annex III provides recommendations for sampling points aiming at the protection of vegetation and natural ecosystems to be located more than 20 km from agglomerations or more than 5 km from other built-up areas, industrial installations or motorways or major roads with traffic in excess of 50 000 cars per day, which means that a sampling point must be located in such a way that the air sampled is representative of air quality in a surrounding area of no less than 1 000 km^2. A Member State may decide to locate a sampling point at a lesser distance or to use it to sample air quality in a less extended area, taking account of geographical conditions or the opportunities to protect particularly sensitive areas. The site selection procedures shall be supported by full documentation gathered at the classification stage, comprising in particular compass-point photographs of the surrounding area and a detailed map. Sites shall be reviewed periodically using the same documentation to check that they still fulfil the selection criteria.

Annex IV details the measurements to be made at rural background locations irrespective of concentration. The key purpose of these measurements is to provide reliable information on background levels. This information is necessary to assess elevated levels in more polluted areas such as urban, industrial or traffic areas, to assess the impact of long-range transport of air pollutants, to support source apportionment analysis or to understand specific pollutants such as particulate matter. In accordance with the principles set out in Annex III, the measurement of PM2.5, in order to describe its chemical composition, must include at least the total mass concentration and the concentrations of the appropriate chemical compounds at least as follows (Table 4.35):

Table 4.35 Scope of measurements

SO_4^{2-}	Na^+	NH_4^+	Ca^{2+}	elemental carbon (EC)
NO_3^-	K^+	Cl^-	Mg^{2+}	organic carbon (OC)

Annex VIII of the Directive contains criteria for the classification and siting of sampling points for the assessment of ozone concentrations. It contains rules on the location of sampling points at the macro scale, including conditions for siting of rural background stations. The representativeness of these stations is to cover the region/ country/ continent level and the area between 1 000 and 10 000 km^2. These stations are to be located in less densely populated areas, e.g. with natural ecosystems, forests, at least 20 km away from urban and industrial centres and away from local emissions. Locations with the potential for locally occurring ground inversions and the tops of higher mountains should be avoided. Coastal locations with locally prevailing diurnal wind cycles shall be discouraged. According to Annex IX there should be one rural background station per 50 000 km^2, with the proviso that in areas with complex terrain there should be one station per 25 000 km^2 . The minimum number of rural background stations shall be 1 per 100 000 km^2.

Although those criteria do not apply in all cases to deposition sampling points for the measurement of deposition, they should be taken into account in view of the cost-effectiveness of locating sampling points at sites suitable for the measurement of air pollutants that are required to be monitored for international observation networks.

Another important document is Directive 2004/107/EC relating to to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons (PAHs) in ambient air.

The preamble to Directive 2004/107/EC notes that the impact of arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons on human health, including via the food chain, and on the environment as a whole, occurs via concentrations in ambient air and via deposition; the accumulation of these substances in soil and the protection of groundwater should be taken into account. In order to facilitate the evaluation of the effectiveness of this Directive, in 2010 the Commission and the Member States should consider promoting research into the effects of arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons on human health and the environment, in particular through deposition.

Scientific evidence shows that arsenic, cadmium, nickel and certain polycyclic aromatic hydrocarbons are genotoxic carcinogens for humans and that there is no identifiable threshold below which these substances that these substances do not pose a risk to human health. Mercury is a very dangerous substance for human health and the environment. It is present throughout the environment and, in the form of methylmercury, has the capacity to accumulate in organisms, and in particular to concentrate in organisms higher up the food chain. Mercury released into the atmosphere can be transported over long distances.

It also notes that it is important to provide reference measurement methods and states that information on concentrations and deposition of regulated pollutants should be forwarded to the Commission as a basis for periodic reports. The public should have easy access to up-to-date information on ambient air concentrations and deposition of regulated pollutants.

Article 8 of the Directive states that for the assessment of benzo(a)pyrene in ambient air, each Member State shall monitor other relevant polycyclic aromatic hydrocarbons at a limited number of sampling points. These compounds shall include at least: benzo(a)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, and dibenzo(a,h)anthracene. The measurement points for these polycyclic aromatic hydrocarbons are located next to the sampling sites for benzo(a)pyrene and are selected so that geographical variation and long-term trends can be identified.

Article 9(4) of Directive 2004/107/EC provides that, irrespective of concentration levels, one sampling point for background monitoring shall be installed every 100 000 km^2 for the indicative measurement in ambient air of arsenic, cadmium, nickel, total gaseous mercury, benzo(a)pyrene and the other polycyclic aromatic hydrocarbons referred to in paragraph 8 and total deposition of arsenic, cadmium, mercury, nickel, benzo(a)pyrene and the other polycyclic aromatic hydrocarbons referred to in paragraph 8. Each Member State shall set up at least one measuring station; however, Member States may set up one or several common measuring stations, covering neighbouring zones in adjoining Member States, to achieve the necessary spatial resolution. The siting criteria for such common measuring stations shall be such that they are also suitable as common measuring stations for PM2,5 as defined in Article 6(5) of Directive 2008/50/EC. Measurement of divalent mercury in the form of dust and vapour is also recommended. Where appropriate where appropriate, monitoring should be coordinated with the European Monitoring and Evaluation of the Long-range Transmission of Air Pollution (EMEP) programme. The sampling points for these pollutants shall be selected in such a way that geographical variations and long-term trends can be determined.

Article 12 states that standardised, accurate measurement techniques and common criteria for the location of measuring stations are important elements in the assessment of ambient air quality, so that the information obtained is comparable throughout the Community.

The detailed criteria for the location of a station measuring substances applicable Directive 2004/107/EC are laid down in Part 1 of Annex III to the Directive. It is also specified there that, where the objective is to assess background levels, the sampling point should be free from the influence of agglomerations or industrial sites in its vicinity, i.e. places closer than a few kilometres.

It also includes recommendations on measurement frequency and data output. In particular, round-the-clock sampling is necessary for the measurement of benzo(a)pyrene and other polycyclic aromatic hydrocarbons. Single samples taken over a period of up to one month may – with due care – be pooled and analysed as a composite sample provided that the method used guarantees the stability of the samples over that period. The three variants benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene can be difficult to separate during the test. In such cases they may be reported as a sum. 24-hour sampling is also recommended for the measurement of arsenic, cadmium and nickel concentrations. Sampling must be spread evenly over the days of the week and throughout the year. For the measurement of deposition rates monthly or weekly sampling throughout the year is recommended. Member States may take wet deposition samples only instead of total deposition samples if they can demonstrate that the difference between them does not exceed 10%. Deposition rates should generally be given as μg/m^2/day.

This sentence in the original text of the Directive reads: “Member States may use wet only instead of bulk sampling if they can demonstrate that the difference between them is within 10%.” In contrast, the Polish version of the Directive as available both in the Database of Legal Acts of the European Union at https://eur-lex.europa.eu/, and on the Chief Inspectorate of Environmental Protection website at https://powietrze.gios.gov.pl/pjp/publications/card/, the fragment is translated incorrectly: "Member States may take wet deposition samples only instead of dry deposition samples if they can demonstrate, that the difference between them does not exceed 10%." The incorrect provision in the Polish documents should be corrected.

Annex IV "Data quality objectives and requirements for air quality models" includes wording on the uncertainty of the methods. The uncertainty of the methods used for the assessment of ambient air concentrations (expressed at the 95% confidence level) will be evaluated in accordance with the principles of the CEN Guide to the Expression of Uncertainty in Measurement (ENV 13005-1999), the methodology of ISO 5725:1994, and the guidance provided in the CEN report "Air Quality – Approach for the estimation of uncertainty in ambient air reference measurement methods" (CR 14377:2002E). The percentages of uncertainty are given for individual measurements, which are averaged over typical sampling times, for a 95% confidence interval. The uncertainty of the measurements should be interpreted as being applicable in the region of the relevant target value. Fixed and indicative measurements must be evenly distributed over the year to avoid biasing the results.

Annex V provides reference methods for the assessment of, inter alia, deposition rates.

The reference method for the sampling of depositions of arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons is based on the exposure of cylindrical deposition gauges of standard dimensions.

In accordance with the requirements set out in the current Regulation of the Minister of Climate and Environment of 11 December 2020 on the assessment of levels of substances in the air,[6] transposing the provisions of Directive 2008/50/EC of the European Parliament and of the Council on ambient air quality and cleaner air for Europe[7] and Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 on arsenic, cadmium, nickel, mercury and polycyclic aromatic hydrocarbons in ambient air[8] and Commission Directive (EU) 2015/1480 of 28 August 2015 amending certain Annexes to Directives 2004/107/EC and 2008/50/EC of the European Parliament and of the Council laying down rules on reference methods, validation of data and location of measurement points for air quality assessment[9]) measurements of total deposition of heavy metals and polycyclic aromatic hydrocarbons are carried out in Poland in at least three regional background measurement points.

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[6] *Regulation of the Minister of Climate and Environment of 11 December 2020 on the assessment of levels of substances in the air (Journal of Laws of 2020, item 2279*)

[7] *Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe (Official Journal of the EU L 152 of 11.06.2008, p. 1 and Official Journal of the EU L 226 of 29.08.2015, p. 4)*;

[8] *Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, nickel, mercury and polycyclic aromatic hydrocarbons in ambient air (OJ EU L 23 of 26.01.2005, p. 3, OJ EU L 87 of 31.03.2009, p. 109 and OJ EU L 226 of 29.08.2015, p. 4)*;

[9] *Commission Directive (EU) 2015/1480 of 28 August 2015 amending certain Annexes to Directives 2004/107/EC and 2008/50/EC of the European Parliament and of the Council laying down rules on reference methods, validation of data and location of measuring points for the assessment of air quality (OJ L 226, 29.08.2015, p. 4*)

Also in accordance with the requirements set out in the above-mentioned Regulation, measurements of air pollution with mercury and total deposition (similarly to heavy metals and PAH) are conducted in Poland at selected regional background measurement stations. This results from the fact that mercury is a substance very dangerous to human health (it has the capacity to accumulate in organisms) and is present in the entire environment. This obligation, as a separate task, was also included in the State Environmental Monitoring Programme in force during the assessment period. The basic objectives of performing those measurements are monitoring of transboundary transfer of pollutants and development of air quality assessments at regional background stations.

Commission Implementing Decision of 12 December 2011 laying down rules for Directives 2004/107/EC and 2008/50/EC of the European Parliament and of the Council as regards the reciprocal exchange of information and reporting on ambient air quality (notified under document C(2011) 9068) (2011/850/EU) requires the monitoring of the substances listed in Part C of Annex I to the Decision. The list includes all pollutants requiring monitoring as referred to in Directives 2004/107/EC and 2008/50/EC. The European Environment Agency maintains a list of pollutants that are subject to reciprocal data exchange between Member States.

The inventory requires monitoring of wet/bulk deposition of the heavy metals: lead, cadmium, arsenic, nickel and mercury (μg/m^2/day) and of deposition of polycyclic aromatic hydrocarbons (PAHs): benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3,-cd)pyrene and dibenzo(a,h)anthracene (μg/m^2/day).

The monitoring obligation covers also concentrations of heavy metals – lead, cadmium, arsenic and nickel in PM10 (Pb in μg/m^3 , Cd, As and Ni in ng/m^3), concentration of mercury as: gaseous elemental mercury, total gaseous mercury, gaseous reactive mercury and solid mercury (all forms in ng/m^3) and concentrations of polycyclic aromatic hydrocarbons (in ng/m^3) in PM10 – benzo(a)pyrene benzo(a)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3,-cd)pyrene and dibenzo(a,h)anthracene. The list includes other constituents requiring monitoring, including five from the group of inorganic gaseous pollutants (SO_2, NO_2, NO_x, O_3, CO), PM10 and PM2.5 particulate matter concentrations, PM2.5 particulate matter composition, volatile organic compounds.

Commission Directive (EU) 2015/1480 of 28 August 2015 amending certain Annexes to Directives 2004/107/EC and 2008/50/EC of the European Parliament and of the Council laying down rules on reference methods, validation of data and the location of sampling points for the assessment of air quality, having regard to Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 on arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, in particular Article 4(15) thereof, and having regard to Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, in particular Article 28(1) thereof, amends in Annex I the reference methods for the sampling and analysis of arsenic, cadmium and nickel in ambient air, of polycyclic aromatic hydrocarbons in ambient air, of mercury in ambient air and of the reference method for the sampling and analysis of the deposition of arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons. In addition, Annex 2 details the revised quality assurance provisions for air quality assessment for data validation, as well as provisions indicating reference methods for the assessment of concentrations of sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter (PM10 and PM2.5), lead, benzene, carbon monoxide and ozone.

Directive 2016/2284 of the European Parliament and of the Council of 14 December 2016 on the reduction of national emissions of certain atmospheric pollutants, amending Directive 2003/35/EC and repealing Directive 2001/81/EC, known as the Ceiling Directive (NEC, National Emission Ceilings), sets out the ceilings for air emissions of primary gaseous pollutants, which are also precursors to secondary particulate matter.

The NEC Directive imposes on EU Member States obligations to reduce emissions of anthropogenic pollutants into the atmosphere: sulphur dioxide (SO_2), nitrogen oxides (NO_X), non-methane volatile organic compounds (NMVOCs), ammonia (NH_3) and fine particulate matter (PM2.5), and includes, inter alia, the requirement to draw up, adopt and implement national air pollution abatement programmes and to monitor emissions of these pollutants and their effects. Poland's emission reduction commitments relate to two periods, which cover the years from 2020 to 2029 and from 2030 onwards. The reduction obligations are set by reference to emissions in the reference year 2005. In the case of sulphur dioxide (SO_2) they amount to 59% each year from 2020 to 2029 and 70% each year from 2030 onwards, for nitrogen oxides (NO_x) – 30% and 39% respectively, for NMVOCs – 25% and 26% respectively, for ammonia (NH_3) – 1% and 17% respectively, and for fine particulate matter PM2.5 – 16% and 58%.

The ceiling directive obliged Member States to draw up, adopt and implement national air pollution abatement programmes and to monitor emissions of the pollutants which they are obliged to reduce and other pollutants listed in Annex I of the Directive, as well as their effects, and to provide information about them.

The “other” pollutants listed in Annex I of the NEC Directive are: carbon monoxide CO; particulate matter PM10; heavy metals: Cd (cadmium), Hg (mercury), Pb (lead); total persistent organic pollutants POPs, including: polycyclic aromatic hydrocarbons PAHs: benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene; and dioxins/furans, polychlorinated biphenyls PCBs, hexachlorobenzene HCB; the last pollutant identified in the Annex requiring monitoring is soot (black carbon).

The directive originally intended to cover substances that cause acidification and eutrophication and the formation of ground-level ozone.

These substances are briefly discussed below. Among those listed first, i.e. as mandatory as a direct result of the Directive, there are:

- SO_2, sulphur dioxide, a substance that contributes to the acidification of the environment, in the process of physicochemical transformation SO_2 is oxidised to sulphate and sulphuric acid, SO_2 and its oxidation products are removed from the atmosphere in the form of dry and wet deposition; despite these transformation and removal processes, sulphur dioxide can be transported over long distances, causing transboundary pollution – atmospheric lifetime for oxidation is usually a few days; the dry deposition of aerobic sulphur is calculated from the concentrations of SO_2 and SO_4^{2-}, and SO_2 is the basis for calculation of the deposition of hydrogen ions, derived from the dry deposition of SO_2; at background stations SO_2 and SO_4^{2-} are measured in the air and these substances should be included in the mandatory set of indicators covered; they are mandatory under EMEP (level 1) and GAW/WMO,

- NO_X, oxides of nitrogen, which include nitric oxide NO and nitrogen dioxide NO_2, NO_2 is a substance contributing to acidification, eutrophication and the formation of ground-level ozone, nitrogen oxides have a lifetime of about one day; in the process of physicochemical transformation of NO_2 it is transformed into nitrate ions which get to the surface in the form of wet and dry deposition; nitrogen oxides participate in the reaction with hydrocarbons (NMVOCs) in the reaction of ground-level ozone formation; oxygen forms of nitrogen in the air at the background stations are measured NO_X at the Puszcza Borecka station, NO_2 at IMWM-NRI stations in Łeba, Jarczew and on Śnieżka, sum of gases and aerosols (HNO_3 + NO_3^-) at all four stations, and as NO_3 aerosol (only) at IMWM-NRI stations – in Łeba, Jarczew and on Śnieżka; on the basis of NO_2 and NO_3^-, concentrations and the sum of (HNO_3 + NO_3^-) dry deposition of aerobic nitrogen are calculated; measurement of the above mentioned substances in the air should be included in the mandatory set of indicators examined in the future network; NO_2, NO_3^- and (HNO_3 + NO_3^-) are mandatory under EMEP (1 level) and GAW/WMO,
- non-methane volatile organic compounds (NMVOCs), NMVOCs react with nitrogen oxides to form ground-level ozone with nitrogen oxides contribute to the formation of ground-level ozone, volatile organic compounds are not measured at background stations, but some NMVOCs are measured at many stations operating within the SEM structure under the supervision of the Chief Inspectorate of Environmental Protection,
- ammonia (NH_3) – a substance contributing to acidification and eutrophication; enters the air mainly as a result of agricultural activities; ammonia undergoes physicochemical transformations and reaches the ground in the form of dry and wet deposition of NH_4^+; at all four background stations are measured as a sum of gases and aerosols (NH_3 + NH_4^+), and as aerosol NH_4^+ only at IMWM-NRI stations in Łeba, Jarczew and Śnieżka; measurements of NH_4^+ and (NH_3 + NH_4^+) are mandatory under EMEP (level 1), both as aerosol and as a sum of gas and aerosol,
- PM2.5 – very fine dust, with an aerodynamic diameter of particles < 2.5 μm; an important source of PM2.5 is the process of its formation in the atmosphere as a result of chemical transformations involving the precursors of dust, which include, among others, sulphur oxides, nitrogen oxides, volatile organic compounds or ammonia; PM2,5 and its precursors may be transported over long distances and thus emissions from distant emitters (apart from local emissions) may affect the level of PM2,5 concentrations in the air in areas distant from emission sources; measured at the Puszcza Borecka station, mandatory under the EMEP programme (level 1); at the Puszcza Borecka station ion and carbon content of PM2.5 is also measured.

The component of air that forms one of the bases for the introduction of the repealed Directive 2001/81/EC, replaced by Directive 2016/2084, is ground-level ozone. Ground-level ozone is a secondary pollutant and is formed, as previously noted, by photochemical reactions of nitrogen oxides and volatile organic compounds in the air. These reactions are accelerated by meteorological conditions, including high air temperature and sunny weather, as well as by circulation conditions. Ozone has the ability to be transported over long distances. Measurement of ground-level ozone is a mandatory component of the EMEP (level 1) and GAW/WMO programmes. Mandatory measurement of this element is also enshrined in EU Directives.

Other substances subject to mandatory emission inventories listed in the NEC Directive include:

- Carbon monoxide CO – carbon monoxide is emitted into the atmosphere as a result of combustion processes and is also formed as a result of the oxidation of hydrocarbons and other organic compounds. It has an atmospheric lifetime of about one month, during which it is further oxidised to carbon dioxide.
- PM10 particulate matter (fine dust, particles of aerodynamic diameter < 10 µm); measurements of air content of PM10 fine particulate matter and of heavy metals (including As, Cd and Ni) and polycyclic aromatic hydrocarbons contained in it shall be carried out at the Puszcza Borecka station, at the Puszcza Borecka station mercury is also measured in the air in gaseous form, in accordance with the Directive 2004/107/EC; PM10 particulate matter is one of the mandatory elements of EMEP (level 1),
- heavy metals: Cd (cadmium), Hg (mercury), Pb (lead) – heavy metals – cadmium and lead – are measured as constituents of PM10 dust, mercury in gaseous form as mentioned before; metal content in dust is measured at the Puszcza Borecka station and at the Zielonka station; cadmium and lead in PM10 dust are listed as EMEP level 2 elements as first priority metals, gaseous mercury (TGM) is also included in the list of parameters measured at EMEP level 2.
- Total persistent organic pollutants POPs, of which
- Polycyclic aromatic hydrocarbons PAHs – Hydrocarbons (and other organic compounds) are released into the atmosphere from various sources related to human activities (e.g. fossil fuel combustion, solvent evaporation) and from some natural sources (e.g. vegetation). Some hydrocarbons pose a direct threat to health, for example, benzene and 1,3-butadiene are carcinogens; although the levels of most hydrocarbons typically observed do not pose a health risk, they are oxidised to form organic oxygen products (some of which can be harmful) and carbon monoxide. Due to the diversity of their structures and differences in their reactivity, the rate and products of hydrocarbon oxidation vary greatly. In the presence of nitrogen oxides, oxidation of hydrocarbons also leads to formation of ozone; PAHs are deposited in the form of wet deposition and dry deposition; measurement of PAHs contained in PM10, including benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene is carried out at the Puszcza Borecka station and at the Zielonka station; these measurements are part of EMEP level 2,
- dioxins/furans and PCBs and hexachlorobenzene HCB are included in the EMEP list at level 2 sites; they do not belong to the scope of testing of background stations listed in the report.

The last parameter that requires monitoring is black carbon (BC); aerosols in the atmosphere contain large part of carbonaceous matter, which generally consists of two components: organic carbon (OC) and black carbon (BC), BC aerosol effectively absorbs solar radiation and warms the atmosphere; at the Puszcza Borecka and Zielonka stations the content of organic carbon (OC) and elemental carbon (EC) in PM2.5 are measured; these elements are mandatory under EMEP level 1.

In addition, the Ceiling Directive requires Member States to monitor the negative impact of air pollution on ecosystems based on a representative network of monitoring stations.

The organisation of monitoring should take into account the biogeographical regionalisation applied in the European Union, according to which Poland is located in zones of the continental and alpine type. Within the analysed biogeographical regions six use categories should be taken into account – meadows, croplands, forests, heaths and shrubs, wetlands, rivers and lakes. Annex V of the NEC Directive proposes the introduction of a category of integrated monitoring, which concerns comprehensive observations of physical, chemical and biological parameters within the extent of a river and lake basin. The effect of this monitoring should be the ability to determine the cause and effect relationships between the atmosphere, soil, water and the living environment.

The presented objectives and tasks of air pollution impact monitoring within the framework of the NEC Directive are to a large extent similar to the programme of Integrated Monitoring of the Natural Environment, IPM. In Europe, the networks under ICP IM – Integrated Monitoring and ICP Forests, whose research programme results from the implementation of the provisions of the LRTAP Convention, operate within such a system.

In accordance with the provisions of the NEC Directive, in terms of air pollution parameters, each Member State should at least take into account areas with high (nationwide) deposition rates of acidifying and eutrophying substances and eutrophication and high ozone concentrations. In addition, for long-term comparisons, reference locations with low deposition/concentration values should also be selected. These low concentrations are precisely the regions where the background measurement stations for EMEP and GAW/WMO purposes are located.

European Parliament resolution of 25 March 2021 on implementation of the Air Quality Directives 2004/107/EC and 2008/50/EC (2020/2091(INI)) (2021/C 494/07) (OJ C of 8 December 2021), considering that the deposition of nitrogen compounds, emitted into the air as NO_x and NH_3, can cause eutrophication, i.e. an over-supply of nutrients, and that sulphur and nitrogen compounds have an acidifying effect, both of which have a detrimental effect on terrestrial ecosystems, and that pollution by toxic metals, such as lead (Pb), mercury (Hg) or cadmium (Cd), can have a detrimental effect on plants and animals as well as humans and although their concentration in the atmosphere may be low, they still contribute to the deposition and accumulation of toxic metals in soils, sediments and organisms, calls on Member States to improve monitoring networks in their territory and to carry out research in this field. Furthermore, it draws attention to the need to revise air quality standards and to extend the monitoring requirement to other unregulated pollutants which have a negative impact on health and the environment in the EU such as ultra-fine particles, soot, mercury and ammonia, and calls on the Member States to improve monitoring networks on their territory and to carry out research in this field. The research is to include spatial and temporal assessment of the data and evaluation of impacts on quality of life and ecosystems. The Resolution also recommends that the public be informed in annual publicly available reports on the results obtained from monitoring networks.

4.5. Precipitation chemistry monitoring requirements under the Convention on the Protection of the Marine Environment of the Baltic Sea Area (HELCOM).

The current guidelines for conducting monitoring of pollutants of atmospheric origin reaching the Baltic Sea and thus affecting their levels in seawater, organisms and bottom sediments are contained in HELCOM Recommendation 37-38/2, which entered into force on 16 June 2016, replacing the previous one. The Recommendation refers to the provisions of the Convention on the Protection of the Marine Environment of the Baltic Sea Area, 1992 (Helsinki Convention), in which States Parties undertake to measure and assess emissions of pollutants reaching the Baltic Sea from point and diffuse sources using jointly developed methodologies based on scientific research. The Recommendation also refers to the provisions of Directive 2008/56/EC of the European Parliament and of the Council of 17 June 2008 establishing a framework for community action in the field of marine environmental policy (Marine Strategy Framework Directive), which imposes an obligation on EU Member States to develop strategies to achieve good environmental status in the marine environment in areas under their jurisdiction. What is an important element in this context is the determination of the type and magnitude of pressures (in this case, atmospheric inputs of pollutants) and, on this basis, action plans reducing the pressures (emission reductions). Directions and action plans to reduce eutrophication and pollution with hazardous substances, to which the Recommendation refers, are also set out in the Baltic Sea Action Plan. According to the Recommendation, monitoring programmes for atmospheric pollutants reaching the Baltic Sea should take into account the EMEP recommendations on atmospheric pollution monitoring and modelling, quality assurance, data reporting, management and production of emission inventories.

The Recommendation recommends to the States Parties to the Helsinki Convention that each States should continuously collect data on air pollution and precipitation that will enable:

- qualitative and quantitative assessment of the inflow of atmospheric pollutants to the Baltic Sea and its catchment areas,
- validation of models used for calculating pollution loads and to assess the pressures on the marine environment resulting from their inflows,
- supporting decisions on emission reduction measures,
- their use in conjunction with models to verify the effectiveness of actions taken to reduce emissions.

According to the Recommendation, each State should have at least one monitoring station on the coast or on an island with simultaneous sampling and measurement of air and precipitation pollution in accordance with the requirements of the monitoring programme in Table 4.36. It is recommended that the monitoring programme in each country should compulsorily include the parameters and pollutants indicated as mandatory programme (Table 4.36, 4.37). Additional pollutants may be monitored voluntarily at some stations. Monitoring of pollutants should include both precipitation (Table 4.36) and air and aerosols (Table 4.37).

Each country should report annually on the data collected by agreed deadlines in an agreed electronic format. Any change in the declared scope of the monitoring, analyses and procedures should be reported and the potential impact of these changes on the information on pollutant loads and data quality should be indicated

Each country should update, at the end of each year, estimates of emissions of selected pollutants in accordance with the Joint EMEP/CORINAIR Atmospheric Emission Inventory Guidebook and agreed data reporting formats within agreed deadlines

The Recommendation also recommends that the institutions responsible in each country for sample collection and analysis should follow standardised procedures: sampling, analysis and quality assurance and control with particular reference to the guidelines in the EMEP Handbook and internationally agreed and recommended procedures.

According to the Recommendation, countries should cooperate to develop the best methodologies for sampling, methods of analysis, contaminant transport models and methods for assessing the pressures associated with atmospheric pollution inputs to the Baltic Sea.

Table 4.36 Mandatory and voluntary scope of monitoring of pollutants in atmospheric precipitation according to HELCOM Recommendation 37-38/2

Pollutants in precipitation		
Type of pollutant	**Mandatory programme**	**Voluntary national or joint programmes**
Maximum sampling time	1 month	1 month
Precipitation	Precipitation amount	
Biogenes	NO3-; NH4+	total phosphorus
Main ions		Na+; Mg2+; Cl-; K+; Ca2+; SO4-; pH; conductivity
Metals	Cd; Pb	Cr; Ni; Cu; Zn; As; Hg and Fe
Persistent organic pollutants		γ-HCH (lindane).
Polychlorinated biphenyls (PCBs)		Congeners 28, 52, 101, 118, 138, 153, 180.
Polycyclic aromatic hydrocarbons (PAHs)		Benzo(a)pyrene

Brominated diphenylethers PBDE (congeners 28, 47, 99, 100, 153, 154) are a parameter not included in the Recommendation for measurement in atmospheric precipitation but important for the assessment of the marine environment. This indicator may be considered as conditional at HELCOM stations.

Table 4.37 Mandatory and voluntary scope of atmospheric pollution monitoring according to HELCOM Recommendation 37-38/2

Air and aerosol pollutants

Type of pollutant	**Compulsory programme**	**Voluntary national or joint programmes**
Maximum sampling time	24 hours	1 week
Biogenes		
air – gas	NO2	
air – gas	HNO3; NH3.	
air – particles	NO3-; NH4+.	
or alternatively		
sum of the phases	(HNO3 + NO3-)	
sum of the phases	(NH3 + NH4+).	total phosphorus
Metals		
air		Hg
particles		Cr; Ni; Cu; Zn; As; Cd; Pb; Hg and Fe
Persistent organic pollutants		γ-HCH (lindane).
Polychlorinated biphenyls (PCBs)		Congeners 28, 52, 101, 118, 138, 153, 180.
Polycyclic aromatic hydrocarbons (PAHs)		Benzo(a)pyrene

4.6. Guidelines for Monitoring under the World Meteorological Organization GAW/WMO Programmes

One of the main aspects of the GAW/WMO mission is to organise, participate in and coordinate the assessment of atmospheric chemistry on a global scale. Thus, GAW provides reliable scientific information for decision makers, supporting international conventions and contributing to a better understanding of climate change and long-range transboundary air pollution.

The basis of the GAW programme is a network of measurement stations, consisting of global and regional measurement stations, supplemented by measurements from cooperating stations. Both global and regional stations are operated by national meteorological services or other national scientific organisations of the host countries. Worldwide, GAW stations operate in more than 80 countries. Currently, GAW coordinates the activities and data from 30 global stations, more than 400 regional stations and about 100 cooperating stations operated by cooperating networks. A list of stations and all information related to their location and operation can be found on the GAWSIS website https://gawsis.meteoswiss.ch/GAWSIS/#/ .

GAW global stations are primarily designed to observe variables under background conditions, i.e. without permanent significant influence of local pollution sources. These stations, in addition to fulfilling the requirements for regional GAW stations, must meet the following conditions:

- measure at least two variables in at least three of the six main areas of GAW, with full implementation of the GAW quality assurance system.

- have a strong research programme in support of the GAW programme, experience in data analysis and interpretation in their country, and if possible support from more than one agency, with demonstrated experience on research campaigns and/or scientific products in the last at least three years of operation as GAW regional stations, have documented quality of research confirmed by audits, and submit data on at least two variables from at least three of GAW's main areas of interest to the respective World Data Centre(s) (WDC) within the last at least three years within one year after the completion of the surveys.

GAW regional stations in particular are to meet the following requirements:

- they shall be located so that the variables measured are representative for the region and not influenced by significant local sources of pollution or at least that the most frequent directions of inflow are the smallest possible amount of pollutants,
- there should be long-term observations of at least two variables among the six main areas of interest for GAW (ozone, aerosols, greenhouse gases, reactive gases, UV radiation, precipitation chemistry/total deposition); to make the data usable for multiple purposes, it is advisable to study more than one of these elements,
- the standard in situ meteorological observations necessary for the accurate determination and interpretation of GAW variables, i.e. at least measurements of temperature, humidity, atmospheric pressure, wind speed and direction, should be carried out with known accuracy and precision,
- conditions must be provided, namely, adequate electrical power supply, air conditioning, premises and means of communication, to enable the continuous acquisition of data series with a completeness of more than 90% (i.e. less than 10% of lost data).
- there should be staff trained in the maintenance of station equipment,
- the observations made there for the purpose of GAW should be of known quality, met the GAW Quality Assurance (GAWQA) principles and procedures, linked to the GAW Primary Standard,
- data and related metadata should be submitted to one of the GAW World Data Centres no later than one year after the observation took place; changes to metadata, including measuring instruments and their location, observation and laboratory procedures, should be reported to the responsible World Data Centre (WDC) in a timely manner (according to the WIGOS metadata standards https://community.wmo.int/activity-areas/wigos),
- when there is a special need, data should be sent to a designated data distribution system in near real time,
- station characteristics and observation programme should be regularly updated in the GAW Station Information System (GAWSIS),
- the station logbook, which contains a record of observations made and actions likely to affect the observations, should be maintained and used in the data validation process.

The Strategy also defines conditions for mobile stations and local stations. The role of local stations is to support local research related to the urban environment and at locations exposed to non-remote emissions (e.g. from biomass burning). GAW local stations fulfil the same requirements as regional stations, except for the location requirements.

The range of measurements recommended by the GAW for the study of precipitation chemistry (WMO GAW No. 228, WMO GAW Implementation Plan, p. 57) includes total deposition, defined as the sum of wet and dry deposition. Direct measurements of dry deposition are difficult to perform due to the requirements for highly sophisticated methods and instrumentation (Wesely and Hicks, 2000), so the best method currently available for determining dry deposition is an estimation technique, which involves measuring the concentrations of gases and particles in the air and multiplying them by their deposition rates obtained from the model (Vet et al., 2014). Measurements of total deposition in the atmosphere include:

- pH of wet deposition,
- wet deposition conductivity,
- alkalinity of wet deposition,
- chemical composition of wet deposition (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, organic acids, NO_2^-, F^-, PO_4^{3-}).

The updated manual for the GAW Precipitation Chemistry Programme, published in November 2004 (GAW Report No. 160, https://www.qasac-americas.org/manual), provides detailed guidelines to be met by stations implementing the GAW precipitation chemistry programme.

Firstly, it provides guidance on the location of precipitation chemistry programme stations.

The choice of the location of measuring stations for the collection of precipitation for the study of its quantity and chemical composition is of fundamental importance in the design of the network of precipitation chemistry stations. First of all, the sites selected for precipitation sampling should be representative for larger areas.

Global stations are intended to provide measurements to address global issues such as climate change or stratospheric ozone depletion, as well as measurements of other key parameters. Global stations are usually located in remote areas and have pollution levels that are very low or at background levels, representative of large-scale atmospheric processes.

Regional stations, on the other hand, provide atmospheric measurements to address regional environmental problems, such as wet and dry acid deposition, long-range transport of pollutants, biogeochemical cycles, biomass burning, biogenic sources and sinks of greenhouse gases and others. Regional stations are located at sites less distant than global stations and have pollution levels representative of an area on the order of several hundred kilometres.

In particular:

1) Global stations should be located in remote areas, e.g. islands, mountain ranges, forest reserves:

a) where no significant changes in land use are expected within a radius of 30-50 km in all directions for up to 50 years;
b) away from major population centres, industrial centres, major motorways and airports;
c) in places where the effects of major natural phenomena such as volcanic eruptions, forest fires and dust storms are absent or very rare;
d) where it can reasonably be assumed that ambient air:
    - is free of local pollution,
    - is free from regional pollution for at least 60% of the time, evenly distributed over the year, and
    - contains only dilute traces of chemicals transported to the site by long-range transport of pollutants from sources at least 30-50 km away;
e) where a full set of measurements from ground-based meteorological stations is available.

2) Regional stations should be located:

a) in rural areas sufficiently distant from centres of population and and industrial centres, so that the contribution from these sources of air pollution is absent for most of the year;
b) in areas normally kept clear of nearby agricultural or other land use sources, e.g. highways and unpaved roads, construction activities, mining activities and mineral extraction;
c) on or near meteorological/climatological stations, at which ground-based observations and possibly radar or radiosonde measurements are conducted.

Care should be taken to ensure that both global and regional stations are representative of the region in terms of natural and anthropogenic emissions and topographical conditions. It should be assumed that the stations will operate for at least ten years.

This document (GAW Report No. 160) also sets out detailed recommendations and requirements for the measurement of the chemical composition of precipitation and wet deposition.

Sites selected for precipitation chemistry and wet deposition measurements should represent the region in which they are located. Sites in the immediate vicinity of urban or industrial areas should be avoided. Table 4.38 provides detailed recommendations for the minimum distances from various sources of anthropogenic and natural emissions at which global and regional stations should be located. This information should be considered as a guideline.

Table 4.38 Guidelines for minimum distances for GAW precipitation chemistry stations (source: GAW Report No. 160)

Potential interference	Minimum distance from station (km)		Examples, comments and local considerations
	global	regional	
Point source of SO_2 or NO_X			If emission sources (such as power plants, refineries, chemical plants, steel mills or other large industrial facilities) are located windward of the collector, the distances should be doubled
>100 tonnes per year	50	20	
>1000 tonnes per year	100	50	
Large industrial complex	150	50	
City, population 1,000-10,000	25	10	Future population growth and associated land use should be carefully considered, particularly for towns and villages near stations. If population centres are located to windward of the collector, the distances should be doubled.
City, population 10,000-25,000	50	20	
City, population 25,000-100,000	100	50	
City, population >100,000	200	100	
Main motorway, airport, railway, shipping lane, port	25	5	Mobile sources of pollution, such as air, ground or waterborne traffic or the road on which they travel (e.g. runway, taxiway, street, tracks or navigable river) should not be within 500 m of a collector.
Secondary road, heavily used	5	1	The local road network around the measurement site is of particular concern. The intensity of intensity and type of traffic as well as the road surface have a major impact on the station.
Secondary road, little used	1	0.5	
Livestock/ fattening farms	50	2	Acceptable distances will vary considerably depending on the size of the farm. Even small concentrations of animals should be kept at a distance of no less than 500m. If there is an odour of feedlot, barn or animal waste in the

Potential interference	Minimum distance from station (km)		Examples, comments and local considerations
	global	regional	
			collector it means that the farm is too close.
Intensive agricultural activities	10	2	Open storage of agricultural products, fuels, vehicles or other materials should be located not less than 500 m from the collector.
Limited agricultural activity	1	0.4	Small storage facilities for agricultural products, fuels or other materials should be located at least 200 m from the collector and be leakproof
Parking area or large paved area	0.5	0.2	Parking areas and manoeuvring yards must not be closer than 300 m from the collector.
Building with fuel combustion	1	0.4	
Waste water treatment plant	20	2	
Active volcanoes, fumaroles, etc.	100	20	Avoid zones of geothermal activity - geysers and springs can be a source of emissions.
Natural sources of salt, dust, alkali	2	2	Samples can be contaminated by wind-borne materials from saline and alkaline plains, as well as by marine aerosols from the coast.
Tree line, building	0.05	0.05	

Ideally, before locating a GAW station, a rigorous assessment of the impact of local emissions on the chemical composition of air and precipitation at the site should be carried out. This assessment would take into account meteorological and topographical conditions, as well as estimated emissions from the sites listed in Table 4.37. In practice, such an assessment could be carried out using data collected at the station over a period of at least one year to assess the representativeness of a station.

Here are some general comments:

- representative exposure to air masses is very important. The station should be located on flat or moderately undulating ground. Valleys should be avoided. If valleys cannot be avoided, the station should be located above the nocturnal inversion layer which usually forms in valleys. Coastal sites with pronounced diurnal wind shifts due to land-sea breeze effects are not recommended. Sites located too close to trees or towers, which may not only change wind speed/direction affecting precipitation uptake but may also emit or absorb certain air pollutants, should also be avoided.
- Stations should not be located close to emission sources. Natural emission sources such as geothermal areas, volcanoes and areas subject to excessive windblown dust should be avoided. Marine aerosols should be avoided by locating the station sufficiently inland from the coastline.
- particular attention should be paid to industrial activities and sources in associated with suburban and urban areas. Power plants, chemical plants and manufacturing facilities should be located at least 50 km from the station, preferably further. These distances should be increased to 100 km if the facilities are located on the side from which the wind is most likely to blow. The same criteria apply to suburban/urban areas with a population of 25 000. The station should be no closer than 100 km or 200 km to human centres of more than than 100 000 if on the windward side. It shall be assumed that those located between 100 km and 200 km industrial and urban sources are sufficiently attenuated by regional air masses.

Additional requirements at the station location

The station should be accessible in both summer and winter and located where the risk of vandalism is low. The location of the precipitation container and a standard rain gauge should meet the following criteria to the extent possible (Figure 4.36):

1. Install the collection container and rain gauge on unaltered natural ground. Naturally vegetated, horizontal areas are preferred, but grassed areas and slopes up to ±15% are acceptable. Sudden changes in slope within a 30 m radius of the precipitation collector should be avoided. There should be ground cover within approximately 30 m of the collector. On agricultural land, a vegetated strip shall be provided around the precipitation collector, at least 30 m away from crops or cultivated soil.
2. Vegetation in the station area shall not extend higher than 0,5 m and not higher than half of the height of the precipitation container or rain gauge, measured from the ground to the opening of the precipitation container.
3. Make sure that objects in the vicinity (obstacles, constructions, buildings) do not project into the precipitation tank or rain gauge at an angle greater than than 45° from the surface, i.e. the angle formed by the surface, the precipitation tank and the top of the object is not greater than 45°; 30° is the optimum setting, but 45° is the largest acceptable setting. As shown in Figure 4.26, the distance from the precipitation tank to the facility must be at least equal to the height of the facility, and preferably twice its height. The buildings should also be twice the height of the rainfall tank and should not be closer than 30 m from the tank when located in the prevailing upwind direction

(windward side). Anemometer towers, poles and overhead wires are considered as structures and shall meet the same requirements.

4. To reduce wind turbulence, the base of the container should not be enclosed for precipitation. No object over 1 m in height that can deflect the wind shall be located within 5 m of the sampler or rain gauge.
5. The rain gauge shall be installed at a distance of between 5 and 30 m from the rainfall sampling tank according to the standards of the hydrological and meteorological service (h-m service), with the inlet area of the rain gauge being no higher than the inlet area of the precipitation tank.
6. In areas where more than 20% of the annual precipitation is in the form of snow, the rain gauge should be fitted with a suitable wind shield. It is recommended that the wind shield is installed by a meteorological expert.
7. In areas where the snow cover extends to more than 0.5 m, the container and rain gauge may be placed on a platform (or platforms). Platforms should not be higher than the maximum predicted snow depth. The precipitation tank should be equipped with a suitably counterbalanced snow roof in areas where snow represents 10% or more of the annual precipitation. If already installed, it can be left on the roof for the entire year.
8. If necessary, fences should be installed to limit vandalism or interference by animals. Open galvanised mesh fencing is recommended. The fence must meet the requirements in 3) and 4) above.

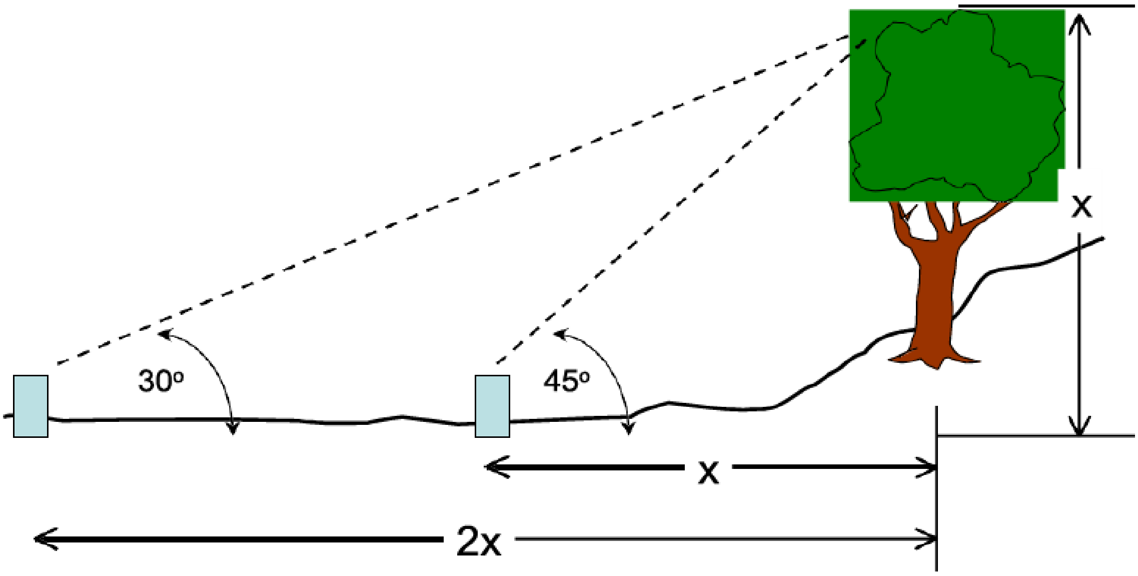

Figure 4.26 Guidance on the location of the precipitation collector and rain gauge in relation to nearby facilities (Source: GAW Report No. 160)

It is recommended that the precipitation chemistry station be located at a standard meteorological station, provided that this station meets the location requirements set out in this chapter. This increases the value of precipitation chemistry data by making meteorological measurements from the same location available for data interpretation. Meteorological data are particularly useful when unusual precipitation measurement results are reported.

A record, documenting each station that participates in precipitation chemistry and wet deposition measurements, should be available on file at the institution to which it reports. A description of the precipitation chemistry and wet deposition stations is provided as Appendix B to GAW Report No. 160 and wet deposition, including forms to document information about the location of GAW stations on a regional scale, a local scale and within the station itself. Periodic completion of these forms allows for documentation of station history that can be useful in interpreting the data. Tracking changes also allows the sponsoring agency to assess whether location criteria are being met.

Description of a GAW precipitation chemistry and wet deposition station

(GAW PRECIPITATION CHEMISTRY and WET DEPOSITION STATION DESCRIPTION) “B”

This appendix contains forms for describing GAW precipitation chemistry and wet deposition measurement stations. While there is no requirement to use these specific forms, documentation for every station should be available from the NMHS or other sponsoring agency. These forms can serve to guide the periodic review or audit of existing stations or the selection of a new or re-located station. Periodic documentation of site characteristics provides a chronology of changes that may be important in understanding the data at a station. Each NMHS or other sponsoring agency is encouraged to adopt these forms as part of their QC programme or create similar ones tailored to their specific needs.

PRECIPITATION CHEMISTRY AND WET DEPOSITION STATION DESCRIPTION

Date (yyyy/mm/dd) (circle one) New Site Site Change Revision

1. GENERAL DESCRIPTION

Identification:	Name	Site code (assigned by GAW):
Address		
Classification	(circle one) Global Regional Other (please specify)	
Coordinates	Latitude N/S (in decimal degrees)	Longitude E/W (in decimal degrees)
Elevation (m)	(above sea level)	

2. ADMINISTRATION

Station Contact Person	
Mailing Address	
Telephone	E-mail:
Laboratory Contact Person	E-mail:
Laboratory Mailing Address	
Laboratory Telephone	E-mail:
Station Ownership	
Operating Agency	
Is site part of another network?	(specify)

3. INSTRUMENTATION

Instrument	Type/Model	Height of orifice above ground (m)
Precipitation Sampler		
Precipitation Gauge		

4. REGIONAL DESCRIPTION OF THE STATION (10 km – 50 km)

Attach a map. Do not leave blanks, indicate none or unknown

Item	North Direction (NW-NE)	East Direction (NE-SE)	South Direction (SE-SW)	West Direction (SW-NW)
Air pollution sources >10 tonnes per year (SO_X, NO_X, NH_3, HCl, etc.) For global site, include air pollution sources >1000 tonnes per year out to 150 km				
Main roads with >5 000 vehicles per day (estimate traffic density)				
Cities with more than 10 000 persons For global site, include cities with a population > 100 000 out to 200 km Give approximate populations				

5. LOCAL DESCRIPTION OF THE STATION (150 m – 10 km)

Position	North Direction (NW-NE)	East Direction (NE-SE)	South Direction (SE-SW)	West Direction (SW-NW)
Roads with estimated traffic densities >1000 vehicles per day				
Airports, railways or ship routes, with estimated traffic densities				
Irrigated fields, farms (type of crop and/or animal/ livestock species), animal confinement facilities				
Air pollution sources >10 tonnes per year (SO_X, NO_X, NH_3, HCl etc.)				
Cities or towns with >1000 persons and their approximate populations				

6. ON-SITE DESCRIPTION (within 150 m)

Attach a sketch. Do not leave blanks, indicate none or unknown

Position	North Direction (NW-NE)	East Direction (NE-SE)	South Direction (SE-SW)	West Direction (SW-NW)
On-site trees, poles, fences, buildings (estimate heights)				
On-site ground cover (estimate percent gravel, grass, bare soil, rock, etc.)				
Slope of the site (range in degrees)				
Next to site: incinerators, domestic heating, parking lots, storage of fuel or agricultural products, poultry or other livestock farms				
Land cover surrounding the site: forest, streams, river, lake, marsh, farms, fields, tundra, desert, grassland, etc.				
Roads (including estimate of traffic density*)				

*Describe roads with >100 vehicles per day for global sites and roads with >1,000 vehicles per day for regional sites.

The following list provides additional valuable documentation to supplement the description in Annex B:

1) A map of the area, preferably a topographic map (scale 1:24 000 or similar), with the location of the station marked on the map with an x in a circle. Neighbouring maps should be included if the site is near a map boundary. If a map is not available, sketches of the region and area of the station should be prepared. The sketches should show the location of air pollution sources and the land use and land cover surrounding the site.

2) A sketch of the station itself showing the location of all instruments and the location of structures, fences and other actual or potential obstacles to the flow of air and the free passage of precipitation to the measuring instruments located at the station.

3) Colour or black and white photographs of the area showing the area surrounding the collector in eight directions (i.e. photographs taken facing N, NE, E, SE, S, SW, W, NW). The photographs should be taken 5 to 7 m from the sampler with the sampler and rain gauge in the foreground. Mark the back of each photo with the station name, date and direction.

Station staff should keep copies of these materials in their own records and for use in periodic site assessments.

The GAW Station Information System (GAWSIS) contains the official directory of GAW stations and cooperating networks. GAWSIS offers users an open database that documents:

1. stations, including descriptions and their status,
2. list of measurement programmes and data availability,
3. authorised contact persons,
4. bibliographical references and supporting documents.

Information on newly established or closed stations should also be reported to GAWSIS.

The WDCPC (World Data Centre for Precipitation Chemistry) does not maintain a record of GAW precipitation chemistry and wet deposition station network documents, i.e. photographs, maps and sketches, site history, site quality assurance information, etc. It is the responsibility of each hydrometeorological service or sponsoring agency to maintain an archive of these records and make relevant information available to interested data users.

It is recommended that each station should be inspected by network staff annually and independently audited every 5 years (Martini and Mohnen, 1994). Any changes should be documented and station description forms, maps and sketches (as described earlier) updated. Copies of the original and updated documentation should be kept in the archives of the hydrometeorological service (the agency conducting/sponsoring the measurements). This applies to changes at regional and local scales, as well as at the station itself. Examples of changes that should be documented include: the construction of a new industrial complex many kilometres away; the development of cities and suburbs not far from the station; the start of new agricultural activities near the station; and the placement of new (interfering) instrument towers near a rainfall harvesting tank or rain gauge. Where changes are considered to have compromised the chemical and spatial representativeness of the site, remedial action should be taken to bring the site back into compliance. If this is not possible, the station may have to be stripped of its global or regional station status, or in extreme cases even terminated from participation in the GAW programme.

When documenting changes at the station, the following guidelines should be complied with:

- relocation of a precipitation container or rain gauge by more than 30 m from the previous location requires new sketches and photographs of the site. The new location shall be marked on a topographic map of the station area.
- If a station is moved by more than 1 km, it is considered a new station. It will be assigned a new station identifier. The new station coordinates and the start dates of the measurements should be entered.
- The reasons for changes in the deployment of equipment or relocation of stations should be documented in writing.

Records of all station changes must be kept by the hydrometeorological service or sponsoring agency and made available to interested data users upon request. Information on changes or station closures must be reported to the WDCPC and GAWSIS.

For precipitation chemistry measurements, wet-only sampling is recommended. GAW recommends a 24-hour sampling period, with sampling taking place at a fixed time each day, preferably at 9:00 am local time. Where the cost of site visits and analytical services makes daily sampling makes daily sampling impractical, a multi-day sampling period of up to 7 days (i.e. weekly sampling) is recommended. The GAW programme strongly advises against sampling over seven days as the chemical composition of the samples changes as the sampling period increases.

Whether samples are taken daily or weekly, it is important to avoid taking samples during precipitation. This reduces the high probability of contamination of the sample during rain or snow. In such a situation, it is best to wait for a break in the precipitation, and if the precipitation has not stopped after a few hours, the sample should be taken and recorded on the sample history form.

At least two measurements shall be reported for each sampling period: the volume of the sample from the collector and the amount of precipitation from a standard rain gauge. These measurements shall be compared with each other for a routine check of the performance of the collector and rain gauge. Significant differences may indicate that a measurement error or failure has occurred in one or both instruments.

Sample volume must be measured gravimetrically because this method is efficient, accurate and less prone to contamination and spillage than volumetric measurements.

Irrespective of the length of the sampling period, there is always the possibility of chemical degradation of the sample in the field during sampling, during transport from the field to the laboratory and prior to analysis in the laboratory. It is recommended practice to refrigerate samples in the laboratory at a temperature below 4˚C prior to analysis.

In addition to sample volume and precipitation amount measurements from a rain gauge, some programmes, such as EMEP, record pH and conductivity measurements in the field. These values are compared with laboratory measurements to assess chemical changes that may occur between the field and the laboratory. GAW does not recommend field chemistry measurements unless they are supported by a comprehensive QA/QC program so that the measurements can be verified.

GAW recommends as mandatory analysis of the following substances in precipitation samples: sulphate, nitrate, chloride, sodium, potassium, magnesium, calcium, ammonium ions, pH and conductivity. Hydrogen carbonate (formerly bicarbonate ion) must either be analysed or calculated. Total nitrogen and total phosphorus may also be important in some regions, but their analyses are not currently required by GAW. Formate and acetate analyses are recommended for areas suspected of having high concentrations of organic acids, and oxalate measurements can be used to track biomass burning.

The list of substances provided for chemical analysis recommended by GAW, together with the preferred analytical method, is presented in Table 4.39 below.

Table 4.39 List of substances provided for chemical analyses recommended by GAW, together with the preferred analytical method (source: GAW Report No. 160)

Component	**Status**	**Preferred method**	**Alternative method**
sulphates, nitrates, chlorides (Cl^-, NO_3^-, SO_4^{2-})	mandatory	IC	
ammonia NH_4^+	mandatory	FIA	IC
calcium, magnesium, sodium, potassium (Ca^{2+}, Mg^{2+}, Na^+, K^+)	mandatory	ICP-AES	IC, FAA
pH	mandatory	electrode	
Conductivity	mandatory	conductivity sensor	
bicarbonates HCO_3^-	mandatory	IC (recommended for pH>6)	calculated from pH
total nitrogen	voluntary	FIA – with digestion	
total phosphorus	voluntary	FIA – with digestion	
organic acids	voluntary	IC	IEC

IC – Ion Chromatography

ICP-AES – Inductively Coupled Plasma Atomic Emission Spectrometry,

FIA – Flow Injection Analysis colorimetry,

IEC – Ion Exclusion Chromatography,

FAA – Flame Atomic Absorption

For bicarbonate (HCO_3^-) the IC method is recommended for stations where precipitation pH is greater than 6, while it can be calculated when precipitation pH is less than 6.

The GAW Manual also contains a detailed discussion of sample handling in the laboratory and the recommended analytical methods.

It also contains information on data handling, analysis and reporting. For several years now, in order to avoid double reporting, data to GAW, but also to HELCOM are transmitted through the EMEP system.

4.7 Information on chemical analysis methods of atmospheric deposition for use in project implementation

Table 4.40 below shows the atmospheric deposition chemical analysis methods recommended for use in project implementation.

Table 4.40 Preferred and alternative (if any) methods for chemical analysis of atmospheric deposition [own work based on EMEP, GAW/WMO and HELCOM documents]

Parameter	Preferred method	Alternative method
Precipitation	rain gauge	
Precipitation amount	gravimetric	
SO_4^{2-}	IC	
NO_3^-	IC	Griess spectrophotometric method after reduction
NH_4^+	FIA	IC, CFA, indophenol
H^+ (pH)	potentiometric	
Na^+	FAAS, ICP-OES	IC, ICP-MS
K^+	FAAS, ICP-OES	IC, ICP-MS
Ca^{2+}	FAAS, ICP-OES	IC, ICP-MS
Mg^{2+}	FAAS, ICP-OES	IC, ICP-MS

Parameter	**Preferred method**	**Alternative method**
Cl^-	IC	mercury (II) rhodanide spectrophotometric method
Electrical conductivity	conductivity	
Pb	ICP-MS, GF-AAS/FAAS	ICP-OES
Cd	ICP-MS, GF-AAS/FAAS	ICP-OES
Cu	ICP-MS, GF-AAS/FAAS	ICP-OES
Zn	ICP-MS, GF-AAS/FAAS	ICP-OES
As	ICP-MS, GF-AAS/FAAS	ICP-OES
Cr	ICP-MS, GF-AAS/FAAS	ICP-OES
Ni	ICP-MS, GF-AAS/FAAS	ICP-OES
HCO_3^- at pH>6 (calculated from pH at pH<6)	IC (recommendation for pH>6)	calculated from pH (for pH<6), titration
Hg	CV-AFS	ICP-MS, CV-AAS
PAHs	GC-MS	HPLC, GC-MS/MS
PCBs (polychlorinated biphenyls)	GC-MS	GC-ECD, GC-MS/MS
total phosphorus	FIA – with sample digestion	spectrophotometric method, CFA
total nitrogen	FIA – with sample digestion	calculation method (sum of NO_3^-, NH_4^+, NO_2^-, Kjeldahl nitrogen), CFA
HCB (hexachlorobenzene)	GC-MS	GC-ECD, GC-MS/MS
DDT/DDE	GC-MS	GC-ECD, GC-MS/MS
HCHs	GC-MS	GC-ECD, GC-MS/MS
Chlordane	GC-MS	GC-ECD, GC-MS/MS

Explanations:

CFA – Continuous Flow Analysis with spectrophotometric detection

CV-AAS – Cold Vapor Atomic Absorption Spectrometry

CV-AFS – Cold Vapour Atomic Fluorescence Spectroscopy

FAAS – Flame Atomic Absorption Spectrometry

FIA – Flow Injection Analysis

GC-ECD – Gas Chromatography with Electron Capture Detector;

GC-MS – Gas Chromatography Mass Spectrometry

GC-MS/MS – Gas Chromatography with tandem Mass Spectrometry

GF-AAS – Graphite Furnace Atomic Absorption Spectrometry

HPLC – High-Performance Liquid Chromatography

IC – Ion Chromatography

ICP-MS – Inductively Coupled Plasma Mass Spectrometry

ICP-OES – Inductively Coupled Plasma Optical Emission Spectrometry

5. Summary

This study analyses Polish and foreign documents and studies, as well as monitoring systems and data of the State Environmental Monitoring in order to design a new system of research and assessment of atmospheric deposition.

This report describes the current monitoring system of atmospheric precipitation chemistry in Poland, consisting of stations conducting measurements within the framework of atmospheric precipitation chemistry monitoring and assessment of deposition to the ground, background monitoring of atmospheric pollution for the needs of EMEP, GAW/WMO, HELCOM and the European Commission, and regional background stations conducting measurements of total deposition of heavy metals, including mercury, and polycyclic aromatic hydrocarbons, in accordance with the provisions of Article 4(9) of Directive 2004/107/EC.

An analysis of precipitation chemistry monitoring systems in selected European countries is carried out, focusing on the multi-program Norwegian experience, an analysis of the Baltic countries to determine the optimum atmospheric chemistry monitoring programme for assessing atmospheric inflow of substances to the Baltic Sea, and an analysis of monitoring programmes in selected countries neighbouring Poland, due to similarities in geographical conditions.

The requirements for precipitation chemistry monitoring stations under EMEP, ICP Integrated Monitoring, ICP Forests, GAW/WMO and HELCOM programmes and European Directives is described.

The methods of chemical analysis of atmospheric deposition recommended for use in the project is presented.

The analysis carried out reveals a number of good practices that are worth using in the new system being designed.

1. NILU:

- The Norwegian monitoring programmes have had a long-term perspective, which makes the observations made of value far beyond national interests. Involvement in international programmes is extremely important in order to develop standardised procedures for activities and to share knowledge on atmospheric composition and deposition. An open data sharing policy is a prerequisite.
- In addition to long-term perspectives, the close cooperation between the research and regulatory sectors in Norway allows for continuous renewal of the monitoring programme. This allows the measurement of pollutant data to move quickly from the screening/innovation level to the monitoring level, with the data providing important input for regulators.
- Different monitoring programmes benefit from sharing infrastructure (observatories, laboratories and databases). This is cost-effective and creates synergies between different environmental issues.
- To understand the effects and sources of air pollution and deposition, many different components need to be measured and confronted. For atmospheric deposition, the challenge is to have a sufficiently representative number of stations,

which is especially difficult in Norway where there are large geographical differences.

2. ČHMÚ:

- To check the precipitation quality data, ion balance calculations performed by the respective laboratory analysing the collected precipitation sample are routinely used. The difference between the amount of cations and the amount of anions in the sample must meet the permitted criteria, which vary slightly between organisations. In addition, a check is made by comparing the calculated and measured conductivity, which must also meet the permitted criteria (the method used so far also within the framework of monitoring of precipitation chemistry and assessment of deposition to the ground in Poland).
- Control is also exercised through the analysis of laboratory blanks, and field blanks are continuously monitored and evaluated to control the work during sampling and to control the changes occurring related to the transport, handling, storage and treatment of samples prior to the actual chemical analysis.

3. SHMU:

- At the Chopok high-mountain station, due to the occurrence of unfavourable weather conditions, sampling is carried out only by the bulk method.

6. Conclusions

In developing a new system of research and evaluation of atmospheric deposition in Poland, it is necessary to take into account the guidelines of international measurement programs and make use of good practices applied in other European countries.

Most of the requirements and recommendations of the international programmes concerning the location criteria and sampling procedures coincide with EMEP. In the manuals (handbooks) of programmes such as ICP IM there are references to the EMEP Manual (EMEP Manual, 2014).

In all international programmes, it is very important that the locations of the measurement points are selected so that they are representative of the larger area and not directly influenced by local emission sources or interferences due to topography. Another very important aspect is the very foundation of the precipitation collector, which should be in accordance with WMO location requirements for rain gauges.

Another important recommendation mentioned in the recommendations of the GAW programme concerning the siting of the precipitation chemistry station is its location near a standard meteorological station provided that the station meets the location requirements specified in this study. Standard meteorological observations conducted at the station (mainly temperature, humidity, atmospheric pressure, wind speed and direction) enable more accurate assessment and interpretation of the results of monitoring studies, which increases the value of the obtained data. Meteorological data are particularly useful when unusual results of precipitation sample analyses are reported.

What is an important issue concerning the operation of a precipitation sampling point is the provision of appropriate technical conditions for the proper and trouble-free collection and storage of samples at the station. The choice of the location of the sampling point should also take into account its accessibility at any time of the year, this is particularly important when it is necessary to take samples to the laboratory or repair of equipment by service staff.

The fact that the main objective of the EMEP level 1 strategy is to provide long-term measurements of physical and chemical atmospheric parameters is very important for the design of the new chemistry monitoring system. According to this strategy, level 1 activities should be a priority in extending the monitoring network in areas with a small number of stations. Bearing this fact in mind, while establishing a new monitoring system of precipitation chemistry in Poland, it is necessary to take into account the existing stations which meet the requirements of representativeness and have long-term measurement series. When selecting new locations, it is necessary to choose such which will ensure the completion of measurements within the next at least 10 years. Conducting monitoring measurements in a long-term perspective makes the observations of significant international value.

Another important point in the design of the precipitation chemistry monitoring network are the methods and frequency of precipitation sampling. The recommended precipitation sampling method for physical and chemical analyses of the basic parameters describing the quality of precipitation is the wet method. Total precipitation sampling is acceptable if there are circumstances that prevent the use of a wet collector or make it impractical. In this case the sampling point shall be located at a sufficient distance from sources of pollution and the recommended sampling frequency sampling frequency of 24 hours is recommended. In case of high costs or problems with daily sampling this period may be extended to a maximum of 7 days. For the determination of additional components such as heavy metals the sampling period may be 1 month.

The basic parameters determining the quality of precipitation are pH and conductivity. They give information on the general composition of a given sample and are important for checking the consistency of chemical analyses carried out. The pH index is the parameter used when calculating the ion balance, which serves to check the correctness of the analyses carried out. This parameter does not have to be measured directly at the monitoring station, as it is currently practised in chemical monitoring stations in Poland, it may be performed later in the laboratory. Possible pH measurements conducted in the field should be supported by a comprehensive QA/QC programme, which ensures quality control of conducted measurements.

Cooperation between countries in international programmes should be used to develop common, standardised methods for the collection and analysis of precipitation samples and procedures for quality assurance and control, and for sharing knowledge of atmospheric composition and deposition.

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