# 1. Commentary on the summary annual tabular survey

## 1.1 Overview of measuring methods

# 1.1.1 Overview of measuring methods in the network of automated monitoring stations (AMS)

Component	Abbreviation	Method	Type of method
$SO_2$	UVFL	ultraviolet fluorescence	reference
NO <sub>x</sub>	CHML	chemiluminescence	reference
$PM_{10}, PM_{2.5}$	RADIO	radiometry	equivalent
	TEOM	tapered element oscillating microbalance	equivalent
CO	IRABS	IR correlation absorption spectrometry	reference
$O_3$	UVABS	ultraviolet absorption photometry	reference
NH <sub>3</sub>	CHML	chemiluminescence	
BTX	GC-FID	gas chromatography – flame-ionization detection	reference
	GC-PID	gas chromatography – photo-ionization detection	
Hg	AFS low-temperature gas atomic fluorescence		
	AMA	atomic absorption spectrophotometry AMA for mercury determination	

## 1.1.2 Overview of measuring methods in the network of manual stations

Component	Abbreviation	Method	Type of method
SO <sub>2</sub>	WGAE	spectrophotometry using TCM and fuchsin (West-Gaeke)	equivalent
	IC	ion chromatography	equivalent
	FUCEL	electrochemical fuel cell	equivalent
	CLM	coulometry	equivalent
NO <sub>2</sub>	CLM	coulometry	equivalent
NO <sub>x</sub>	FUCEL	electrochemical fuel cell	equivalent
	GUAJA	guajacol (modified Jakobs-Hochheiser) spectrophotometry	equivalent
	TLAM	triethanolamine spectrophotometry	equivalent
SPM, PM <sub>10</sub> , PM <sub>2.5</sub>	GRV	gravimetry	reference
TK/HM	AAS	atomic absorption spectrometry	reference
	PLRG	polarography	equivalent
	ICP-AES	inductively coupled plasma – atomic emission spectrometry	equivalent
	XRF	X-ray fluorescence	equivalent
	ICP-MS	inductively coupled plasma – mass spectrometry	reference
SO <sub>4</sub> <sup>2-</sup>	IC	ion chromatography	equivalent
$\sum NO_3^-$	IC	ion chromatography	
$\sum NH_{4}^{+}$	FIA-BERTH	spectrometry: flow injection analysis (FIA) with indophenol, Berthelot reaction	
VOC	GC-VOC	gas chromatography	reference
Benzene	PD	passive sampler	
PAH	GC-MS	gas chromatography with mass detection	
	HPLC	high performance liquid chromatography	
	GC-MS/PUF	gas chromatography - mass spectroscopy (only PUF)	
	GC-MS/QUA	gas chromatography - mass spectroscopy (only QUARTZ)	
EC [elemental carbon	HD_FID	heat decomposition_FID	
OC [organic carbon]	HD_FID	heat decomposition_FID	

### 1.1.3 Overview of measuring methods of supplementary meteorological elements

Component	Abbreviation	Method
Wind direction and velocity	OPEL	optoelectronically
	U-SONIC	ultrasonic anemometer
Global radiation (GLRD)	TDM	temperature difference method
Atmospheric pressure	APRESS	atmospheric pressure measurement
Relative air humidity	CAP	capacitance sensor
	HAIR	hair hygrometer
Temperature	PT100	resistance method
RAD	RAD	dosimeter
Precipitation amount	RAIN	automatic pluviometer

### 1.1.4 Sampling procedure and description of the used methods

### FAAS - flame atomic absorption spectrometry

The aerosol of the analysed sample is directly driven to the acetylene-air flame supplied by the light beam from the respective spectral lamp. The decline of the intensity of the light after passing through the flame is indicated and it is proportional to the concentration of the determined element in the sample.

Use: see GF-AAS

### GF-AAS - graphite furnace atomic absorption spectroscopy with electrothermic atomization

The constant microvolume of the acidified precipitation sample and the modifier is dosed to the graphite furnace of the electrothermal atomiser (ETA). Then evaporation, pyrolysis and atomization occur. ETA is located in the optical axis of the beam emitted from the respective spectral lamp. The indicated decline of the light intensity after passing through the furnace is proportional to the concentration of the determined element.

Use: determination of metals e.g. in precipitation samples from the stations of the precipitation monitoring network.

### Spectrophotometry, FIA (flow injection analysis) with indophenol, Berthelot reaction

Sampling on filters is carried out in a sampling head which is drawn through air for 24 hours a day.

Ammonium ions are captured on the first located paper filter, gaseous  $NH_3$  is captured on the filter impregnated with citric acid in methanol,  $NH_4^+$  is determined by the method of Bertholet reaction after the filters are eluted by demineralized water.  $NH_4^+$  reacts with alkaline solution of phenol and hypochlorite at 60 °C and the resulting indophenol is determined spectrophotometrically at 630 nm using flow analyzer FIA. The sum of  $NH_4^+$  (in  $\mu g \cdot m^{-3}$ ) is calculated from both analyses of the filters. In precipitation  $NH_4^+$  is determined similarly as in the aqueous elution from the filters.

Use: sum  $NH_4^+$  in the ambient air at manual stations and  $NH_4^+$  at the stations of the precipitation network.

#### Coulometry

Electrochemical method where electrolytical current is proportional to gas concentration according to Faraday's law. *Use:* SO<sub>2</sub>, NO<sub>2</sub>

### El. fuel cell

A semiautomatic method, APM analyzer of City Technology Corp. with a selective micro-fuel cell. Use:  $SO_2$ ,  $NO_x$  at Health Institutes stations

#### Gravimetry

The sample is taken through continuous filtration of ambient air on selected filtering material (membrane filters made of cellulose derivates or teflon with appropriate pore size or of glass fibre; capturing efficiency > 99.5 %). The difference between the weight of the filter prior to and after the exposure is determined gravimetrically.

Use: SPM,  $PM_{10}$ ,  $PM_{2.5}$  at manual stations, in CHMI filters with diameter 47 mm are used for detecting  $PM_{10}$ ,  $PM_{2.5}$  – Whatman GF/C (for simple gravimetry) and Merck Millipore SSWP (for gravimetry with the subsequent analysis of HM).

### Guajacol (modified Jakobs-Hochheiser) spectrophotometry

After oxidation  $NO_2$  is absorbed into the solution of NaOH with addition of guajacol and is converted to nitrites. Reaction in acid medium of  $H_3PO_4$  with a solution of sulfanilamide and N-(1-naphthyl)ethylene diamine dihydrochloride (NEDA) follows to form a red colour. The intensity of the colour is measured spectrophotometrically at 560 nm.

Use:  $NO_x$ ,  $NO_2$  at manual stations

### Mass spectrometry with inductively coupled plasma

Fractional sampling on membrane filters made of cellulose derivates, after gravimetry acid digestion and ICP-MS (mass spectrometry) analysis, elemental analysis – separation by element mass and their detection with electron multiplier detector.

Use: Detection of metals in SPM,  $PM_{10}$  and  $PM_{2.5}$  at manual stations, in CHMI for detecting metals in  $PM_{10}$ ,  $PM_{2.5}$ , Merck Millipore SSWP filters with diameter 47 mm, ICP-MS analysis, digestion in microwave field (Milestone Ethos Plus).

#### Chemiluminescence

Nitrogen molecule excitation by ozone. With the conversion of the molecule into the basic energetic level, release of radiation as chemiluminescence occurs. This radiation is detected by a photomultiplier.

Use: NO, NO<sub>2</sub>, NO<sub>x</sub>

### Ion chromatography

It is used for the determination of anions in precipitation and in the ambient air. The precipitation sample is analyzed directly, the air sample is drawn through a filter to capture sulphate and nitrate particles. Another filter impregnated with hydroxide captures sulphur dioxide and gaseous nitric acid. The exposed filters are leached out using deionized water and the sulphate and nitrate ion are determined by ion chromatography. Nitrates and gaseous nitric acid are determined as the sum of nitrate ion. Ion chromatography is based on the separation of anions in the colon filled with anion exchanger and their gradual elution and subsequent detection.

Use: Fluorides, chlorides, nitrates and sulphates in precipitation and  $SO_2$ , sulphates and sum of nitrate ion in the ambient air at manual stations

### IR-correlation absorption spectrometry

The radiation from an infra-red source passes through two parallel cells, one of which contains a non-absorbing background gas, the other contains the analyzed flowing sample of ambient air. The difference in energy between the sample and the reference cell is proportional to the carbon monoxide concentration.

Use: CO at AIM stations

#### Low-temperature gas atomic fluorescence

Mercury vapour is captured in the block with ultra-clean golden absorbent in the form of amalgam from which mercury is released by heating and decoded.

Use: Hg at AIM stations

### **Optoelectronic method**

The wind direction and velocity are measured using a wind vane and an anemometer. The position of the vane is taken optoelectronically or transferred to electrical voltage using a circular potentiometer.

The rotation speed of the anemometer sensor is measured optoelectronically or transferred to electrical voltage using a tachodynamo.

Use: wind direction and velocity at AIM stations

### Tapered element oscillating microbalance

It measures the mass of the sample captured on a replaceable filter according to the oscillating tapered element frequency variation. The air sample passes through a filter where the dust particles are captured and runs through a hollow tapered element to a vacuum pump with an electronic flow control.

*Use:*  $PM_{10}$  at AIM ZU stations

#### Passive sampler

The sampling method – the measured air pollutant is captured at the medium (usually impregnated filter or a tube with sorbent) by passive diffusion. After the capture the pollutant reacts with the impregnation agent, or the pollutant is bound with sorbent. The captured pollutant is extracted or released from the sorbent and its concentration is determined by appropriate analysis. Based on the detected concentration and the length of exposure the average pollutant concentration in the monitored area for the period of exposure is calculated using the experimentally set coefficients. The exposure time is usually 1–2 weeks.

Use: screening measurements for first assessment of air pollution levels in the given area; determination of benzene at air pollution monitoring stations.

### Gas chromatography - photo-ionization detection

Continual measurement of aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes) by BTX analyzers Syntech and gas chromatography method. It is a case of standard linkage to a sampling probe in a container. The method is based on photoionization detection.

Use: Ústí n. L., Praha-Libuš, Pardubice-Rosice

### Gas chromatography - flame-ionization detection

Continual measurement of aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes) by BTX analyzers Chrompac and gas chromatography method. It is a case of standard linkage to a sampling probe in a container. Ionization of organic substances in flame (hydrogen- air), increase of ion current proportional to the concentration of the measured substances at constant gas flow.

Use: Praha-Libuš, Praha-Strahovský tunel, Rudolice, Mikulov-Sedlec, Most, Ostrava-Přívoz

### Gas chromatography

Persistent organic pollutants (POP) are captured on glass-fibre and polyurethan filters using high-volume pump sampling. Exposed filters are eluated with dichlormethane. After purification and preconcentration the selected POP are measured by gas chromatography with mass detection.

Use: CHMI- MS Košetice, ZÚ stations

### Gas chromatography

Volatile organic compounds (VOC) are determined by gas chromatography. Air samples taken in special vacuum steel canisters on Monday and Thursday of each week at 12:00 UTC for a period of 10 minutes (CHMI). At Health Institutes' (ZÚ) stations the 24-hour samples are taken every 6th day during the heating period (November–March) and every 12<sup>th</sup> day in the non-heating period (April–October). Samples from transportation canisters are modified by cryogenic concentration prior to the GCH analysis.

Use: CHMI and ZÚ stations

### **Polarography**

Sampling on membrane filter, acid decomposition, differential pulse polarography DPPAFW.

Use: HM at ZÚ stations up to 1991–1993

### **Potentiometry**

Potentiometric titration to equiv. point pH 4.5

Use: SO<sub>2</sub> at ORGREZ stations

### Radiometry – absorption of beta radiation

It stands on beta-ray absorption in a sample captured on filtering material. The difference between the beta-ray absorption of the exposed and non-exposed filtering material, which is proportional to the mass of the captured suspended particulate matter, gives the information on its concentration.

Use: SPM,  $PM_{10}$ ,  $PM_{2.5}$  at AIM stations

### X-ray fluorescence

Non-destructive analysis with sampling on teflon filter exposed to X-rays.

Use: metals and sulphates in SPM

### Spectrophotometry with TCM and fuchsin - West-Gaeke

The sulphur dioxide is absorbed into a sodium tetrachloromercury solution (TCM) containing Chelaton III. The compound formed reacts with fuchsin and formaldehyde in acid medium to yield a red-purple colour, which is measured spectrophotometrically at 586 nm.

Use: SO<sub>2</sub> at manual stations

### **Temperature difference method**

Energy of solar radiation (GLRD) is measured in W.m<sup>-2</sup> using temperature difference method. The temperature difference of black and white coloured segments of sensor surface with different reflection to short-wave solar radiation is measured.

#### Triethanolamine spectrophotometry

After oxidation NO<sub>2</sub> is absorbed into the solution of thiethanolamine with sulfanilic acid in acid medium of H<sub>3</sub>PO<sub>4</sub> using NEDA. The intensity of the colour is measured spectrophotometrically at 540 nm.

Use: NO<sub>x</sub> at manual ZÚ stations

### Ultrasonic anemometer

Comparison of the times taken for an ultrasonic puls to travel between ultrasonic transducers.

Use: wind velocity measurement

#### **UV** absorption

The method rests upon absorption of radiation with the wavelength of 254 nm by ozone in the analyzed sample. The radiation source is an UV-lamp and clean air (zero) and the sample itself are alternately measured in cell.

Use: ozone at AIM stations

#### **UV fluorescence**

The analysed sample is exposed to UV-lamp irradiation with energetic excitation of SO<sub>2</sub> molecule. With the backward conversion of the molecule into the basic energetic level, energy as fluorescing radiation is released. This radiation is proportional to the sulphur dioxide concentration and is detected by a photomultiplier.

Use: SO<sub>2</sub>, H<sub>2</sub>S at AIM stations

### High performance liquid chromatography

### Gas chromatography - mass detection (for PAH)

Samples are captured on a filter and further adsorbing material for PAH in gaseous phase. The samples are processed in a chemical laboratory and analyzed by the HPLC method or GCH-MS method.

### **Heat decomposition FID**

Organic carbon (OC) and elemental carbon (EC) are determined from aerosol  $PM_{10}$  and  $PM_{2.5}$  by capture on silicon filters. The cut sample is inserted into silicon furnace flushed with helium. The resulting products, created by thermal decomposition, are oxidized by manganese dioxide to  $CO_2$  which is converted to methane and measured by flame ionization detector as OC. During the second thermal programme elemental carbon is oxidized in the oxidation mixture of oxygen and helium and is measured in the same way.

Use: EC, OC

### 1.1.5 Overview of sampling types and analytical methods in the CHMI precipitation monitoring network

Observed components in precipitation	Sampling period	Sampling type	Analytical methods in laboratory
amount of precipitation	daily	rain gauge	
conductivity	weekly	wet-only	EC-meter
рН	weekly	wet-only	pH meter
F-	weekly	wet-only	ion chromatography
Cl <sup>-</sup>	weekly	wet-only	ion chromatography
SO <sub>4</sub> <sup>2-</sup>	weekly	wet-only	ion chromatography
NO <sub>3</sub>	weekly	wet-only	ion chromatography
Na <sup>+</sup>	weekly	wet-only	flame atomic absorption spectrometry
Mg <sup>2+</sup> Ca <sup>2+</sup>	weekly	wet-only	flame atomic absorption spectrometry
Ca <sup>2+</sup>	weekly	wet-only	flame atomic absorption spectrometry
K <sup>+</sup>	weekly	wet-only	flame atomic absorption spectrometry
NH <sub>4</sub> <sup>+</sup>	weekly	wet-only	spectrophotometry, FIA with indophenol, Bertholet reaction
As, Cd, Co*, Cr*, Cu*, Fe*, Ni, Mn*, Pb, Se*, V*, Zn*	weekly	wet-only	inductively coupled plasma - mass spectrometry

#### Notes:

At the station in Košetice monthly bulk samples are also collected as well as monthly throughfall samples. In addition, daily wet-only samples are also collected there using the analysis of commonly determined ions incl. the analysis of POPs-PCB and POPs-PAH. Wet-only sampling is realized by automatic collectors NSA 181/KHD and NSA 181/S supplied by Eigenbrodt Co.

Bulk sampling is realized by Precipitation Collector RS1 supplied by NILU Products AS, a subsidiary of the Norwegian Institute for Air Research (NILU).

Metals signed by \* are not accredited by the Czech Accreditation Institute.

### 1.2 Database of the annual processing and Air Quality Information System

The periodically published Tabular Survey is a result of the statistical processing of air pollution data systematically stored over the calendar year in the air pollution database from all significant networks monitoring air pollution in the country. From the statistical tables it is apparent from how many monitoring stations data were stored and processed in 2013.

Since 1992, the up-to-date information technology has been utilized in the CHMI to establish the Air Pollution Information System (IIS), later integrated in the database system Air Quality Information System (ISKO) which is further developed.

Since the establishment of the ISKO system there have been a lot of changes in data collecting and publishing and the requirements to extend the utility function of the database system have increased. Therefore the new data model ISKO2 project was developed and implemented in 2003 under RDBMS Oracle. ISKO2 meets the growing demands on the presentation of measurement results in various forms incl. internet publication. The new model enables much larger possibilities of data storage, verification, export and further processing. This applies also to metadata, i.e. data about localities and measuring programmes used in these localities. ISKO2 provides the strong, constantly developing software support facilitating the activities connected with the measured data and metadata processing and presentation.

The Air Quality Information System ISKO collects and provides access to further processing of data gathered within significant air pollution monitoring networks and data from the monitoring networks for chemical composition of atmospheric precipitation and atmospheric deposition. It thus allows more effective general utilization of these expensive data. The integrated regionalised evaluation of air pollution levels, and analysis of the development over time of the status of air pollution in this country would not be feasible without collecting and archiving systematically at one place all the air pollution data available. The continuous need to make this assessment objective also necessitates simultaneous accessibility of emission, meteorological and climatic data and geographic information on the locations of pollution sources, the extent and location of forest growth, residential areas, roadways and similar information.

Fig. 1 schematically depicts ISKO's links to data sources and co-operating systems. The scheme outlines the interconnection of air quality monitoring networks and sources of data on emissions with data processing and information layers represented by ISKO, and the linkage to a higher-level layer – "cross-sectional" information systems.

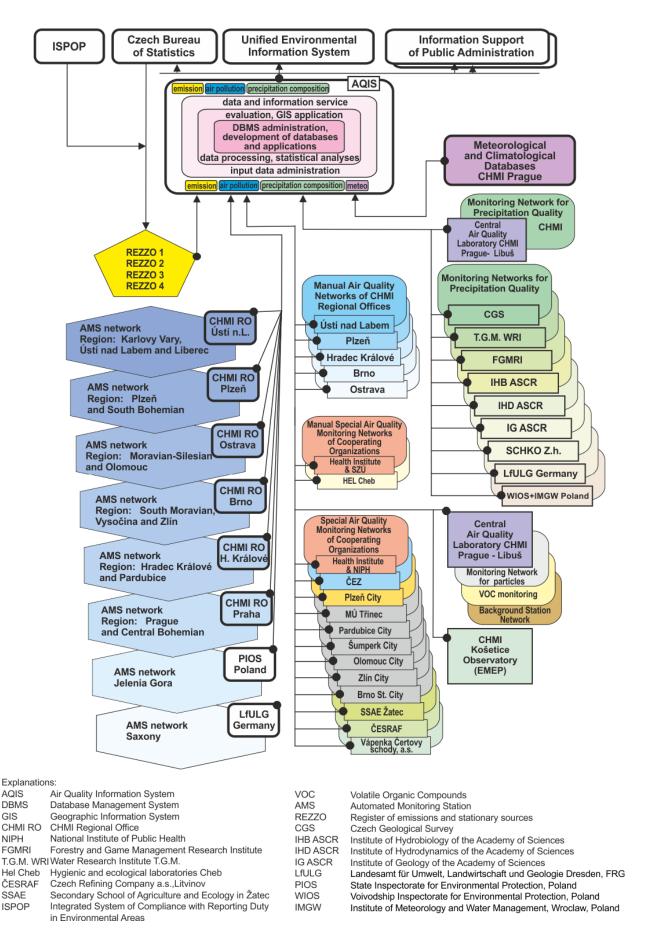


Fig. 1 Scheme of ISKO's links to data sources and cooperating systems in 2013

#### 1.2.1 Computer system

Starting from 1993, both the Tabular Survey and the Graphic Yearbook were completely prepared using a computer system with the SUN database server with the installed Ingres multi-user relative database system under the SOLARIS operating system. In 2003 there was a change to RDBMS Oracle. The data core of the information system is implemented under RDBMS with predominant utilization of client–server architecture. The concept of the system is based on distributed processing in the local network at working stations and personal computers with direct access of processing and analytical programmes, such as the ARC/INFO and ArcGIS geographical information systems, the statistical programmes SPSS, Systat, tabular and graphical programmes, to the data in the CHMI central database with features of uninterrupted and backed-up operation.

The Czech Hydrometeorological Institute has its regional offices throughout the Czech Republic; they are mainly concerned with measurements, data collection and initial processing within their respective regions, including the laboratory analysis. The offices are connected to the central system in Prague via CHMI's packet private data network and via the virtual private network (VPN).

### 1.2.2 Air pollution assessment

In 2012 Clean Air Act No. 201/2012 Coll. and Decree No. 330/2012 Coll., about the way of assessment and evaluating the level of pollution, extent of informing the public about the level of pollution and during the smog situations. The limit values and margins of tolerance set by the Act No. 201/2012 Coll. and Decree No. 330/2012 Coll. are published in the introductory part.

### 1.3 Commentary on the contents of the tables

### 1.3.1 Survey of the station networks

As mentioned in the Preface, the yearbook gives a very extensive survey of the air pollution data for the Czech Republic. It includes the measuring results collected by several organizations. The tabular part begins with the summary statistical table giving the numbers of localities from which data were actually received, based on the individual regions and on the owners. The next tables show: the numbers of localities measuring basic pollutants and supplementary quantities at AMS stations, based on the regions and the owner; the numbers of localities measuring basic pollutants and supplementary quantities by manual and semiautomatic methods, based on the regions and the owner; the total number of localities with special measurements, based on the owner giving the types and numbers of stations in individual regions, based on the owner and the type of the measured quantity. These surveys include the localities (measuring sites) on the territory of the Czech Republic from which the measured data were supplied to ISKO in 2013.

#### 1.3.1.1 Survey of localities and measuring programmes

The survey contains all localities and air pollution measuring programmes registered in the ISKO database with at lest one registered measurement in the year 2013. Each locality is supplemented by the list of measuring programmes registered in ISKO and their characteristic (name, code, classification, type and registered measurement). The overview of localities is ordered by regions, districts and names of localities.

The maps of the zones and agglomerations (regions) of the Czech Republic are presented showing the localities and measuring programmes with the respective codes and the old ISKO numbers.

Finally, the list of stations of the atmospheric precipitation and atmospheric deposition monitoring networks and their localities are presented.

### 1.3.1.2 Types of measuring programmes

Owing to the transition to the new ISKO2 database model there are some modifications as concerns the terminology of the types of the stations used earlier to correspond with the state of the art. ISKO2 defines the locality (measuring site). Each locality operates one or more measuring programmes. The list of measuring programmes used in 2013 is given in the following table.

## Air pollution

Code of measuring programme	Measuring programme	Type of measurement	Analogue values collection and treatment	
M	manual	manual	all manual, processing in laboratory	
A	automated	continuous	automatic collection and processing in measuring site	
K	combined	manual and semiautomatic	partly automatic collection and evaluation on the measuring site and partly processing out of the measuring site	
P	PAH	manual	all manual, treated in laboratory	
Н	PAH within project solution	manual	all manual, treated in laboratory	
T	heavy metals in SPM	manual	all manual, treated in laboratory	
0	heavy metals in PM <sub>10</sub> ,	manual	all manual, treated in laboratory	
5	heavy metals in PM <sub>2.5</sub>	manual	all manual, treated in laboratory	
V	VOC	manual	all manual, treated in laboratory	
D	PD –passive samplers	manual	all manual, treated in laboratory	
Z	EC/OC in PM <sub>2.5</sub>	manual	all manual, treated in laboratory	

## **Precipitation quality**

Code of measuring programme	Measuring programme	
В	Bulk samples	
F	Wet-only - autom. sampler	
Y	Daily cumulated samples	
S	Throughfall (spruce)	
I	I Throughfall (pine)	
Q	Throughfall (birch)	
R	Throughfall (oak)	
Е	Throughfall (beech)	
U Daily rain		
N	Surface water	

## 1.3.1.3 Codes of localities and measuring programmes

Since 2003 the localities have been defined by a four-letter code as follows: letter 1: abbreviation for the region;

letters 2–4: abbreviation for the measuring site (locality)

The code of the measuring programme is formed by a five-letter code. The first four letters define the locality and the fifth one is the code of the measuring programme (see 1.3.1.2).

### 1.3.1.4 Classification of air pollution stations

Classification of air pollution monitoring stations for the year 2013 is presented in tabular surveys – Stations and air quality measurement methods registered in IIS-Air Quality Information System and Summary overviews of air pollution standard exceedances and max. values at stations of the Czech Republic in 2013.

This classification of stations for the purpose of exchange of information (EoI) was presented for the first time in the Council Decision 97/101/EC and was obligatory for the EU Member States.

As the above Decision was the only document bringing the official European classification it was applied to all localities in the Czech Republic registered in the ISKO database. The application procedure is described in Sládeček, J., Blažek, Z. (2000): Application of criteria for the classification of stations and station networks pursuant to the EoI Decision 97/101/EC and Criteria for EUROAIRNET to the stations included in the air quality assessment process. The Report on the task DU01-1.E1 of the R&D Project VaV/740/2/00, CHMI, Prague.

The classification of localities is designed with respect to the reporting requirements set in the Commission Implementing Decision 2011/850/EU, 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, the so called e-reporting. E-reporting is to be implemented for the first time in autumn 2014, when the data for the year 2103 will be reported. The procedure is based on the current classification of localities (97/101/EC), which is stored in the ISKO database and will be used for the 2013 yearbook. This classification was supplemented by e-reporting requirements, additional items were included particularly with regard to the most accurate description of the locality for the introduction of parametrization. The analysis of the current state of classification, the parametrization of the territory and the draft of the complex classification of localities are described in the final report of the contract: Project of the classification of monitoring stations incl. parametrization of the territory. Individual items of the new classification will be gradually introduced into the ISKO database.

The complete EoI classification (97/101/EC) consists of 3 fundamental letters divided by strokes; at most stations it was officially affirmed by an expert team in accordance with local criteria. In some cases the classification was derived mainly from the purpose of the station establishment.

The third column of the table shows only the examples of the combinations of zone characterisation. Any logical combination is possible and the order of letters in the abbreviation is meaningful – the first position is of the highest priority.

#### Exchange of Information (EoI) site classes

Type of locality		Type of z	one (area)	Characterisation of zone (area)	
Traffic	(T)	Urban	(U)	Residential	(R)
Industrial	(I)	Suburban	(S)	Commercial	(C)
Background	(B)	Rural	(R)	Industrial	(I)
				Agricultural	(A
				Natural	(N)
				Residential/Commercial	(RC)
				Commercial/Industrial	(CI)
				Industrial/Residential	(IR)
•				Residential/Commercial/Industrial	(RCI)
				Agricultural/Natural	(AN)

### Source:

Council Decision 97/101/EC of 27 January 1997 establishing a reciprocal exchange of information and data from networks and individual stations measuring ambient air pollution within the Member States. [Rozhodnutí Rady 97/101/EC z 27. ledna 1997 zavádějící reciproční výměnu informací a dat z měřicích sítí z jednotlivých stanic měřících znečištění vnějšího ovzduší mezi členskými státy.]. Official Journal of the European Communities, No. L 35/14. EC, 1997.

Larssen, S. et al. (1999) Criteria for EUROAIRNET. The EEA Air Quality Monitoring and Information Network. [Kritéria pro EUROAIRNET, Monitorovací a informační síť pro čistotu ovzduší agentury EEA.]. Technical Report no. 12. EEA, Copenhagen.

Subcategories B/R (2001/752/EC, Criteria for EUROAIRNET, Technical Report no. 12, EEA):

**near-city**, **code NCI**, located in rural/agricultural areas, with a distance of 3–10 km from built-up areas and other major sources, radius larger than about 5 km.

**regional, code REG**, located in rural/agricultural areas, with a distance of 10–50 km from built-up areas and other major sources, radius larger than about 20 km.

**remote, code REM,** located in rural/natural areas, with a minimum distance of 50 km to built-up areas and other major sources, radius larger than about 60 km.

Since 2004 specialized automated monitoring stations, indicated as traffic hot spots, have been introduced gradually. These are the following AMS: Prague 2-Legerova, Ústí n. L.-Všebořická, Brno-Úvoz and Ostrava-Českobratrská. These measuring sites are exclusively traffic-oriented which results in their air pollution load. These localities meet the criteria for the location of samplers oriented at traffic according to the Degree No. 330/2012 Coll.

### 1.3.2 Tabular part of air pollution characteristics

In the part Summary overviews of limit values exceedances and maximum values of air pollution characteristics at localities of the Czech Republic in 2013 stations and values for those pollutants whose limit values are set by the above Government Order are presented. The stations at which the limit values including the margin of tolerance were exceeded have dark grey background and the data are printed in bold type. Stations at which the limit values were exceeded have light grey background.

For individual pollutants, the stations are presented according to the regions and districts.

The data from the network of measuring stations of the Saxony Region in Germany and of the south-west border region of Poland are also included each year. These stations are presented always in the end of individual tabular sets.

The Tabular Survey presents air pollution characteristics for those pollutants whose air pollution limit values are set in the tables Hourly, daily, quarterly and annual air pollution characteristics with the assessment for the year 2013. Other pollutants are presented in the form of tables Monthly and annual average concentrations and supplementary air pollution characteristics. The headings of most tables show air pollution limit values for the selected pollutants. The detailed tabular overview of daily averages at the stations is also published.

The monthly and annual air pollution characteristics are calculated from the daily data. Daily averages are calculated from 6:00 to 6:00 UTC for the comparison with manual sampling once a day. All daily values, both measured and calculated, are marked with the beginning of measurements, i.e. 6:00 UTC.

The tabular overviews present the values of air pollution characteristics for the individual pollutants and for individual measurements requested by the above Government Order [25<sup>th</sup> highest hourly (25MV) and 4<sup>th</sup> highest 24-h (4MV) SO<sub>2</sub> concentration, 36<sup>th</sup> highest 24-hour PM<sub>10</sub> concentration, 19<sup>th</sup> highest hourly (19MV) NO<sub>2</sub> concentration and maximum daily 8-h running average of ozone and CO] with the respective dates of their occurrence. In accordance with the above Government Order requirements also AOT40 for ozone is presented. Further, numbers of exceedances of the given air pollution limit values or target air pollution limit values (VoL) and numbers of exceedances of air pollution limit values including the margin of tolerance (VoM) are given. Quarterly arithmetic means are given instead of monthly means, as well as the number of values from which they are calculated (X1q, C1q, ...).

The overview of heavy metals is also presented for which air pollution limit values and target limit values are set. The table of monthly concentrations was updated: quarterly arithmetic averages and annual characteristics were added.

In the tables, for each measurement the monthly arithmetic average and the monthly frequency (Xm, mc) are given in two subsequent lines. Further, the daily maximum for the year and the date of occurrence (MAX. DAT), 95<sup>th</sup> percentile (95%kv), 50<sup>th</sup> percentile (50%kv), and 98<sup>th</sup> percentile (98%kv), or 90th percentile (90%kv) are given as well as the annual arithmetic average and standard deviation (X, S), annual geometric average and standard geometric deviation (XG, SG), number of measurements in the year and the length of the longest continuous shut-down (N, dv).

Since 1994 the table presenting measured concentrations of VOCs at CHMI stations has been included, the measurement is carried out within the EMEP programme. Since the year 2000 this et of tables has included also VOC measurements at  $Z\dot{U}$  stations carried out within the project MZSO (Population Health State Monitoring) with regard to ambient air.

Since 1997 continual measurement of aromatic hydrocarbons has also become part of the Tabular Survey.

The measurement of persistent organic pollutants (POPs), presented in two tabular sets, have been included since 1997 as well. Polyaromatic hydrocarbons (PAHs) are included in the first set and polychlorinated biphenyls (PCBs) in the second set.

### 1.3.2.1 Principles of data presentation and validity of air pollution characteristics

New calculation criteria pursuant to Annex I to the Directive 2008/50/EC and Annex IV to the Directive 2004/107/EC were implemented for air quality evaluation in this yearbook. The above annexes set the data quality objectives for ambient air quality assessment. Pursuant to Annex I to the Directive 2008/50/EC and Annex IV to the Directive 2004/107/EC only data from the measuring stations may be used for ambient air quality evaluation for which the requirement for minimum data capture amounting to 90 % is fulfilled. The requirements for the calculation do not include losses of data due to the regular calibration or the normal maintenance of the instrumentation. Without prejudice to Annex I to Directive 2008/50/EC, the criteria set in Annex XI of the same directive shall be used when aggregating data and calculating statistical parameters. Due to these changes some of the data presented in previous yearbooks may slightly differ as compared with the data presented in this yearbook.

The measured data are given in this Tabular Survey if the relative share of primary data per year is greater than 16 %.

The calculated air pollution characteristics could be presented and regarded as valid if they fulfil the conditions given in the following tables. There are two types of measurement: continuous and indicative.

### **Continuous measurement**

In intervals longer than one day recalculation is done for individual days and then the evaluation of validity of the calculated characteristics is carried out according to the conditions presented in the following table.

Data input interval	Calculated characteristic	Minimum number of data
30min	1h	2
30min	8h	12
30min	1d	36
30min	1r	15 768
1h	8h	6
1h	1d	18
1h	1r	7 884
1d	1M	23
1d	3M	68
1 <b>d</b>	6M	162
1d	1r	329

### **Indicative measurement**

For presentation and validity assessment of the calculated characteristics the indicative measurement is theoretically converted to continuous measurement by re-calculating according to the interval of the sampling length to the time span of the sampling frequency (re-calculated to the surroundings). Then the validity assessment of the calculated characteristics is carried out according to the conditions presented in the following table.

Data input interval (sampling length/frequency)	Calculated characteristic	Minimum number of data
10min/4d	1M	27
10min/4d	3M	68
10min/4d	1r	302
10min/4d	1r	94
14d/14d	1M	23
14d/14d	3M	68
14d/14d	1r	302
14d/14d	1r	24
14d/1m	1M	23
14d/1m	3M	68
14d/1m	1r	151
14d/1m	1r	11
14d/3m	1M	23
14d/3m	3M	68
14d/3m	1r	50
14d/3m	6M	2
14d/3m	1r	4
1d/2d	1M	23
1d/2d	3M	68
1d/2d	1r	324
1d/2d	1r	165
1d/3d	1M	23
1d/3d	3M	68
1d/3d	1r	324
1d/3d	1r	110
1d/4d	1M	23
1d/4d	3M	68
1d/4d	1r	302

Data input interval (sampling length/frequency)	Calculated characteristic	Minimum number of data
1d/4d	1r	83
1d/5d	1M	23
1d/5d	3M	68
1d/5d	1r	324
1d/5d	1r	66
1d/6d	1M	23
1d/6d	3M	68
1d/6d	1r	324
1d/6d	1M	23
1d/6d	3M	68
1d/6d	1r	302
1d/6d	1r	55
1d/6d	1r	47
1m/1m	1M	23
1m/1m	3M	68
1m/1m	1r	324
1m/1m	1r	11
7d/1m	1M	23
7d/1m	3M	68
7d/1m	1r	76
7d/1m	1r	11
7d/3m	1M	23
7d/3m	3M	68
7d/3m	1r	25
7d/3m	6M	2
7d/3m	1r	4
7d/7d	1M	23
7d/7d	3M	68
7d/7d	1r	302
7d/7d	1r	47

### 1.3.2.2 Differentiation of types of letters

**Bold** – exceedance of air pollution limits LV (the condition of the tolerated number TE of exceedances needn't be fulfilled) assuming that the data fulfil the requirements for validity of data for calculation of the annual air pollution characteristics.

**Dark grey background** – exceedance of air pollution limits LV incl. the condition of the tolerated number TE of exceedances assuming that the data fulfil the requirements for validity of data for calculation of the annual air pollution characteristics.

### 1.3.3 Data on chemical composition of atmospheric precipitation and wet deposition

The Tabular Survey also gives the chemical composition of precipitation and atmospheric deposition. The localities for which data are given for 2013 are depicted on the map; the table 2.3 gives more detailed information on stations (altitude, sampling methods and organizations). The stations are ordered alphabetically according to the regions and districts, included are data from the stations operated by CHMI, and from the stations of cooperating organizations ČGS, VÚV TGM, VÚLHM and HBÚ AV ČR, which are submitted to the ISKO database. Data from boarder areas with Poland and Germany are also included.

Data on chemical composition of atmospheric precipitation are given in the tables as separate daily, weekly, monthly or irregular analyses. One-week interval complies with the international EMEP's methodology (Tuesday – Tuesday sampling). For the measuring programmes with one-week sampling interval re-calculated monthly concentrations are also presented.

The Tabular Survey of precipitation quality and wet deposition monitoring contains also the tables presenting the annual average concentrations weighted by rain amounts and the annual wet depositions given for individual stations and measured parameters. While calculating the monthly (annual) concentrations (depositions) the average concentration for the week covering the end and start of the two months (years) is weighted by daily precipitation. For instance, at the turn of the years 2005/2006 the concentration from the week between 30.12.2005 and 5.1.2006 is first multiplied by precipitation from 30. and 31.12.2005. This deposition is then added to December 2005 and, consequently, to the year 2005. The same concentration is then multiplied by the total precipitation for 1.–5.1. 2006. This result deposition is added to the deposition for January 2006 and, consequently, to the year 2006.

The measured quantities are designated in the tables by the common chemical nomenclature symbols, cond is the measured sample conductivity, rain is the total precipitation. The total precipitation is measured by the standard method directly at the sampling site or, in case of CHMI, at a climate or precipitation station that is considered to be meteorologically representative for the given site.

### 1.4 Data quality assurance

#### 1.4.1 Assurance of the quality of the measured data

In 2005 CHMI air pollution monitoring obtained the Accreditation Certificate for testing laboratory No. L 1460 accredited by the Czech Accreditation Institute for testing and sampling listed in the Annex Accreditation Certificate (see www.cai.cz, section Accredited Bodies). The accreditation covers ambient air pollution and atmospheric precipitation monitoring, incl. sampling. The quality assurance handbook and further air pollution monitoring documentation were compiled in compliance with the standard CSN/EN/ISO 17025 according to which the CHMI air pollution monitoring has been accredited.

The quality assurance of air pollution measurements by means of automated methods and their calibration, the manual methods of air pollution, aerosols and the subsequent quality control of the data obtained from CHMI stations are in charge of the Central air pollution laboratories (CLI), CHMI Prague and laboratories in regional offices in Brno, Hradec Králové, Ostrava and Ústí nad Labem. The quality of the measured data is thus controlled at all levels. The quality of atmospheric precipitation sampling from the CHMI stations is in charge of the respective CHMI branches, the quality of chemical analysis of atmospheric precipitation is in charge of CHMI (CLI).

For continuous measurements within the AIM network analyzers of gaseous pollutants ( $SO_2$ ,  $NO_x$ , CO,  $O_3$ ) are used. They are equipped with the zero-span check system carried out in a 23-hour interval (72-hour interval at the stations without diluting systems). Twice a year the analyzers are checked by five-point calibration using portable calibrator HORIBA ASGU 364 calibrated in the CHMI Air Pollution Calibration Laboratory which has been accredited for air pollution measurements and has a role of a reference centre on air pollution monitoring.

Manual sampling methods for air pollution measurements, aerosol composition monitoring and precipitation quality are controlled among others by parallel sampling at selected sites and with the use of blank samples. The quality assurance and control of the activity of chemical laboratories is carried out according to the requirements for trace and ultra-trace chemical determination.

Air Pollution Laboratories participate regularly in international interlaboratory tests organized by World meteorological organization (WMO/GAW) and the European monitoring network EMEP. CLI are involved in international programmes and research projects. The central CHMI air pollution laboratories also perform regular interlaboratory tests  $NO_2$  for guajacol method both for the laboratories of CHMI regional offices and for other cooperating organizations.

The accuracy of laboratory determinations is controlled regularly by the analysis of the certified reference materials. The precision of laboratory determinations is evaluated by repeated analyses of the same sample. The relative uncertainty of determination covers the accuracy and precision of laboratory determination. The presented uncertainties are expanded uncertainties (expansion coefficient k=2). Due to the fact that concentrations of many analytes range close to the margin of detection the users should accept that the presented uncertainties of measurements are relatively high. The detailed description of uncertainty calculation is given in the standard operating procedure (SOP) for each method and the respective sampling of the monitored pollutant. The total combined expanded uncertainty including sampling is used in the table.

## Detection limit values and uncertainty – manual air pollution measurement methods

	Total uncertainty		Calibration
Method	Relative Expanded [%]	Margin of detection [μg·m <sup>-3</sup> ]	range up to [mg·l <sup>-1</sup> ]
SO <sub>2</sub> (West-Gaeke method)	10	3	3
SO <sub>2</sub> (IC)	5.2	0.045	50
SO <sub>4</sub> <sup>2-</sup> (IC)	5.3	0.028	50
$\sum NO_3^-$ (IC)	7.1	0.052	30
NO <sub>x</sub>	23 / 46	1.1	3
$\sum$ NH <sub>4</sub> <sup>+</sup> (FIA-BERTH)	34	0.022	4.0
	without concentration level 21  up to 14 μg · m <sup>-3</sup> 76		
PM <sub>10</sub> , PM <sub>2.5</sub> with sampling	14–24 μg · m <sup>-3</sup> 31	2	
	over 24 μg · m <sup>-3</sup> 13		
	at 50 μg · m <sup>-3</sup> 10		
Benzene ( PD)	22	0.10	

## Detection limit values and uncertainty – automatic air pollution measurement methods

Pollutant	Margin of detection	Standard u	ncertainty
Ponutant	[μg · m <sup>-3</sup> ]	abs. [μg · m <sup>-3</sup> ]	rel. [%]
SO <sub>2</sub> TEI-43 A,B,C (UV fluorescence)	2.5	2.5	8
SO <sub>2</sub> TEI-43 S (/UV fluorescence)	0.5	0.5	
NO TEI-42 A,C (chemiluminescence)	1.5	1.5	8
NO TEI-42 S (/chemiluminescence)	0.2	0.2	
NO ESA-AC32M (chemiluminescence)	0.5	0.5	
NO <sub>2</sub> TEI-42AC (chemiluminescence)	2	2	10
NO <sub>2</sub> TEI-42 S (chemiluminescence)	0.4	0.4	
NO <sub>2</sub> ESA-AC32M (chemiluminescence)	1	1	
NO <sub>x</sub> TEI-42 A,C (chemiluminescence)	2	2	10
NO <sub>x</sub> TEI-42 S (chemiluminescence)	0.4	0.4	
NO <sub>x</sub> ESA-AC32M (chemiluminescence)	1	1	
CO TEI-48A,C,S (IR correlation spectrometry)	120	120	8
O <sub>3</sub> TEI-49 A,C (UV absorption photometry)	2	2	8
PM <sub>10</sub> FH62IR (radiometry)	2		20
PM <sub>10</sub> ESA-MP101M(radiometry)	0.5		·
BTX Chrompack, Syntech, ESA-VOC71 (gas chromatography)	0.2		20

The given deviations are provisional. The values will be further specified.

## Detection limit values and uncertainty - particles and trace elements in the air

	UNCERTAINTIES			
Method	<b>Standard</b> <b>Expanded</b> [μg·m <sup>-3</sup> ]	Relative Expanded [%]	Margin of detection [μg·m <sup>-3</sup> ]	Concentration level [μg·m³]
PM <sub>10</sub> , PM <sub>2.5</sub> (with sampling)	3.7	21		without giving
	7.6	76		up to 14
	5.6	31	2	14–24
	4.7	13		over 24
	5.0	10		at 50

Element	Calibration range up to [µg · m <sup>-3</sup> ]	Margin of detection [μg·l <sup>-1</sup> ]*	Margin of detection $[ng \cdot m^{-3}] **$
As (ICP-MS)	362	0.082	0.030
Cd (ICP-MS)	362	0.020	0.007
Co (ICP-MS)	362	0.012	0.004
Cr (ICP-MS)	362	0.998	0.362
Cu (ICP-MS)	362	0.218	0.079
Fe (ICP-MS)	362	5.97	2.17
Mn (ICP-MS)	362	0.097	0.035
Ni (ICP-MS)	362	0.256	0.139
Pb (ICP-MS)	362	0.103	0.037
Se (ICP-MS)	362	0.269	0.097
V (ICP-MS)	362	0.017	0.006
Zn (ICP-MS)	362	0.520	0.188

<sup>\*</sup> margin of detection of the analyte in mineralizate

\*\* margin of detection of the analyte on the filter at approx. 55 m³ of the sucked air

Element	Analysis uncertainty level LV [%]	Combined uncertainty (incl. sampling) level LV [%]	Expanded uncertaint level LV [%]
As	5	7	15
Cd	10	12	23
Co*	12	13	26
Cr*	14	26	51
Cu*	13	16	32
Fe*	22	23	46
Mn*	14	15	29
Ni	13	14	27
Pb	9	10	20
Se*	21	25	50
V*	20	21	42
Zn*	14	19	38

mean concentration level (without limit value)

# Detection limit values and uncertainty – precipitation quality monitoring

Mathad	UNCERTAINTIES	Manain Classic	Calibration range up to	
Method	Standard Total expanded	Margin of detection		
рН	0.4	0.01	3–8	

Method	UNCERTAINTIES Relative Total expanded [%]	Margin of detection [μS.cm <sup>-1</sup> ]	Calibration range up to [μS.cm <sup>-1</sup> ]
conductivity	20	0.4	1.4–500

	UNCERTAINTIES (incl. sampling)		Calibration range	
Method	Combined expanded [%]	Margin of detection [μg·l <sup>-1</sup> ]	up to [mg·l <sup>-1</sup> ]	
F (IC)	21	7.5	4.2	
Cl <sup>-</sup> (IC)	15	11.2	25	
NO <sub>3</sub> (IC)	55	40.1	21	
SO <sub>4</sub> <sup>2-</sup> (IC)	50	29.2	21	
Na(AAS)	105	6	10	
K (AAS)	119	4	10	
Mg (AAS)	36	2	10	
Ca (AAS)	31	15	10	
NH <sub>4</sub> (FIA-BERTH)	5	18	4.0	
As (ICP-MS)	63	0.115	0.5	
Cd (ICP-MS)	35	0.004	0.5	
Cr (ICP-MS)	18	0.023	0.5	
Cu (ICP-MS)	25	0.149	0.5	
Co (ICP-MS)	51	0.003	0.5	
Fe (ICP-MS)	171	3.53	0.5	
Mn (ICP-MS)	35	0.023	0.5	
Ni (ICP-MS)	51	0.023	0.5	
Pb (ICP-MS)	23	0.028	0.5	
Se (ICP-MS)	80	0.307	0.5	
V (ICP-MS)	55	0.012	0.5	
Zn (ICP-MS)	61	0.636	0.5	

### 1.4.2 Air pollution data control and validation

Air pollution data submitted to ISKO are checked in compliance with the Operation rules of the National air pollution network and the Operation rules of ISKO air pollution data administration.

The measured results are checked twice: the first, monthly control is in charge of the regional network administrator. This is done prior to data affirmation or supply to ISKO, CHMI. The second control is implemented by ISKO, and namely for each quarter of the current year.

Both procedures are based on the control of formal and logic parameters aimed at the detection and elimination of gross errors which could affect and lower the quality of statistical characteristics of the data file.

Within the second control of the measured results unreliable data are detected from the currently stored national files of daily averages of air pollution data using the database application.

After the finished collection of air pollution data for the given period and their input into ISKO database the air pollution data administrator reports this to the researcher responsible for the control of data.

The primary detection of unreliable data in the newly stored national files of daily averages of air pollution data is carried out by using the database application. This procedure based on mathematical and statistical methods detects suspicious data; the days with suspicious data are supplemented by daily averages and data on five preceding and five subsequent days incl. the daily averages at other seven nearest stations for the same time span. The application is launched automatically upon each ISKO database update (i.e. input of new data, correction of the stored data etc.) and its output in the form of html page is given at disposal of the researcher responsible for the reliability control of the stored data.

In addition to the basic data application there are further methods of data verification developed for ISKO2, which are given at disposal of the researcher responsible for the control of air pollution data.

The researcher responsible for the control of data considers the results of verification and then contacts the data supplier and requests the verification of suspicious data and, if necessary, the approval to eliminate the data from the database.

The supplier sends the corrected data to the ISKO data administrator who stores the corrected data to the database.

In some cases the suspicious data, confirmed by the suppliers as erroneous, are identified by the respective researcher responsible for data control with error codes and are sent to the database administrator for elimination. At present the application for recording the error values can be used; the suspicious values are eliminated from the ISKO database tables and transferred to error tables. The records about such transfers are archived.

After the collection of data for the period of one year the researcher responsible for the control of data accuracy carries out also the control of reliability of all measured and calculated (aggregated) air pollution data exceeding the limit values.