CONCEPT OF MODERNISATION AND OPTIMISATION OF DEPOSITION MEASUREMENTS IN POLAND

Task 2: Determination of optimum ranges of substances and parameters to be studied within the framework of precipitation chemistry (wet precipitation)

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, Climate Change Mitigation and Adaptation sub-programme, funded by the European Economic Area Financial Mechanism 2014-2021

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Table of contents

List of Tables

List of Figures

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, as well as 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.

The assessment of physicochemical composition of precipitation in Poland is one of the subsystems of air quality monitoring. This task is carried out by the Chief Inspectorate of Environmental Protection (CIEP), based on the *Executive Programme of State Environmental Monitoring for 2022 Air Quality Monitoring* (Executive Programme...2022).

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 for the Study

The basis for the study is Agreement No. GIOŚ/ZP/380/2021/DMŚ/MFEOG, concluded on 22.12.2021 between the State Treasury – the Chief Inspectorate of Environmental Protection and the Institute of Meteorology and Water Management – National Research Institute.

4. Scope of the Study

This report shall include a proposed range of measurements and physicochemical analyses, together with information on precipitation sampling methods for wet deposition, aerosol measurements (relevant for dry deposition estimation) and physicochemical analysis methods, for each individual substance, as well as a proposal for the sampling regime and the physicochemical analysis regime.

5. Guidelines affecting the proposed scope of physicochemical measurements and analyses

5.1 Information on changes in wet deposition of selected substances across Poland and tracking trends in this area and determining the loads of substances deposited to the ground

The developed proposal of the measurement range ensures provision of information on changes in wet deposition of selected substances in the whole area of Poland and monitoring of trends in this respect, as well as determination of loads of substances deposited to the ground. The necessary condition to provide such information are homogeneous data series obtained from measurements complying with the following conditions:

- uniform methodology for collecting samples,
- as few laboratories as possible performing qualitative and quantitative compositional analyses of samples taken to maintain the quality and comparability of analyses,
- uniform analytical methodologies,
- universal sampling devices adapted to the environmental conditions of the sampling points: automatic wet-only or manual collectors, or bulk collectors in locations with particularly difficult weather conditions (occurrence of high snowfall and strong winds in mountainous areas and strong winds in coastal areas),
- permanent one-person supervision and responsibility for sampling at the measuring point (as recommended by the NILU).

In order to provide information on changes in wet deposition of selected substances throughout Poland, it is necessary to select appropriate locations, considering:

- selection of measurement points of atmospheric pollution background in areas with the smallest influence of anthropogenic pollution of various origin (according to the NILU recommendations),
- selection of measurement points which will provide a qualitative and quantitative assessment of the inflow of atmospheric pollutants into the Baltic Sea and its catchment area,
- the selection of non-urban and suburban measurement points with the lowest contribution of anthropogenic pollution from traffic and heating sources,

Statistically significant long measurement series are needed to follow trends in wet deposition results. The Norwegian NILU experience indicates the need to obtain averages over at least five years of survey periods to reduce the impact of annual fluctuations (NILU Report, 2021). Measurement stations should be located in such a way as to ensure that measurements are made over at least a ten-year period.

5.2 Information on wet deposition of substances for water management purposes

Water management covers groundwater and surface water, distinguishing between inland surface water (standing and running), territorial sea and internal marine waters, transitional waters and coastal waters, which are main unit spatial unit of management water management Journal of Laws item 2233 of 03.12.2021, the Water Law). Specific supervision covers:

- bodies of water intended for the extraction of water for human consumption,
- bodies of water intended for recreational purposes (bathing waters),
- areas sensitive to eutrophication caused by pollution from municipal sources, defined as the enrichment of waters with nutrients, in particular nitrogen or phosphorus compounds, causing an accelerated growth of algae and higher forms of plant life, resulting in undesirable disturbance of the biological balance of the aquatic environment and a deterioration in the quality of these waters,
- areas designated for the protection of habitats or species referred to in the provisions of the Nature Conservation Act of 16 April 2004, for which the maintenance or improvement of the state of the waters is an important factor in their protection,
- areas designated for the protection of aquatic animal species of economic importance.

The deposition of pollutants with wet precipitation is one of the sources of area pollution and can negatively affect the aquatic environment. The diversity of ecosystem responses to acid deposition makes it very difficult to assess the change in environmental status caused by acidification. Therefore, the following measurement set is proposed as required to determine the mineralization of wet precipitation: pH, conductivity, Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+} as well as total nitrogen and total phosphorus are very important in areas near large water bodies.

Precipitation is characterised by a high degree of mineralisation. Acid rain is the result of air pollutants emitted into the atmosphere, mainly acid-forming sulphur and nitrogen compounds. The emitted gases: sulphur dioxide, nitrogen oxides, ammonia undergo chemical reactions with water in the atmosphere, transforming into proper mineral acids. They pose a threat not only to the natural environment and cause negative changes in the structure and functioning of terrestrial and aquatic ecosystems, but also to the technical infrastructure (e.g. water structures, hydrotechnical equipment, power lines). Describing acid-forming compounds in precipitation, we mention hydrogen ions H^+, oxygen compounds of sulphur and nitrogen (sulphates, nitrites and nitrates) and chlorides. When discussing the acidity of precipitation we talk about the concentration of free hydrogen ions contained in it. One of the basic factors characterising the acidifying properties of precipitation is the presence and inflow of hydrogen ions to the ground. The parameter that determines the reaction of precipitation water is the pH index. For many years, due to the presence of acidifying substances in the atmosphere, precipitation waters in Poland have been on average acid waters (pH below 5.6). The occurrence of acidification of precipitation waters is confirmed by research commissioned by the State Environmental Monitoring, Inspection of Environmental Protection *(Monitoring of precipitation chemistry and assessment of deposition to the ground in the years 2021-2022, Annual Report for 2020).*

The values and variability of the most important soil and water parameters, which depend on the deposition of acidifying substances, including those found in rainwater, are the result of complex catchment processes.

Impact of reducing the deposition of sulphur and nitrogen on surface waters is the subject of much research. The directions of changes in the chemical composition (pH and alkalinity) of waters are not always as predicted. However, many rivers and lakes, especially less acidified ones, do not show such rapid signs of reversal of chemical changes or do not show them at all. This may be related to the phenomenon of a simultaneous decrease in base cation concentrations along with a decrease in sulphate and nitrate concentrations, resulting in no reduction in acidification. The chemical changes in soils and waters of the catchment caused by the decrease in acid deposition are also influenced by other factors related to the circulation of elements in nature and the intensification of certain elements. These include, for example, changes in the nitrogen cycle through an increase in nitrogen uptake by vegetation and microorganisms in the catchment associated with improving environmental conditions. The influence of global climate change on the variability of the chemical parameters of the environment is increasingly being taken into account. An important element of the research work is the assessment of trends in chemical and biological changes in the waters. This is important for determining the necessary degree of reduction in pollution emissions into the atmosphere and allows predictions of changes in catchment areas depending on from changes in size deposition. Surface water at sites that are poorly exposed to local emissions are very good indicators of global change, responding to it more quickly and clearly than soils or forest ecosystems (Rzychoń D., 2009).

Another important factor in water management is eutrophication, or overfertilization. Eutrophication consists in the enrichment of water bodies with nutrients, biogenic elements, mainly nitrogen and phosphorus, but also potassium and sodium, which cause excessive production of algal biomass or cyanobacteria, manifested for example by blue-green algae bloom. Water quality is determined by its trophic state. An increase in trophicity is associated with an increase in the growth of aquatic organisms. Accelerated growth of aquatic organisms results from high concentrations of phosphorus and nitrogen, which enter the water bodies in mineral form or as organic matter. Eutrophication is a cause of organisms dying off, so it is important to be able to assess the impact of various sources of pollution, including from wet atmospheric deposition. The experience of long-term studies of “monitoring of precipitation chemistry and assessment of pollutant deposition to the ground” shows that nitrogen deposition from wet precipitation to catchment areas of selected rivers in 2020 reached or exceeded the permissible load for nitrogen (according to Vollenweider 1 $g/m^{2} \cdot y$ N = 10 kg/ha·y) for 18 catchments (28% of selected catchments), located mainly in the south of the country.

The number of catchments that met or exceeded the allowable load indicates improved conditions for the water environment in relation to 2019 (29 catchments – 45% of catchments) and at the same time a large improvement in relation to the amount of deposition with precipitation in 2017 (in 2017, 98% of catchments exceeded the allowable annual surface nitrogen load). If the entire nitrogen load deposited with wet precipitation were to enter surface water, then in some catchments, the rains themselves could pose a threat of eutrophication to natural standing water bodies, artificial water bodies and to water retained in dam reservoirs *(Precipitation Chemistry Monitoring and Deposition to Ground Assessment 2021-2022, Annual Report 2020).*

For fish farming, which is an important element of water management, apart from eutrophication, the biggest problem is heavy metals: Cd, Cu, Pb, Zn, Fe, Hg, delivered to water bodies also with wet precipitation. Due to the ability of heavy metals to accumulate in the tissues of aquatic animals, studies have proved necessary to differentiate the metal content in individual organs depending on the species. In fish, the highest heavy metal content is accumulated in gills, bones and liver. Accumulation of metals in animal tissues is directly related to their content in the environment (Formicki G., 2010). Their presence in fish tissue samples makes it impossible to consume fish, and therefore to carry out fishery operations.

The total annual loads of heavy metals carried with precipitation represent only about 1% of their average content in soil. The majority of heavy metals are microelements, which in very small quantities are necessary for normal life processes. At the same time, however, they are toxic substances with a high capacity to accumulate in living organisms. They are easily absorbed by living organisms directly from the air.

Heavy metals also pose a threat to agricultural production (in vegetable crops) especially in industrialised areas. Plants may be contaminated not only from soil, but also through aboveground parts, which easily retain metals on their surface. Fertilisers containing biogenic compounds and heavy metals, as well as plant protection products, which during periods of precipitation are flushed from fields and feed water bodies, are also a problem for water management. Heavy metals also pose a threat in water catchment areas. The threat to water supply catchments is greatest in the spring, because during the winter season metals in precipitation are accumulated in the snowpack and only transported during the melt season, increasing their content in snowmelt waters.

The deposition of heavy metals with wet precipitation is important information for water management due to the presence of metals (Cd, Ni, Pb, Hg) in the list of priority substances of the Water Framework Directive (WFD). This information is included in the Polish law – the Water Law, which is established in the Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy and its amending Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 in European water protection legislation.

The list of priority substances also includes POPs ingredients. These are synthetic substances which are foreign to the environment. Information on how much of these substances present in surface water comes from precipitation can be important in determining remediation programmes.

The activity of the state in the field of protection of the natural environment, with simultaneous rational use of its resources, should consist in limitation of human inputs of any substances into natural ecosystems. Most of all, those which disturb their functioning (e.g. nutrients accelerating eutrophication). In the case of priority substances, the national policy should be more strict and consist in gradual (in accordance with the principles of sustainable development) reduction. In the case of priority hazardous substances, it should consist in a complete ban on their introduction into ecosystems, with the ultimate aim of achieving a state in which their concentration corresponds to the natural background concentration, and in the case of synthetic substances is close to zero. Knowledge of the natural background level is very important and is a reference for current research at different locations of measurement points.

The atmospheric deposition measurement range proposed in the study includes indicators of great importance for water management, namely pH, conductivity, Cl^- , $SO4^{2-}$, $NO3^-$, $NH4^+$, Na^+ , K^+ , Ca^{2+} , Mg^{2+} as well as total nitrogen, total phosphorus and heavy metals Cd, Cu, Pb, Zn, Hg.

5.3 Information on wet deposition of substances for the purposes of the Convention on the Protection of the Marine Environment of the Baltic Sea Area (HELCOM)

HELCOM Recommendation 37-38/2, which came into force on 16 June 2016, refers to the provisions of the Convention on the Protection of the Marine Environment of the Baltic Sea Area, as well as 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 requires EU Member States to develop strategies to achieve good environmental status of the marine environment in areas under their jurisdiction. The directions and action plans referred to in the Recommendation are also set out in the Baltic Sea Action Plan. According to this Recommendation, monitoring programmes for atmospheric pollutants reaching the Baltic Sea should take into account EMEP recommendations on atmospheric pollution monitoring and modelling, quality assurance and data reporting.

The atmospheric deposition measurement range proposed in the study includes indicators that are mandatory for monitoring according to HELCOM Recommendation 37-38/2: NO_3^- and NH_4^+ biogenic compounds and heavy metals Cd and Pb. Additionally, it also includes optional pollutants such as: total phosphorus, Na^+, Mg^{2+}, Cl^-, K^+, Ca^{2+}, SO_4^{2-}, pH, conductivity, Cu, Zn, As, Cr, Ni, PAHs and polychlorinated biphenyls.

More information on the HELCOM programme can be found in section 4.5 of the Report entitled “Analysis of Polish and foreign documents and studies, as well as monitoring systems and data of the State Environmental Monitoring in terms of designing a new system of conducting research and assessments of atmospheric deposition.”

5.4 Links between precipitation chemistry and climate change

The relationship between precipitation chemistry and climate change can be considered in two ways:

- climate change may affect precipitation chemistry both in terms of magnitude and spatial distribution due to changes in meteorological conditions. Therefore, in this context, it is important to obtain long measurement series for trend analysis,
- monitoring, as part of precipitation chemistry, of components that also influence climate change (e.g. elemental carbon – EC) or play a role in climate change mitigation, but importantly are emitted from anthropogenic sources such as transport, industry, agriculture and domestic heating, which also emit other greenhouse gases. Changes in emissions from these sources will affect both air quality, atmospheric deposition and climate.

Climate is a natural resource, significantly influencing civilisation development. Its changes, under the influence of anthropogenic and natural factors, expressed by particular climatic and weather-forming elements, may have various consequences. The observed climate change may lead to depletion of civilisation climate resources, which necessitates systematic monitoring of the climate system, taking actions that slow down or even eliminate the causes of contemporary climate change, as well as forecasting climate system change scenarios and developing adaptation strategies, i.e. undertaking adaptation actions (Klimat Polski 2020, 2021). Adaptation actions may be expressed through modification of economic and social life or updating the assumptions of the environmental monitoring system, including atmospheric deposition.

One of the most important weather and climate-forming factors is atmospheric circulation. Thanks to it the weather in a given area changes from day to day or even several times a day. One of the frequent methods of describing atmospheric circulation is to characterise it by giving the direction of air mass advection over a selected area and by defining the character of air movement (cyclonal or anticyclonal). In a given season of the year those parameters allow to determine thermal and humidity features of air masses flowing over the studied area, which is also important for the direction of inflow of pollutants over a given area (Klimat Polski 2020, 2021).

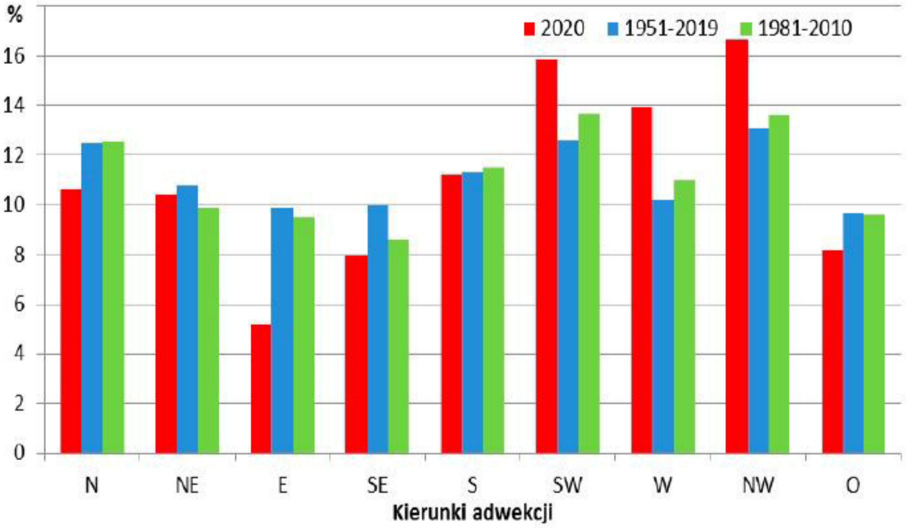
The variability of climatic conditions can be considered in global, regional or local terms in different time frames. To determine thermal variability, 30-year data should be analysed.

The average values of air temperature in particular decades of the period 1951-2020 range between 7.1°C in the decade 1961-1970 and 9.3°C in the last decade 2011-2020. Here, the increase is unequivocal, from 7.2°C in the 1951-1980 period to 8.7°C for the last 30-year period, i.e. 1991-2020. This means an increase, in terms of 30-year norms, of 1.5°C. The last 20-year period is the warmest since the middle of the 20th century. In the last 20 years, only once, in 2010, was the average annual air temperature lower than the multi-year average value for the period 1981-2010. The anomaly was -0.8°C, and was a consequence of an extremely cold beginning of the year (January-February) and a cold December.

Studies show that the rate of warming is rising steadily. The trend coefficients calculated for the period 1901-2020 are higher than those for the period 1851-2020, and those calculated for the period since 1951 are even higher. The values of the trend coefficients increased sharply in the period after 1980.

Progressing warming is also visible in particular meteorological stations located in different physiogeographic regions of Poland and characterised by different location features (coastal station, big-city station, high-mountain station, station in a small town) (Klimat Polski 2020, 2021).

Analysis of the circulation index calendar allows us to conclude that in 2020 air masses coming from the west (from SW to NW) prevailed. Their total share was almost 47%. In the assessment of variability of that circulation in relation to the normal period, the frequency of air masses coming from the west was by almost 8% higher than in 1981-2010 and by almost the same amount than in the period since 1951. The share of air masses coming from the northern sectors (from NW to NE) was large, for it amounted to 38%. The frequency of air masses coming from the south (from SE to SW) was almost 35% (Fig. 5.1) (Klimat Polski 2020, 2021).



Advection Direction

Figure 5.1 Calendar of circulation index in Poland, 2020 (Klimat Polski 2020, https://www.imgw.pl/index.php/badania-nauka/klimat, 2021)

Changes in the circulation affect the direction of inflow, including the highs and lows system, at which air stagnates or not and pollution persists or not in an area. Chemical compounds may contribute as condensation nuclei to increasing the amount of precipitation in an area. Analysis of the dependence of deposition on the amount of precipitation indicates the possible phenomenon of dilution or accumulation of pollutants depending on the length of the period preceding the precipitation.

With higher precipitation there is a dilution of pollutants, but high precipitation means high deposition. It should also be borne in mind that, according to studies, most pollution enters the ground with the precipitation in the first few minutes. The longer precipitation lasts the cleaner the water. It is only when there is a long period without rain, e.g. a drought, that the accumulation of pollutants in the air takes place and as a result of precipitation the atmosphere may become clean at the cost of pollution of ecosystems. Therefore it is necessary to analyse the condition of the environment by assessing, among other things, the magnitude of critical loads, which was conducted in the KLAPS project entitled “Climate Change, Air Pollution and Exceedance of Critical Loads in the Polish-Saxon Border Region” implemented under the Operational Programme Cross-border Cooperation Poland-Saxony 2008-2014.

The project concluded that there was a significant reduction in the deposition of sulphur compounds and nitrogen oxides between 2000 and 2010. It was also found that ammonium nitrogen deposition remained practically at the same level. Ammonium nitrogen is currently the main source of nitrogen deposition to ecosystems in the border area between Poland and Saxony. These trends are expected to continue in the future. Climate change, determined regionally, in particular a decrease in precipitation, will contribute to a further slight reduction in the deposition of sulphur and nitrogen compounds in the study area.

Through the analysis of critical loads, the maximum amount of deposition of sulphur and nitrogen compounds, which does not cause harmful effects in ecosystems, was assessed. Contemporary changes in emissions and deposition of atmospheric pollutants are also reflected in positive changes in exceedances of critical loads. In the case of acidification, only about 10% of forest areas and other natural ecosystems are at risk of excessive deposition. Analyses for future emission change scenarios indicate that this problem will be completely eliminated by 2030. Reducing nitrogen oxide emissions by 2030 will only slightly reduce this problem. An assessment of the impact of climate variability on loads critical for eutrophication has shown that they will have a negative impact, which should be taken into account in the formation of the air protection policy (https://www.umwelt.sachsen.de/umwelt/klaps/wyniki_projektu.htm, accessed 15.02.2022).

The study shows that it is necessary to assess the variability of wet deposition of precipitation based on climate change expressed by the variability of the amount of precipitation and its nature, i.e. the increase in the frequency of rain-free periods and the intensity of torrential rains.

The variability of precipitation in Poland results, among other things, from the diversity of landforms. The distribution of total precipitation for the multi-year period 1991-2020 is characterised in Figure 5.2.

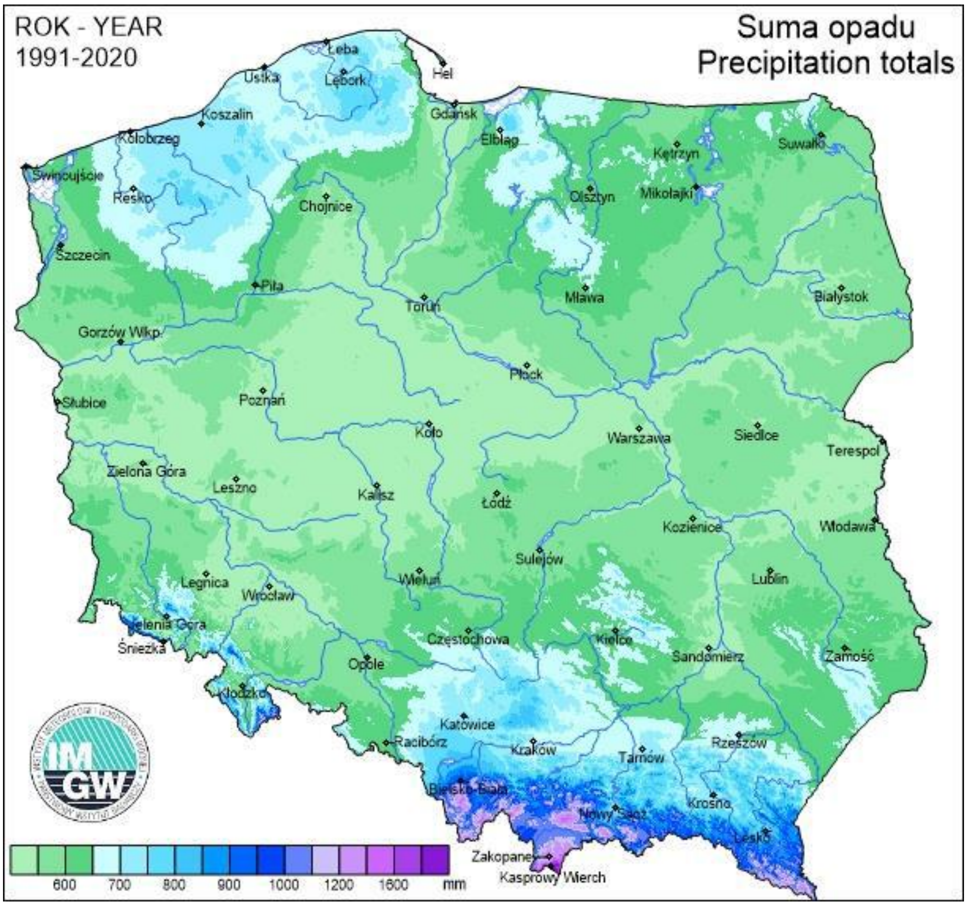


Figure 5.2 Distribution of total precipitation in Poland, 1991-2020 (http://klimat.imgw.pl)

In order to assess the variability of precipitation, there was carried out an analysis of data from meteorological stations in Poland was carried out, e.g. within the framework of the study "Strategic Adaptation Plan for Sectors and Areas Sensitive to Climate Change up to 2020 with an Outlook up to 2030" for the period up to 2002 (SPA 2020).

As a result of the analyses it was found that the precipitation structure had changed in the majority of Poland. An increase in the number of days with heavy precipitation (daily precipitation ≥50 mm) was observed, especially in ranged the southern regions. The longest precipitation sequences in the period 1961-2000 from 11 to more than 40 days on average. The increasing trend in the number of days with precipitation of ≥50 mm is marked in the figure below (Figure 5.3) by blue dots, the size of which indicates the degree of intensification of the changes. The red colour indicates a decreasing trend, while the green colour indicates no trend. Heavy rainfall with intensities exceeding 5 mm/min and seasonal probability (V-IX) ≥10% occurs most frequently in the whole belt of Subcarpathia, the Swietokrzyskie Mountains, a meridionally arranged belt from Opole and Częstochowa to the Olsztyn region, western part of Roztocze and includes a fragment of the Nysa Kłodzka river basin (in the period 1966-1985).

On the other hand, the assessment of the length of rainless periods (number of days without precipitation or with precipitation below 1 mm) shows that in the period of the last 12 years (1991-2002) in the whole eastern Poland (from the Vistula River to the east) the rainless period has been lengthened, even by 5 days/decade. This is the region of the country which in the period 1991-2002 was most frequently affected by drought (including hydrological drought). Periodical occurrence of droughts is a characteristic feature of Polish climate. In the 20th century it occurred 24 times, and since the beginning of the 21st century, i.e. in 2001-2011, droughts have occurred 9 times in different periods of the year (SPA 2020).

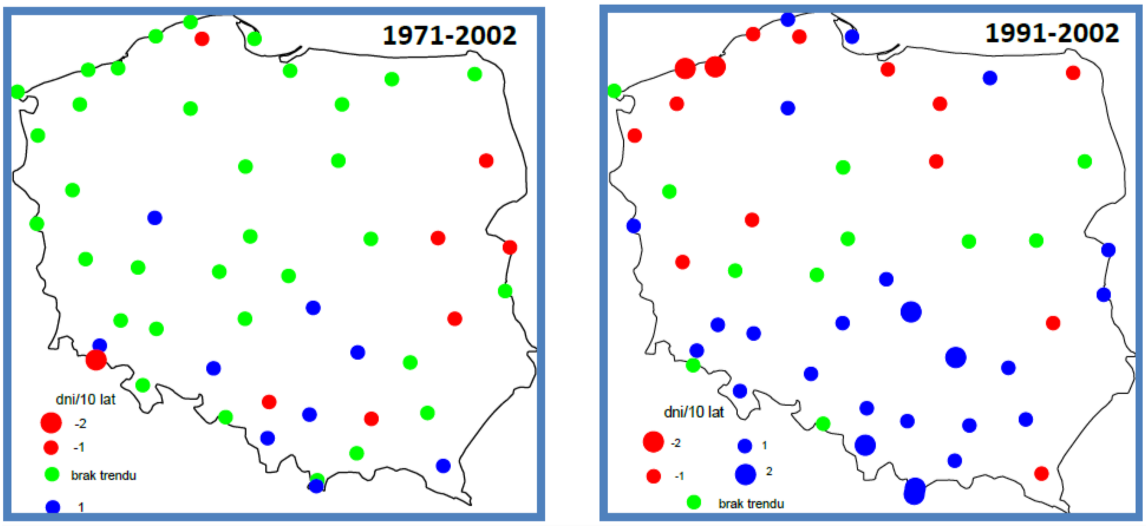
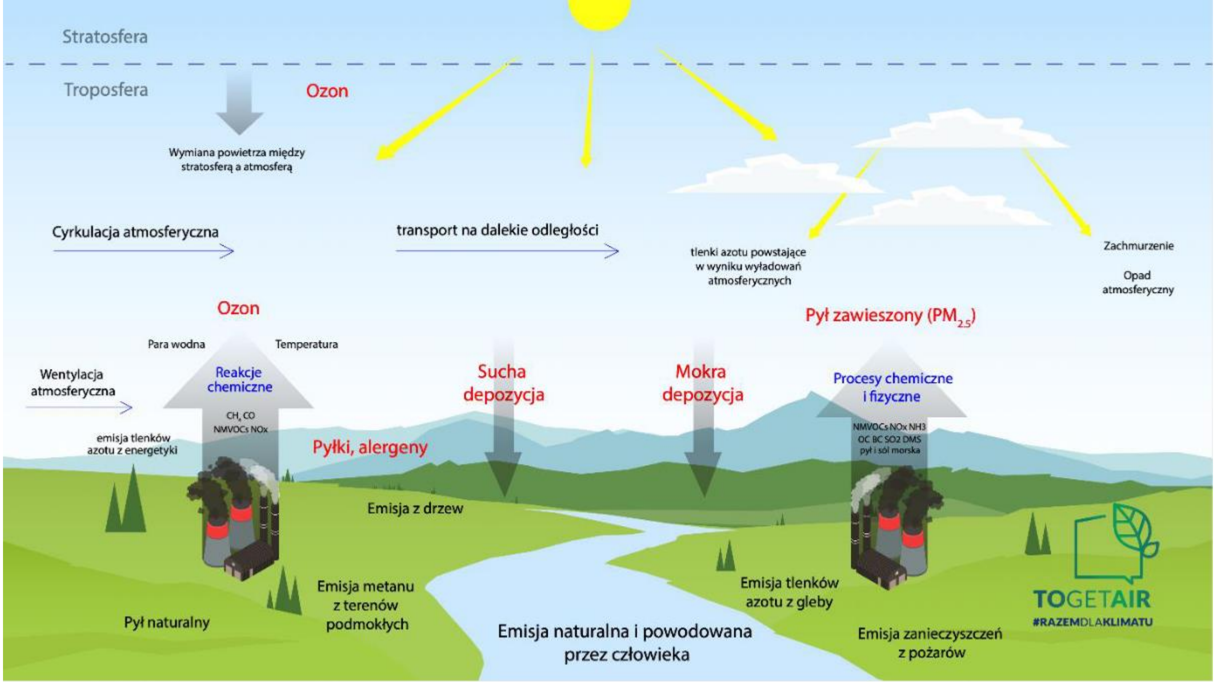


Figure 5.3 Distribution of days with precipitation ≥ 50 mm for multi-year periods 1971-2002 and 1991-2002 (SPA 2020)

In the case of wet deposition, the main determinant is the amount of precipitation, while the variability of air pollutant concentrations must also be taken into account.

The interactions between air pollution and climate are complex. Both atmospheric emissions affect climate change and climate change affects air quality, with aerosols playing an important role in this process (https://raport.togetair.eu/czlowiek/ludzie-swiat-klimat/aerozol-w-atmosferze-a-zmiany-klimatu, accessed 15.02.2022).



Atmospheric circulation / long-range transport /
Nitrogen oxides created by lightning / Cloud cover / Precipitation
Ozone / Particulate matter (PM$_{2.5}$)
Water vapour / Temperature
Atmospheric ventilation / Chemical reactions / Dry deposition / Wet deposition / Chemical and physical processes
Emission of nitrogen oxides from the energy sector / CH$_4$ CO NMVOCs NO$_x$ / Pollens, allergens / NMVOCs NO$_x$ NH$_3$ OC BC SO$_2$ DMS dust and sea salt
Emissions from trees
Natural dust / Emission of methane from wetlands / Natural and anthropocentric emissions / Emission of nitrogen oxides from the soil / Emission of pollutants from fires

Figure 5.4 Circulation of pollutants in the environment (https://raport.togetair.eu/czlowiek/ludzie-swiat-klimat/aerozol-w-atmosferze-a-zmiany-klimatu, accessed 15.02.2022)

The Klimada 2.0 project stresses that the assessment of the emission of pollutants into the atmosphere a well-recognised process which influences the greenhouse effect, where the so-called greenhouse gases, i.e. carbon dioxide or methane, are mainly referred to. However, aerosols emitted into the atmosphere from natural and anthropogenic sources also have a direct and indirect impact on climate change. Natural sources include: volcanic eruptions, evaporation of salt water from the oceans, emissions of volatile organic compounds from plants. The main anthropogenic sources, on the other hand, are the combustion of fossil fuels in electricity generation, industry and households, and the combustion of liquid fuels in transport (Figure 5.4) (https://raport.togetair.eu/czlowiek/ludzie-swiat-klimat/aerozol-w-atmosferze-a-zmiany-klimatu, accessed 15.02.2022).

It is some of these that cause heat to be retained in the atmosphere, while others scatter and reflect solar radiation reaching the Earth. This effect is called "radiative forcing" in the literature, which determines the occurrence of the greenhouse effect contributing to the currently observed trends of temperature and precipitation changes. Moreover, climate change may cause a feedback loop, favouring in some regions the formation or disappearance of aerosol in the atmosphere (K. Juda-Rezler, B. Toczko 2016). The main components of atmospheric aerosol are inorganic compounds (such as sulphates, nitrates, ammonia, sea salt), organic compounds (often referred to as organic aerosol), soot (dust particles containing significant amounts of carbon resulting from incomplete combustion of solid fuels and biomass), mineral fractions (mainly desert dust and dust lifted from dry areas) and biological particles from plants. Research indicates that anthropogenic sources are responsible for the presence of soot, sulphates, nitrates and ammonia in the atmosphere, while sea salt, most mineral dust and organic compounds are mainly of natural origin.

The amount of a given type of aerosols in the atmosphere (concentration) and their properties (absorbing or reflecting radiation) affect the climate of a given region. The difficulty in assessing the impact of different aerosol types on climate is mainly due to the incomplete understanding of the complex processes between natural and anthropogenic emission sources and their interaction with the thermal and hydrological cycle (https://raport.togetair.eu/czlowiek/ludzie-swiat-klimat/aerozol-w-atmosferze-a-zmiany-klimatu, accessed 15.02.2022).

Climate change may affect atmospheric aerosols through (https://raport.togetair.eu/czlowiek/ludzie-swiat-klimat/aerozol-w-atmosferze-a-zmiany-klimatu, accessed 15.02.2022):

- changes in air temperature, which affect the rate of chemical reactions in the atmosphere and the formation of secondary aerosols,
- changes in atmospheric humidity, which affects the type and rate of chemical reactions in the atmosphere and the reduction of tropospheric ozone,
- changes in the frequency and intensity of lightning discharges, resulting in impacts on ozone precursors and an increase in the likelihood of natural fires,
- changes in atmospheric cloudiness affecting the composition and energy balance of the atmosphere and the rate of chemical reactions occurring in the atmosphere,
- changes in the frequency and intensity of precipitation (effects on the leaching of pollutants from the atmosphere and changes in the deposition of pollutant loads reaching the ground),
- ocean temperature changes (effects on atmospheric circulation, formation of marine aerosol and sulphate aerosols),
- changes in the general circulation of the atmosphere (effects on dispersion and transport of pollutants in the atmosphere).

Similarly to the effects on aerosols, the influence of atmospheric conditions on air pollution by dust of natural as well as anthropogenic origin was analysed. Natural sources are considered to be biological pollutants, sea salt, volcanic emissions, gas precursor processes or secondary dusting of natural ground surfaces. On the other hand, the sources of dust of anthropogenic origin are biomass burning, dust from fossil fuel combustion and secondary dust from the surface of anthropogenically transformed areas.

As it has been mentioned above, variability of dust concentrations in the atmosphere is a result of physical and chemical processes that occur under the influence of a complex of meteorological factors. Without going into the mechanism of formation of such dependencies, it is possible to indicate single meteorological elements which, at least intuitively, have an impact on dust concentrations in the atmosphere. As a result of long-term observations, it has been found that, apart from the conditions of thermo-dynamic stability of the atmosphere, these are: solar radiation; air temperature; air humidity and precipitation; anemological conditions.

Therefore, deposition rates should be considered as a sequence of relations linking the variability of meteorological conditions resulting from local conditions influenced by climate change and the variability of the amount of pollutants in the air resulting from physicochemical processes in the atmosphere.

5.5 Information on pollutant deposition as referred to in the NEC Directive (Directive (EU) 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)

In 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 Ceilings Directive (NEC, National Emission Ceilings), set the ceilings for air emissions of primary gaseous pollutants, which are also precursors to secondary particulate matter.

In accordance with the Directive, the national emission inventory covered the following pollutants and their groups:

- sulphur dioxide, nitrogen oxides, ammonia, carbon monoxide,
- particulate matter (total – TSP, and fine fractions: PM10, PM2.5 and BC),
- heavy metals (including mandatory reporting to UNECE/EMEP: cadmium, mercury and lead and those reported so far on a voluntary basis: arsenic, chromium, zinc, copper and nickel),
- non-methane volatile organic compounds (NMVOCs),
- Persistent organic pollutants – POPs (including dioxins and furans, polychlorinated biphenyls, hexachlorobenzene, benzo(a)pyrene and three other polycyclic aromatic hydrocarbons (PAHs), namely: benzo(b)fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene.

In order to arrive at a value for total deposition, it is necessary to measure parameters that enable the calculation of dry deposition. Dry deposition is calculated on the basis of the concentration of a given substance in the air multiplied by the speed of its deposition.

Of these substances, the following are proposed for measurement:

- SO_2, sulphur dioxide, a substance contributing to the acidification of the environment, dry deposition of oxygen sulphur and hydrogen ions, derived from dry deposition of SO_2, is calculated on the basis of SO_2 concentrations; SO_2 is measured at background atmospheric pollution stations and should be included in the compulsory set of indicators to be surveyed; measurement of the component is mandatory under the EMEP (level 1) and GAW WMO programmes,
- SO_4^{2-}, sulphate ions are a substance that contributes to the acidification of the environment, dry sulphur deposition is calculated on the basis of the concentration of SO_4^{2-}; at background sites, SO_4^{2-} in the air is measured and this substance should be included in the mandatory components; measurement of the component is mandatory under the EMEP (level 1) and GAW WMO programmes,
- NO_x, nitrogen oxides, these include nitric oxide NO and nitrogen dioxide NO_2, NO_2 is a contributor to acidification, eutrophication and ground-level ozone formation, dry deposition of oxygenated nitrogen is calculated on the basis of NO_2 concentration; the measurement should be included in the mandatory set of indicators of the future network; NO_2 is a mandatory parameter under the EMEP (level 1) and GAW WMO programmes,

- NO_3^- aerosol is a substance that contributes to acidification, eutrophication and ground-level ozone formation, dry deposition of oxygenated nitrogen is calculated on the basis of NO_3^- concentration; the measurement should be included in the mandatory in the set of indicators for the future network; measurement of $NO3^-$ is mandatory under the EMEP (level 1) and GAW WMO programmes,

- (HNO_3+NO_3^-), total airbound nitrate compounds, contributes to acidification, eutrophication and ground-level ozone formation; dry deposition of aerobic nitrogen is calculated on the basis of (HNO_3+NO_3^-) concentration; the measurement should be included in the mandatory set of indicators of the future network; the measurement of (HNO_3+NO_3^-) is mandatory under the EMEP (level 1) and GAW WMO programmes,
- NH_4^+, ammonium ions – contribute to eutrophication; enters the air mainly as a result of agricultural activities; NH_3 ammonia undergoes physicochemical transformations and reaches the ground in the form of dry and wet deposition of NH_4^+; measurements of NH_4^+ are mandatory under the EMEP (level 1) and GAW WMO programmes and should be included in the set of indicators of the future network,
- (NH_3+NH_4^+), total airborne ammonium compounds, contribute to eutrophication; ammonia (NH3) undergoes physicochemical transformations and reaches the ground in the form of dry and wet deposition of NH_4^+; measurements of (NH_3+NH_4^+) are mandatory under the EMEP (level 1) and GAW WMO programmes and should be included in the set of indicators of the future network.

For more information on the NEC Directive see section 4.4 of the Report entitled “Analysis of Polish and foreign documents and studies as well as monitoring systems and data of the State Environmental Monitoring in view of designing a new system of atmospheric deposition research and assessment.”

5.6 Information on the integration of research on precipitation chemistry with the research carried out for the EMEP programme under the Convention on Long-range Transboundary Air Pollution

The proposed selection of indicators, methods and frequency of precipitation sampling for chemistry monitoring is integrated with the EMEP programme. At all stations, there has been proposed determination in precipitation of inorganic compounds and heavy metals, which are the first priority under the EMEP strategy, such as: SO_4^{2-}, NO_3^-, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, pH, conductivity and Cd and Pb. At selected stations, depending on the characteristics of the region, heavy metals that are the second priority of EMEP will be measured: Cu, Zn, As, Cr and Ni. For stations designated as EMEP level 1 or 2 stations, a full precipitation measurement programme required by the programme has been proposed. Additionally, it is recommended to measure total nitrogen and total phosphorus at the EMEP stations, selected as required parameters for precipitation chemistry monitoring stations for water management purposes.

Precipitation sampling will be carried out as wet precipitation with the proviso that total precipitation sampling is acceptable where circumstances prevent the use of a wet precipitation collector or render it impractical. The recommended sampling frequency is 24 hours with the possibility, in cases of high costs or problems with daily sampling, to extend it to a maximum of 7 days.

For more information on EMEP see sections 4.1 and 4.3 of the Report entitled “Analysis of Polish and foreign documents and studies as well as monitoring systems and data of the State Environmental Monitoring in view of designing a new system of atmospheric deposition research and assessment.”

6. Scope of substances and parameters proposed for measurements under the framework of precipitation chemistry

Having analysed Polish and foreign documents and studies and monitoring systems, including the requirements of international programmes, as well as the data of the State Monitoring of the Environment, a list of sampling methods, ranges of measurements and analyses recommended for the monitoring of precipitation chemistry of the new system of studies and assessments of atmospheric deposition have been compiled.

Sampling methods for the monitoring of precipitation chemistry

Wet precipitation sampling is recommended. Total precipitation sampling is acceptable where circumstances prevent the use of a wet precipitation collector or render it impractical. In this case, the sampling point should be located sufficiently far from pollutants and local dust sources and the sampling frequency should be 24 hours (Source: GAW Manual No. 160, 3.2.1.1).

A total precipitation collector can be used to sample precipitation for heavy metals determination if it is proven to be quantitatively equivalent to the recommended method. Collectors of this type may overestimate metal concentrations due to the delivery of dry deposition components to the sample, but in many areas there are no differences between the use of these two types of collectors (Source: EMEP Manual 3.10.3.1).

Time resolution of sampling for precipitation chemistry monitoring

According to the recommendations and requirements of the GAW programme the recommended sampling time resolution is 24 hours. In case of high costs or problems with daily sampling this period can be extended up to a maximum of 7 days, as shown in Table 6.1. (Source: GAW Manual No. 160, 3.2.2.).

The recommended methods and time resolution of precipitation sampling for precipitation chemistry are presented in Table 6.1.

Table 6.1 Sampling methods and time resolution recommended for precipitation chemistry monitoring studies (own work based on EMEP and GAW-WMO)

Parameter	**Recommended (permissible) time resolution**	**Collection methods**
precipitation	daily	rain gauge
precipitation amount	daily (weekly)	wet precipitation (total precipitation)
SO_4^{2-}	daily (weekly)	wet precipitation (total precipitation)
NO_3^-	daily (weekly)	wet precipitation (total precipitation)
Cl^-	daily (weekly)	wet precipitation (total precipitation)
NH_4^+	daily (weekly)	wet precipitation (total precipitation)
Na^+	daily (weekly)	wet precipitation (total precipitation)
Mg^{2+}	daily (weekly)	wet precipitation (total precipitation)
Ca^{2+}	daily (weekly)	wet precipitation (total precipitation)
K^+	daily (weekly)	wet precipitation (total precipitation)
HCO_3^-	daily (weekly)	wet precipitation (total precipitation)
H^+ (pH)	daily (weekly)	wet precipitation (total precipitation)
specific electrical conductivity	daily (weekly)	wet precipitation (total precipitation)
total phosphorus	daily (weekly)	wet precipitation (total precipitation)
total nitrogen	daily (weekly)	wet precipitation (total precipitation)
Hg	weekly	total precipitation
Cd, Pb (first priority), Cu, Zn, As, Cr, Ni (second priority)	weekly (1 collector) or monthly (2 collectors)	wet precipitation (total precipitation)
POPs (PAHs, PCBs, HCB, chlordane, HCHs, DDT/DDE)	weekly	wet precipitation

For bicarbonate ion measurements, it is additionally important to note that its analysis is recommended when the pH value of the precipitation sample is greater than 6, while its concentration can be calculated when the pH value of the sample is lower than 6 (source: Manual GAW No. 160, 4.1).

Analytical methods for the study of precipitation chemistry

A proposal of analytical precipitation methods for precipitation chemistry monitoring studies is presented in Table 6.2.

Table 6.2 Summary of proposed analytical methods used to study precipitation chemistry (own work based on EMEP and GAW-WMO)

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
Cl^-	IC	spectrophotometric method with mercuric rhodanide (II)
specific 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
Ace	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
WWA	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 (dichlorodiphenyltrichloroethane / dichlorodiphenyldichloroethylene)	GC-MS	GC-ECD, GC-MS/MS
HCHs	GC-MS	GC-ECD, GC-MS/MS
Chlordan	GC-MS	GC-ECD, GC-MS/MS

Explanations:

CFA - Continuous Flow Analysis with spectrophotometric detection

CV-AAS – Cold Vapour – 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

Methods of sampling and analysis for gases and aerosols

Sampling on a daily basis is mandatory. Samples for the determination of SO_2 and SO_4^{2-} , nitrate and ammonium aerosol and nitrate and ammonium aerosol gas sums are taken on filters. Samples for NO_2 determination are collected on NaI impregnated glass frit. Another recommended sampling method for SO_2 and NO_x is continuous automatic measurement.

Table 6.3 Range of measurements, sampling and analytical methods recommended for testing gases and aerosols needed for dry deposition estimation (own work based on EMEP and GAW-WMO)

Parameter	**Measurement period**	**Collection frequency**
Gas		
SO_2	24 hours	daily
NO_2	24 hours	daily
Aerosol		
SO_4^{2-}	24 hours	daily
NO_3^-	24 hours	daily
NH_4^+	24 hours	daily
Gas + aerosol		
HNO_3(g)+NO_3^- (a),	24 hours	daily
NH_3(g)+NH_4^+ (a)	24 hours	daily

Analytical methods for aerosol measurements

On the basis of the analyses carried out, a proposal of recommended gas and aerosol measurement parameters, which are presented in Table 6.3, and measurement and analytical methods, which are presented in Table 6.4, was put together.

Pursuant to the analysis carried out earlier, these include:

- oxygenated sulphur compounds – in the form of gas and aerosol, i.e. SO_2 and SO_4^{2-},
- oxygenated nitrogen compounds – as gas and aerosol and/or as sum of gas and aerosol, i.e. NO_2 and NO_3^- and (HNO_3+NO_3^-),
- oxygen-free nitrogen, in the form of aerosol and the sum of ammonium compounds, i.e. NH_4^+ and (NH_3+NH_4^+).

The recommended method for the determination of gases and aerosols is the IC method, alternatives include: the thorine method for SO_2 and SO_4^{2-}, the Griess method and the Griess spectrometric method after reduction for NO_2, NO_3^- and total nitrate compounds respectively, and the indophenol method for ammonium compound ions – single component and sum of ammonium compounds.

Table 6.4 Measurement and analytical methods recommended for testing gases and aerosols needed for dry deposition estimation (own work based on EMEP)

Parameter	Field sampling methods	Laboratory methods
Gas		
SO_2	KOH impregnated filters	IC / Torin method
NO_2	NaI impregnated glass frit	IC / Griess method
Aerosol		
SO_4^{2-}	aerosol filter	IC / (Torin)
NO_3^-	aerosol filter after denuder	IC / Griess spectrometry method after reduction
NH_4^+	aerosol filter after denuder	IC / indophenol
Gas + aerosol		
HNO_3(g)+NO_3^-(a),	filter pack	IC / Griess spectrophotometric method after reduction
NH_3(g)+NH_4^+(a)	filter pack	IC / indophenol

IC = ion chromatography

Summary of selected parameters and physicochemical analysis methods with justification

Justification for the proposed scope of measurements and physicochemical analyses of wet (total) precipitation samples as part of the monitoring of precipitation chemistry:

1. Ions: SO_4^{2-} – parameter mandatory under EMEP and GAW/WMO, recommended as voluntary in the HELCOM programme; in case of combining EMEP and HELCOM stations, it can be used as supplementary information, recommended in regional monitoring at each location and for each type of station. For analyses, the method preferred by GAW/WMO and EMEP, IC – ion chromatography, is recommended.
2. Ions: Cl^- – parameter mandatory under EMEP and GAW/WMO, recommended as voluntary in the HELCOM programme; in case of combining EMEP and HELCOM stations, it can be used as supplementary information, recommended in regional monitoring at any location and for any type of station. For analyses, the method preferred by GAW/WMO and EMEP, IC – ion chromatography, is recommended, or alternatively the mercury (II) rhodanide spectrophotometric method.
3. Ions: Na^+ K^+ Ca^{2+} Mg^{2+} – parameters mandatory under EMEP and GAW/WMO, recommended as voluntary in the HELCOM programme; in case of combining EMEP and HELCOM stations, they can be used as supplementary information, recommended in regional monitoring at each location and for each type of station. For analyses, the method preferred by GAW/WMO and EMEP, the FAAS flame atomic absorption spectrometry or the ICP-OES inductively coupled plasma optical emission spectroscopy are recommended, or alternatively the IC – ion chromatography method and the ICP-MS – inductively coupled plasma mass spectrometry method.
4. Ions: HCO_3^- parameter analysed to ensure the quality of chemical analyses performed through control of the ion balance for precipitation samples; recommended in EMEP and HELCOM international programmes. For analyses (for pH values above 6), the method preferred by GAW/WMO and EMEP, IC – ion chromatography, is recommended. For pH below 6, the concentration can be calculated from the pH value. As an alternative method, titration may be used.

5. pH – the basic parameter to be analysed as part of the mandatory EMEP and GAW/WMO, recommended as voluntary in HELCOM programme; in case of combining EMEP and HELCOM stations, it can be used as supplementary information, recommended in regional monitoring at each location and for each type of station. It is a mandatory parameter, necessary to assess rainwater mineralisation, its acidification, to determine the degree of sample contamination and for the purpose of quality assurance of the chemical analyses performed through control of the ion balance for precipitation samples. To perform the measurement, the potentiometric method is preferred by GAW/WMO and EMEP.
6. Specific electrical conductivity – mandatory parameter for GAW/WMO, preferred as voluntary in the HELCOM programme; in case of combining EMEP and HELCOM stations, it can be used as supplementary information, preferred in regional monitoring at any location and for any type of station. It is a mandatory parameter, necessary to assess rainwater mineralisation, to determine the degree of sample contamination and for the purpose of quality assurance of the chemical analyses performed through control of the ion balance for precipitation samples. To perform the measurement, the conductometric method is preferred by GAW/WMO and EMEP.
7. NO_3^- (nitrate ions) – parameter mandatory under EMEP and GAW/WMO; nitrate levels in marine waters affect eutrophication processes; therefore, deposition assessment is of primary importance for the assessment of nitrate pressures. The parameter is used to verify the model for nitrate deposition to the Baltic Sea (e.g. MSC-W Technical Report 3/2020) and is preferred for regional monitoring at each location and station type. It is a mandatory parameter necessary for the assessment of rainwater mineralisation, its acidification and influence on eutrophication processes. For analyses, the GAW/WMO and EMEP preferred method is IC – ion chromatography, or alternatively the Griess spectrophotometric method after reduction.
8. NH_4^+ (ammonium ions) – parameter mandatory under EMEP and GAW/WMO; sea water ammonium ion levels influence eutrophication processes and therefore assessment of deposition is of fundamental importance for assessing nitrate emission pressures; this parameter is used to verify a model determining the deposition of ammonium ion to the Baltic Sea (e.g. MSC-W Technical Report 3/2020), recommended in regional monitoring at each location and for each type of station. It is a mandatory parameter, necessary to assess rainwater mineralization, its acidification and its impact on eutrophication processes. For analyses, the GAW/WMO and EMEP preferred method is the FIA method is recommended, or alternatively one of the following: IC – ion chromatography, CFA – continuous flow analysis with spectrophotometric detection or the indophenol method.
9. Total phosphorus – parameter voluntary within GAW/WMO, phosphorus level in marine waters influences eutrophication processes, similarly in freshwater areas and therefore assessment of its deposition is essential for evaluation of emission pressures, recommended in regional monitoring at each location and for each type of station. For analyses, the GAW/WMO and EMEP preferred method is the FIA – flow injection analysis with sample digestion or alternatively one ofthe following: the spectrophotometric method or the CFA – continuous flow analysis with spectrophotometric detection.
10. Total nitrogen – recommended parameter under ICP Forests, voluntary under GAW/WMO; the level of nitrogen compounds in marine waters influences eutrophication processes, similarly in freshwater bodies and therefore assessment of its deposition is crucial for the assessment of emission pressures; recommended for regional monitoring at each location and for each type of station. For analyses, the GAW/WMO and EMEP preferred method is the FIA – flow injection analysis with sample digestion or alternatively one of the following:

the calculation method (sum of NO_3^- , NH_4^+ , NO_2^- , Kjeldahl nitrogen) or the CFA – continuous flow analysis with spectrophotometric detection.

11. Cd (cadmium) - heavy metal considered to be very harmful. Parameter to be mandatory under EMEP, total deposition monitoring mandatory Cadmium also results from Directive 2004/107/EC (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). In marine environmental monitoring, Cd is studied in various ecosystem components: fish, bivalves, bottom sediments and seawater. It is included as a core indicator in assessments of the state of marine environment (https://helcom.fi/wp-content/uploads/2019/08/Metals-HELCOM-core-indicator-2018.pdf). The parameter used to validate the model for cadmium deposition to the Baltic Sea (e.g. MSC-W Technical Report 3/2020) and is recommended for regional monitoring at each location and station type. The parameter is included in the list of priority substances under the Water Law as a hazardous substance. It poses a threat to fish farming. The source in the air and at the same time in atmospheric precipitation is the metallurgical industry (mainly zinc smelters), the chemical industry, battery factories. The source of cadmium contamination may be e.g. dust from power plants fired with brown coal. Phosphates used as mineral additives in animal feed may be an indirect source of cadmium. Cadmium is easily absorbed by plants, animals and humans. For analyses, the following GAW/WMO and EMEP preferred methods are recommended: the ICP-MS – inductively coupled plasma mass spectrometry, the GF-AAS – graphite furnace atomic absorption spectrometry, or the FAAS – flame atomic absorption spectrometry, or alternatively the ICP-OES – inductively coupled plasma optical emission spectroscopy.
12. Pb (lead) – heavy metal considered to be very harmful; parameter that is mandatory under EMEP. Within the framework of the monitoring of the marine environment, it is studied in different components of the ecosystem: fish, bivalves, bottom sediments seawater. It is included as a core indicator in marine assessments (https://helcom.fi/wp-content/uploads/2019/08/Metals-HELCOM-core-indicator-2018.pdf); it is the parameter used to validate the model determining lead deposition to the Baltic Sea (e.g. MSC-W Technical Report 3/2020), recommended in regional monitoring at each location and for each type of station. The parameter is included in the list of priority substances under the Water Law as a hazardous substance. It is a threat to fishery operations. Lead compounds are emitted into the atmosphere, therefore mainly aboveground parts of plants are exposed to pollution. The main source is human activity – mines, smelters, road transport, industry and agriculture (fertilizers and pesticides). Lead, coming mainly from precipitation, is deposited in the surface layers of soil and surface waters. For analysis, one of the following methods preferred by the GAW/WMO and EMEP is recommended: the ICP-MS – inductively coupled plasma mass spectrometry, the GF-AAS – graphite furnace atomic absorption spectrometry or the FAAS – flame atomic absorption spectrometry or alternatively the ICP-OES – inductively coupled plasma optical emission spectroscopy.
13. Cu (copper) – a heavy metal considered to be very harmful; a parameter mandatory under EMEP, in marine environmental monitoring it is studied in various ecosystem components: fish, bivalves, bottom sediments and seawater. From 2021 it is included as a core indicator in assessments of the state of the

marine environment and therefore expanding the information on copper deposition to the Baltic Sea may be very important for pressure assessment, recommended in regional monitoring for a selected group of stations depending on the region of Poland, e.g. the part of western Poland where copper is present. For analyses, one of the following GAW/WMO and EMEP preferred methods is recommended: the ICP-MS – inductively coupled plasma mass spectrometry, the GF-AAS – graphite furnace atomic absorption spectrometry or the FAAS – flame atomic absorption spectrometry, or the alternative method ICP-OES inductively coupled plasma optical emission spectrometry.

14. Zn (zinc) – parameter mandatory under EMEP, recommended as voluntary under HELCOM; in case of combining EMEP and HELCOM stations, it can be used as supplementary information and to support assessment of the state of the Baltic Sea environment, recommended in regional monitoring for a selected group of stations depending on the region of Poland. In the environment, elevated zinc content occurs mainly in close vicinity of industrial plants processing this metal, which is discharged to the atmosphere in the form of fine zinc oxide particles. Zinc, similarly to cadmium, usually accompanies lead in contaminations. For analyses, one of the following GAW/WMO and EMEP preferred methods is recommended: the ICP-MS – inductively coupled plasma mass spectrometry, the GF-AAS – graphite furnace atomic absorption spectrometry or the FAAS – flame atomic absorption spectrometry or alternatively the ICP-OES – inductively coupled plasma optical emission spectroscopy.
15. As (arsenic) – parameter analysed within EMEP, obligation to monitor total arsenic deposition also results from Directive 2004/107/EC; parameter recommended as voluntary under the HELCOM programme; in case of combining EMEP and HELCOM stations, it can be used as supplementary information and to support assessment of the state of the Baltic Sea environment, given that it has been obligatorily introduced into the monitoring of the Baltic Sea within the framework of the State Environmental Monitoring as an indicator of potential contamination by CW agents from dumped chemical weapons (tested in fish and bottom sediments), recommended in regional monitoring for a selected group of stations depending on the region of Poland. Anthropogenic emissions of arsenic air supply come mainly from copper smelting (approx. 50%) and processing of other non-ferrous metals (10%) and coal combustion, especially low-quality brown coal (about 20%). It is carcinogenic. The adverse effects of industrial emissions of arsenic on humans and the environment are associated not only with direct inhalation exposure (i.e. inhalation of arsenic-containing dust), but also with its accumulation in soil or waters associated with precipitation of contaminated dust. For analyses, one of the following GAW/WMO and EMEP preferred methods is recommended: the ICP-MS – inductively coupled plasma mass spectrometry, the GF-AAS – graphite furnace atomic absorption spectrometry or the FAAS – flame atomic absorption spectrometry or alternatively the ICP-OES – inductively coupled plasma optical emission spectroscopy.
16. Cr (chromium) – parameter mandatory under EMEP, recommended as voluntary under HELCOM; in case of combining EMEP and HELCOM stations, it can be used as supplementary information and to support assessment of the state of the Baltic Sea environment, recommended in regional monitoring for a selected group of

stations, depending on the region Poland. The presence of chromium in ambient air is a result of radioactive dust reaching the ground, volcanic activity and emissions from industrial sources (power plants firing coal containing chromium, cement works, water coolers where chromates are used as rust inhibitors). The cause of chromium contamination of water and soil is atmospheric precipitation, leaching and weathering of rocks, discharge of industrial effluents, etc. It is absorbed into the human body in the respiratory system, the digestive system and through the skin. Solubility of the compounds in water and the particle size of the aerosol have a significant impact on the amount of absorption. For analyses, one of the methods preferred by GAW/WMO and EMEP is recommended: the ICP-MS – inductively coupled plasma mass spectrometry, the GF-AAS – graphite furnace atomic absorption spectrometry or the FAAS or alternatively the ICP-OES – inductively coupled plasma optical emission spectroscopy.

17. Ni (nickel) - parameter mandatory under EMEP, total nickel deposition monitoring is also mandatory under Directive 2004/107/EC; recommended as voluntary in the HELCOM programme; in case of combining EMEP and HELCOM stations, it can be used as supplementary information and to support assessment of the state of the Baltic Sea environment, recommended in regional monitoring for a selected group of stations, depending on the region of Poland. The parameter is on the list of priority substances according to the Water Law as hazardous substance. Nickel is absorbed into the organism primarily via the respiratory system. Nickel tends to accumulate in lung and lymphatic tissue. Nickel is a trace metallic element commonly found in nature. It enters the soil and groundwater with wind and rainfall. The main source of nickel in the environment is the combustion of solid fuels, especially coal, and the burning of oil, waste, and steel production and plating processes. In air contaminated with nickel compounds, the metal can be found in the form of sulphates, sulphides and nickel oxides. For analyses, one of the methods preferred by GAW/WMO and EMEP is recommended: the ICP-MS – inductively coupled plasma mass spectrometry, the GF-AAS – graphite furnace atomic absorption spectrometry or the FAAS – flame atomic absorption spectrometry, or alternatively the ICP-OES – inductively coupled plasma optical emission spectroscopy.
18. Hg (mercury) – heavy metal considered to be very harmful, parameter analysed under EMEP level 2; monitoring of total mercury deposition is also mandated under Directive 2004/107/EC; in marine environmental monitoring, it is measured in various ecosystem components: fish, bivalves, seabed sediments and seawater. It is included as a core indicator in assessments of the state of the marine environment (https://helcom.fi/wp-content/uploads/2019/08/Metals-HELCOM-core-indicator-2018.pdf). It is a parameter used to verify the model for the deposition of mercury to the Baltic Sea (e.g. MSC-W Technical Report 3/2020); it is a Level 2 parameter of the EMEP programme, definitely required to be included in measurements performed at HELCOM stations, recommended in regional monitoring for a selected group of stations, depending on the region of Poland. The parameter is on the list of priority substances according to the Water Law as hazardous substance. Mercury is released into the atmosphere by coal-fired power stations and mining activities. The harmful substance then takes on different chemical forms, circulating between air, soil and water in a complex cycle. Mercury is particularly dangerous in the sea, where it accumulates in fish in the form of highly toxic methylmercury. It is a major threat to water management, including fisheries management. For analyses, the recommended, GAW/WMO and EMEP preferred method is CV-AFS – cold vapour atomic fluorescence spectrometry or alternatively, one of the following methods: the ICP-MS – inductively coupled plasma mass spectrometry or cold vapour atomic absorption spectrometry.

19. PCBs (polychlorinated biphenyls) – congeners 28, 52, 101, 118, 138, 153, 180 - EMEP level 2 parameter, recommended as voluntary under the HELCOM programme; in case of combining EMEP and HELCOM stations, it can be used as supplementary information and to support assessment of the state of the Baltic Sea environment; it is included as a core indicator in assessments of the state of the marine environment (https://helcom.fi/wp-content/uploads/2019/08/Polychlorinated-biphenyls-PCBs-dioxin-and-furan-HELCOM-core-indicator-2018.pdf); the congener PCB 153 is a parameter used for verification of the model determining its deposition to the Baltic Sea (e.g. MSC-W Technical Report 3/2020). MSC-W Technical Report 3/2020), recommended in monitoring for a selected group of locations and for a selected type of stations connected to EMEP stations of Programme 2. PCB 118 (and others) is included in the list of priority substances, identified as a priority hazardous substance according to the Annex to the Regulation of the Minister of Maritime Affairs and Inland Navigation of 1 March 2019 on the list of priority substances under Article 114 of the Act of 20 July 2017 – the Water Law (Journal of Laws 2018, item 2268 and 2019, item 125). For analyses, the recommended, GAW/WMO and EMEP preferred method is the GC-MS – gas chromatography mass spectrometry or alternatively one of the following: the GC-ECD – gas chromatography with electron capture detector or the GC-MS/MS – gas chromatography with tandem mass spectrometry.
20. PAHs (polycyclic aromatic hydrocarbons) – parameter placed at EMEP Level 2, obligation to monitor total PAH deposition also results from Directive 2004/107/EC and NEC Directive (2016/2284/EC); recommended as voluntary under the HELCOM programme; in case of combining EMEP and HELCOM stations, it can be used as supplementary information and to support assessment of the state of the Baltic Sea environment; it is included as a core indicator in marine environmental assessments (https://helcom.fi/wp-content/uploads/2019/08/Polyaromatic-hydrocarbons-PAHs-and-their-metabolites-HELCOM-core-indicator-2018.pdf); recommended for EMEP Level 2 and HELCOM stations. Benzo(a)pyrene should be included in the mandatory measurement. Benzo(a)pyrene is a parameter used to verify the model to determine its deposition to the Baltic Sea (e.g. MSC-W Technical Report 3/2020) and is recommended for regional monitoring for a selected group of stations and station type. The parameter is included in the list of priority substances under the Water Law as a hazardous substance. It is toxic, carcinogenic, mutagenic, toxic for reproduction and dangerous for the environment. It can cause cancer, hereditary genetic defects and can impair fertility. May cause harm to the unborn child. Very toxic to aquatic organisms; may cause long-term adverse effects in the aquatic environment. At the EMEP Level 2 stations, in addition to benzo(a)pyrene, other PAHs should be measured, namely benzo(b)fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene, benzo(a)anthracene, benzo(j)fluoranthene and dibenzo(a,h)anthracene. As the three variants of benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene can be difficult to separate in a test, they can, according to Directive 2004/107/EC, be reported as a total. For analyses, the recommended, GAW/WMO and EMEP preferred method is the GC-MS – gas chromatography mass spectrometry, or alternatively one of the following methods: the HPLC – high-performance liquid chromatography or the GC-MS/MS – gas chromatography with tandem mass spectrometry.
21. DDT/DDE (dichlorodiphenyltrichloroethane and dichlorodiphenyldichloroethylene) – parameter placed at Level 2 of the EMEP programme, can be found on the list of priority substances under the Water Law as a hazardous substance. Widely used

in the mid-20th century. It is particularly hazardous to living organisms because its high fat solubility contributes to accumulation in the body. Recommended in monitoring for EMEP Level 2 stations. For analyses, the recpmmended, GAW/WMO and EMEP preferred method is the GC-MS – gas chromatography mass spectrometry or alternatively one of the following methods: the GC-ECD – gas chromatography with electron capture detector or the GC-MS/MS – gas chromatography with tandem mass spectrometry.

22. HCB (hexachlorobenzene) – parameter placed at EMEP Level 2, it is on the list of priority substances under the Water Law as a hazardous substance. Recommended in monitoring for EMEP level 2 stations. It was used as a fungicide, as an semi-finished product in organic synthesis and as a wood preservative. The use of this fungicide is prohibited under the international Stockholm Convention as a persistent organic pollutant (POPs). For analyses, the recommended, GAW/WMO and EMEP preferred method is the GC-MS – gas chromatography mass spectrometry, or alternatively one of the following methods: GC-ECD – gas chromatography electron capture detector or GC-MS/MS – gas chromatography tandem mass spectrometry.
23. HCHs (hexachlorocyclohexane) – this parameter is on the list of priority substances under the Water Law as a hazardous substance, placed at EMEP Level 2, where GC-MS – gas chromatography mass spectrometry is the preferred method of analysis. Recommended for monitoring at EMEP level 2 stations.

    For analyses, the recommended, GAW/WMO and EMEP preferred method is the GC-MS – gas chromatography mass spectrometry or alternatively one of the folowing methods: the GC-ECD – gas chromatography with electron capture detector or GC-MS/MS – gas chromatography tandem mass spectrometry.
24. Chlordane – parameter placed at EMEP level 2, it is on the list of priority substances under the Water Law as a hazardous substance. Recommended in monitoring for EMEP level 2 stations.

    For analyses, the recommended, GAW/WMO and EMEP preferred method is the GC-MS – gas chromatography mass spectrometry, or alternatively one of the following methods: the GC-ECD – gas chromatography with electron capture detector or the GC-MS/MS – gas chromatography tandem mass spectrometry.

An additional parameter not included in the recommendations:

1. Brominated diphenylethers PBDEs (congeners 28, 47, 99, 100, 153, 154) – parameter used in the assessment of the state of the marine environment and water bodies. Current concentrations of total congeners remain above the applicable threshold value, which is very low (a revision of the threshold value is planned). Given that PBDEs levels are indicative of poor environmental status, testing of these compounds in precipitation samples should be considered to determine atmospheric deposition. This indicator may be considered as a conditional at HELCOM stations. Gas chromatography is recommended for analysis.

Tables 6.5, 6.6, 6.7 present parameter summaries for the specific type of chemistry monitoring stations: basic stations, specialised stations (regional monitoring), basic stations combined with EMEP level 1 and 2 stations and basic stations combined with EMEP level 1 and 2 and/or HELCOM stations.

Table 6.5 Summary of proposed parameters for basic and specialised chemistry monitoring stations, regional monitoring (own work)

Basic chemistry monitoring stations	**Specialised chemistry monitoring stations**
SO_4^{2-}	SO_4^{2-}
NO_3^-	NO_3^-
NH_4^+	$NH4^+$
H^+ (pH)	H^+ (pH)
Na^+	Na^+
K^+	K^+
Ca^{2+}	Ca^{2+}
Mg^{2+}	Mg^{2+}
Cl^-	Cl^-
conductivity	conductivity
Pb	Pb
Cd	Cd
total nitrogen	total nitrogen
total phosphorus	total phosphorus
	Cu*
	Zn*
	As*
	Cr*
	Hg*
	PAHs*

* parameters depending on the region of Poland

Table 6.6 Summary of proposed parameters for basic chemistry monitoring stations combined with EMEP level 1 and level 2 stations (own work)

Basic chemistry monitoring stations + EMEP level 1	**Basic chemistry monitoring stations + EMEP level 2**
SO_4^{2-}	SO_4^{2-}
NO_3^-	NO_3^-
NH_4^+	NH_4^+
H^+ (pH)	H^+ (pH)
Na^+	Na^+
K+	K+
Ca^{2+}	Ca^{2+}
Mg^{2+}	Mg^{2+}
Cl^-	Cl^-
conductivity	conductivity
Pb	Pb
Cd	Cd
total nitrogen	total nitrogen
total phosphorus	total phosphorus
Cu	Cu
Zn	Zn
As	As
Cr	Cr
Ni	Ni
HCO_3^-, at pH>6 (calculated from the pH at pH<6)	HCO_3^-, at pH>6 (calculated from pH at pH<6)
	Hg
	PAHs*
	PCBs (polychlorinated biphenyls)
	HCB (hexachlorobenzene)
	chlordane
	HCHs (hexachlorocyclohexane)
	DDT/DDE (dichlorodiphenyltrichloroethane/ dichlorodiphenyldichloroethylene)

PAHs* - mandatory for benzo(a)pyrene, where possible also benzo(b)fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene, as well as benzo(a)anthracene, benzo(j)fluoranthene and dibenzo(a,h)anthracene.

Table 6.7 Summary of proposed parameters for basic chemistry monitoring stations in combination with EMEP level 1 and 2 and/or HELCOM stations (own work)

Basic chemistry monitoring stations + EMEP level 1 + HELCOM	**Basic chemistry monitoring stations + EMEP level 2 + HELCOM**	**Basic chemistry monitoring stations + HELCOM**
SO_4^{2-}	SO_4^{2-}	SO_4^{2-}
NO_3^-	NO_3^-	NO_3^-
NH_4^+	NH_4^+	NH_4^+
H^+ (pH)	H^+ (pH)	H^+ (pH)
Na^+	Na^+	Na^+
K^+	K^+	K^+
Ca^{2+}	Ca^{2+}	Ca^{2+}
Mg^{2+}	Mg^{2+}	Mg^{2+}
Cl^-	Cl^-	Cl^-
conductivity	conductivity	conductivity
Pb	Pb	Pb
Cd	Cd	Cd
total nitrogen	total nitrogen	total nitrogen
total phosphorus	total phosphorus	total phosphorus
Cu	Cu	Cu
Zn	Zn	Zn
As	As	As
Cr	Cr	Cr
Ni	Ni	Ni
HCO_3^-, at pH>6 (calculated with pH at pH<6)	HCO_3^-, at pH>6 (calculated from pH at pH<6)	-
Hg	Hg	Hg
PAHs*	PAHs**	PAHs*
PCBs (polychlorinated biphenyls)	PCBs (polychlorinated biphenyls)	PCBs (polychlorinated biphenyls)
PBDEs***	HCB (hexachlorobenzene)	PBDEs***
	chlordan	
	HCHs (hexachlorocyclohexane)	
	DDT/DDE (dichlorodiphenyltrichloroethane and dichlorodiphenyldichloroethylene)	
	PBDEs***	

PAHs* – mandatory benzo(a)pyrene

PAHs** – benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, benzo(a)anthracene, benzo(j)fluoranthene and dibenzo(a,h)anthracene

PBDEs*** – brominated diphenylethers PBDE (congeners 28, 47, 99, 100, 153, 154) – additional parameter not included in the recommendations, considered conditional

Proposed sampling regime and physicochemical analysis regime

As mentioned above, wet precipitation sampling is recommended. Total precipitation sampling is acceptable if there are circumstances that prevent the use of a wet precipitation collector or make it impractical. As recommended and required by the GAW programme, the recommended sampling frequency is 24 hours. In case of high costs or problems with daily sampling, this period can be extended to a maximum of 7 days.

Therefore, we recommend for basic and specialised chemistry monitoring stations (regional monitoring) a weekly basis for precipitation collection, and a daily basis for EMEP and HELCOM stations.

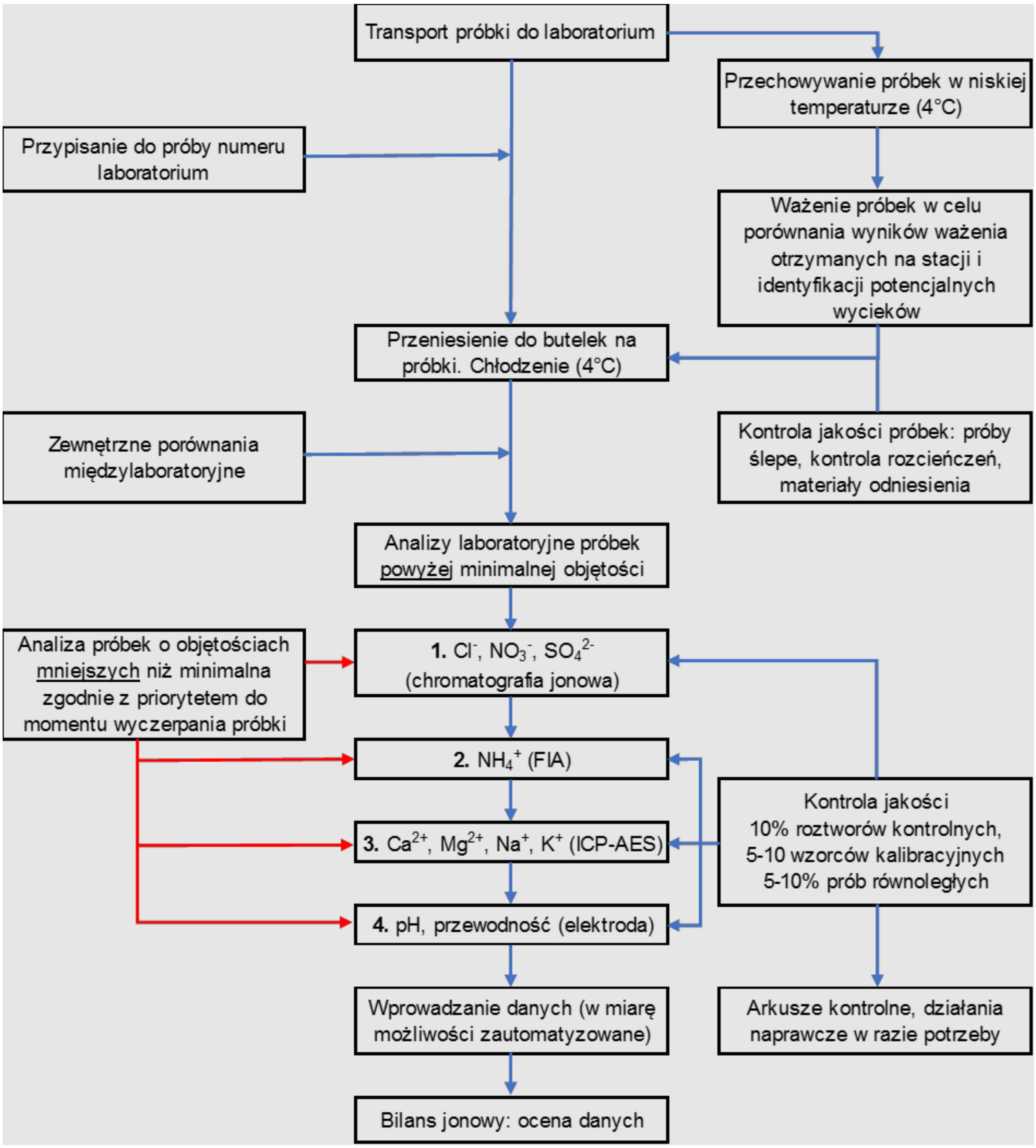
Experience from the regional background sites in Osieczów, Puszcza Borecka and Zielonka shows that sampling for determination of total deposition of heavy metals and total deposition of PAHs should be conducted in two separate collectors. These two groups of components have different methodological considerations, different requirements for the preparation of the collector for testing and experience has shown that the samples of total precipitation are heterogeneous, which makes it difficult to properly separate samples for the determination of PAH and heavy metals. In addition, heavy metals tend to settle on the walls and remain on the walls when the sample is decanted. If one wanted to use samples collected in a single collector, one could first pour out part of the sample for PAH determination and acidify the remaining part and use it for heavy metals determination, but there is a concern that no part of the sample would properly represent the actual heavy metal and PAH contents. Therefore, for EMEP level 2 and HELCOM stations it is recommended to use two separate collectors for sampling.

Monthly transmission of samples to laboratories is recommended and will be possible for stations with regular service and the possibility to store weekly samples in refrigeration units. For stations without regular service, samples should be collected more frequently, depending on the type and technical possibilities of the collectors used at the stations.

It is recommended that laboratories conduct analyses of weekly samples on a monthly basis. In order to ensure the high quality of the analyses performed, it is recommended to select as few laboratories as possible for the analysis of samples from chemistry monitoring stations.

The laboratory shall aim to measure all required components for each sample. It is necessary to predetermine the minimum volume required to perform a complete set of tests. For samples with less than the required volume, the laboratory must be guided by specific priorities for the importance of the tests. The order recommended by GAW/WMO is shown in Figure 6.1.

Where possible, analyses should be carried out without long delays between individual measurements, minimising the possibility of chemical changes and deterioration of the sample. Ideally, anions and the ammonium ion should be measured on the same day and the pH measurement was carried out immediately afterwards. The ammonium ion is usually the least stable of the mandatory components and should be analysed as soon as possible. Where metals can only be analysed individually, the suggested order is calcium, magnesium, sodium and potassium. The following parameters should be determined next: total phosphorus and total nitrogen, heavy metals or PAHs and POPs.



Assigning laboratory number to the sample / External comparisons between laboratories / Analysis of samples with volumes below the minimum in accordance with the priority until exhaustion of the sample
Transport of the sample to the laboratory / Transfer into sampling bottles. Cooling (4°C) / Laboratory analyses of the samples above the minimum volume / 1. Cl^-, NO_3^-, SO_4^{2-} (ion chromatography) / 2. NH_4^+ (FIA) / 3. Ca^{2+}, Mg^{2+}, Na^+, K^+ (ICP-AES) / 4. pH, conductivity (electrode) / Entering data (as automated as possible) / Ion balance; data assessment
Storage of samples in low temperature (4°C) / Weighing the samples to compare weighing results obtained from the stations and identify possible leaks / Sample quality control; blind samples, control of dilutions, reference materials / Quality control of 10% of control solutions, 5-10 calibration standards, 5-10% of parallel samples / Control sheets, remedial actions as needed

Figure 6.1 Example of a flow chart of the priority of measurements performed in a laboratory (source Manual GAW No. 160, 4.1)

7. Summary

The present study presents the scope of measurements and physicochemical analyses along with information on sampling methods of precipitation wet deposition, measurements of gases and aerosols (important for the estimation of dry deposition) and methods of physicochemical analyses for the network of precipitation chemistry monitoring stations. For each substance, a justification for the selection was presented based on information on changes in wet deposition of selected substances in the area of Poland and tracking trends in this area, as well as determination of loads of substances deposited to the ground, information on wet deposition for water management purposes, for HELCOM and information on deposition of pollutants referred to in the NEC Directive. The links between precipitation chemistry and climate change and the integration of chemistry studies with studies for EMEP are traced. The sampling method and the procedure of physicochemical analysis were also proposed.

8. Conclusions

As a result of an in-depth analysis of domestic and international documents in the scope of air and precipitation chemistry studies, with particular emphasis on precipitation chemistry, contained in the Report entitled “Analysis of Polish and foreign documents and studies, monitoring systems and data of the State Environmental Monitoring in the context of designing a new system for the study and assessment of atmospheric deposition”, there was developed the list of parameters necessary for monitoring wet deposition chemistry in Poland.

The recommended list of parameters, together with the range of analytical test methods and measurement methodology, ensures that Poland meets the requirements for participation in the implementation of research tasks under international programmes.

An appropriate choice of locations for monitoring stations will complement the range of precipitation chemistry measurements.

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