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Organic components in the different types of precipitation - Ružomberok experimental area

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Abstract. The aim of this study was to collect different precipitation types including air water (air humidity), rain water and solid water samples (snow and frost deposit) in the close surroundings of Mondi SCP, Inc., which is the most significant source of pollutants in the Ružomberok area, and one of the highest polluters in Slovakia. Subsequently, the samples were analysed using colorimetry (photometry) and gas chromatography. Colorimetry was used to measure the concentrations of ions dissolved in the samples including chlorides Cl^-, sulphates SO_4^{2-}, carbonates CO_3^{2-}, ammoniacal nitrogen $N\text{-}NH_4$, nitrates NO_3^- and phosphates PO_4^{3-}. Results were processed by the correlation analysis in combination with PCA and ANOVA by the STATISTICA programme. Gas chromatography/mass selective detection (GC/MSD) was used to detect and identify potential organic pollutants present in the samples. The sampling started in May 2015 and continued to March 2016. In addition, the day levels of carbon dioxide (CO_2), relative humidity, temperature, ground level ozone and PM_{10} dust particles were monitored during the whole period of sampling. The results of the statistical analysis show 7 different effects that influenced the level of ions in a different type of water as well as in a different season. The most occurring organic compounds detected by the chromatographic analysis were: alcohols, alkenes, aromatic hydrocarbons (including terpenes), carbonyl compounds (aldehydes and ketones), carboxylic acid esters, carboxylic acids, derivatives of ammonia, biphenyl or mercaptan, ethers, PAHs (including pyrenes), phosphoric acid esters (including chlorinated organophosphates) and phthalates.

Key words: organic pollutants, gas chromatography/mass selective detection (GC/MSD), atmospheric deposition, colorimetry, paper and pulp production

Introduction

Modern society is characterised by the use of paper for a wide variety of purposes. Taking this into consideration, the manufacturing of paper and pulp is an inseparable part of the recent industrial economy. Although pulp and paper industry representatives have stated that the environmental pollution generated by their companies is not toxic and hazardous, to a large number of people across the world they pose a rapidly growing problem from the chipping of forests to the pollution of air, water, land and organisms (Carriere *et al.* 1996). Pulping and bleaching processes have the most serious environmental impacts (Bajpai 2015). The main environmental pollution resulting from paper and pulp activities can be divided into emissions to air and emissions to water (EA 2011). The air pollution includes emissions of various gasses, smoke, fumes, dust particles, which impair the quality of air. In accordance with the Toxic Release Inventory (TRI), emissions to air from paper production are the third among industrial sectors (Bajpai 2015).

Different types of substances are emitted in each step of paper production. Major toxic substances produced by paper and pulp industry were discussed in a number of studies. The most common are chlorine (Cl), sulphur dioxide (SO_2), sulphuric acid fumes, nitrous oxides (NO_X), volatile organic compounds (VOCs), carbon monoxide (CO), dust particles, persistent organic pollutants - POPs (dioxins, furans), formaldehyde (CH_2O), polycyclic aromatic hydrocarbons -PAHs, metals, ammonia (NH), chloroform ($CHCl_3$) in waste gasses and a number of other.

To understand the source of pollutants resulting from paper and pulp manufacturing begins with the knowledge of raw material composition - the wood. It consists of polysaccharides cellulose and hemicellulose. The main component of wood and the most important component for the production of pulp is cellulose (Browning 1975). Both, cellulose and hemicellulose differ in the type of chemical bonding and produced pollutants at once. There is also a difference between hardwood and softwood. For example, hardwood contains methyl groups in its chains, which is the main reason of a methanol formation (Servos 1996). The type of wood, its composition, the type of manufacturing methods, which all can vary, influence what kind of pollutants is produced during the paper and pulp production. However, wood alone is not the only component that makes paper and pulp industry possible. It requires plenty of energy and clean water.

Processes used in paper manufacturing

The determination of pollutants formed in the paper and pulp production depend on the knowledge about manufacturing processes. The production of pulp is composed of several processes including mechanical, chemical pulping and their combinations to produce cellulose fibres by the breaking down of wood. As it was mentioned, all processes are environmentally consuming. The most common manufacturing method is a kraft process, which takes approximately 16 million m^3 of water daily.

Ten percent of the production is represented by mechanical pulping. Its advantage is that no chemicals are added during this process. Mechanical pulp results in the production of slurry from wooden chips. The highest percentage (85%) of pulp production represents chemical pulping. During this stage, lignin is removed and the softness is enhanced by the separation of fibres. Combinations of these processes is followed by the use of various chemicals such as the NaOH solution during chemical - mechanical pulping to allow maceration. SO_2 is used to avoid darkening. Some of these are used to reduce the time of boiling, for example sodium sulphite (Na_2SO_3), sodium sulphate (Na_2SO_4) or bisulphite (HSO_3^-) during the semi-chemical process that represents approximately 5% of manufacturing. In the neutral semi-chemical pulping is wood treated with liquor consisting of Na_2SO_3 produced by the combustion of sulphur and sodium carbonate (Na_2CO_3) (Beschkov 2009).

Obviously, paper manufacturing poses a potential environmental risk and has to be controlled for the emissions of chemicals released during production processes.

Air pollution in paper and pulp mill surroundings

In general, air pollution by paper industry tends to be regarded as less important than water pollution. However, it remains important in some areas, especially at the places where the combination of negative meteorological conditions and regional sources of emissions to air might be the cause of pollution.

The most common potential air pollutants include:

- Carbon monoxide CO – it is a colourless, odourless gas emitted in the process of combustion; can have harmful effects on human health by the reducing of oxygen transport to organs and tissues; it belongs to the so-called "criteria pollutants" together with O_3, Pb, SO_X, NO_X and particulate matter (EPA 2016a).
- Carbon tetrachloride CCl_4 - a clear liquid that has a sweet odour; poses potential health problems when inhaled; chronic inhalation can cause kidney or liver damage; EPA has classified CCl_4 as a Group B2, probable human carcinogen; it can be present in the contaminated drinking water (EPA 2000).
- Formaldehyde CH_2O - a colourless, flammable gas with a strong odour; formed during combustion as well as in natural processes; can irritate the skin, nose, eyes, throat (EPA 2016b).
- Hydrogen chloride HCl - a colourless aqueous solution or gas with an irritating odour; has corrosive effects to eyes, skin and mucous membranes (EPA, 2016c); produced in recovery boilers (Andrews *et al.* 1996).
- Chlorinated phenolics and other chlorinated organics, as well as phenol and methanol (Bajpai 2015).
- Chlorinated solvents - responsible for global warming and the ozone layer breakdown. These chemicals are of environmental significance because they are released into the local environment and may also be transported over large distances from the mill (Bajpai 2015).
- Chlorine dioxide ClO_2 - a yellow gas, unstable in light, used for bleaching in paper and pulp industry (EPA 2000). Itself, it is an air pollutant of great concern, especially in relation to the possibility of leaks and fugitive emissions in the plant (Bajpai 2015).
- Side reactions during the ClO_2 bleaching lead to the formation of chloroform $CHCl_3$. It has adverse effects on the nervous system (EPA 1997).
- Oxides of nitrogen NOX - refer to the sum of NO and NO_2 concentrations. NO has an acute health effect, but is very reactive and it is converted to NO_2. They participate in photochemical processes in the atmosphere, are products of combustion processes and all NO_X contribute to the greenhouse effect. Together with oxides they form acid rains, some of them irritate the respiratory system (Envitech 2015).
- Persistent Organic Pollutants POPs - include dioxins which are soluble in fats; are formed as a product of the combustion of wood; have a high ability of bioaccumulation; affect the immune and nervous system, but mostly through the food chain, not air (Envitech 2015). They have a characteristic tendency to long-range transport in the atmosphere beyond national borders. The consequence is a global pollution, which was confirmed by the detection of these substances in areas remote from industrial sources, such as polar regions in which they have never been used or produced, and harm both humans and wildlife organisms (Landlová 2006).
- Sulphur dioxide SO_2 - the most important component of acid rains. SO_2 is considered as a major pollutant from sulphite pulp mills. It can be emitted during pulp washing, cleaning and screening operations. If not controlled, they might be the reason of significant SO_2 emission sources (EPA 1996).
- Total Reduced Sulphur compounds TRS - the most common are:
    a) Hydrogen sulphide H_2S - a colourless gas with characteristic smell of rotten eggs having a sweet taste; the olfactory threshold limit for people is between 0.0007 - 0.014 mg.m^{-3}. It is formed by the decomposition of organic matter with the presence of sulphur or its compounds in a not sufficient O_2 level. The most of H_2S in the ambient air has a natural origin (e.g. from geothermal earth activities, sulphur lakes, springs or salt marches). Industrial emissions are the results of coke, oil, yarn production and of the production of cellulose by sulphate methods.
    b) Methyl mercaptan CH_3SH - a colourless gas with a smell of garlic or rotting cabbage; the olfactory limit is 0.04 mg.m^{-3}. The main natural source is the microbial degradation of freshwater algae. A major industrial source is paper and pulp industry, production of pesticides, fungicides, sewage treatment plants, etc.
    c) Dimethyl sulphide DMS - a yellow liquid with a characteristic smell of rotten vegetable. The olfactory threshold limit is between 0.0007 - 0.014 mg.m^{-3}. It results from biological decomposition. Major industrial emission sources are oil refineries, pulp, kraft and leather industry.
    d) Dimethyl disulphide DMDS - a colourless liquid with a characteristic smell of rotting fish. The olfactory threshold limit is between 0.003 - 0.014 mg.m^{-3}. It occurs naturally and it is a part of the sulphur cycle. It originated in sea water, soil and microbiological activities. It is pro-

duced by the decaying of organic matter during the degradation of amino acids containing sulphur. As air contaminants they originate from wood production, sewage treatment plants, distilleries etc. (Drímal *et al.* 2013).

- VOCs - a volatile organic compound is every organic compound that has an anthropogenic and biogenic origin and it is not methane. It is able to form photochemical oxidants in the reaction with NOx in the presence of sunlight. (NRSR 2010). They play an important role in the reactions forming O_3. They have been found mainly in the vent gases of mills that use 100% ClO_2 substitution (Bajpai 2015).

Atmospheric deposition and its function in the formation of pollutants

Atmosphere is a medium which is responsible for the transport of organic and inorganic substances. These substances take part in important processes during which chemicals are removed via dry and wet deposition (Morales-Baquero *et al.* 2013). Snow functions as an absorbent of pollutants deposited through wet deposition. The dominant indicators that result from wet deposition include NO_3^- and SO_4^{2-} (Morales-Baquero *et al.* 2013). Substances resulting from dry deposition usually come from local pollution sources, while those of wet deposition might be transported from further distances (Balestrini 2000). Gaseous SO_2 and NO_X from anthropogenic sources react in air together with O_3 and OH radicals and produce the so-called "secondary aerosol" in which SO_4^{2-}, NO_3^- and NH_4^+ are present. Aerosols stay in the atmosphere until deposition takes place and due to the residence time, approximately after a week, are responsible for the long-range transport of nitrogen and sulphur (Ruijgrok *et al.* 1995).

Snow has the ability to wash out pollutants from the atmosphere. In addition, gaseous atmospheric contaminants might be adsorbed via the large surface area of snow crystals (Wania and Haugen 1999). Movement of contaminants in the snow cover is controlled by diffusion and ventilation. These processes are probably responsible for the distribution of substances in snow and/or changes in the composition of chemical mixtures in time (Herbert *et al.* 2006). Substances can be released out from snow by volatilisation or they can drain with snow water. Draining of substances bounded to different particles depend on the properties (size, hygroscopic properties, concentration) of snow (Landlová 2006). The diffusion of substances in snow is a very important process which influences the movement of contaminants between the atmosphere and snow cover, and depend on the concentration and temperature gradients (Wania *et al.* 1998). Pollutants may be released from snow in different ways depending on their physical properties. These processes include volatilization, deposition into soil or transport into ground water (Burkow and Kallenborn 2000). For example, POP loss from the fresh snow is significant. Heavier less volatile compounds remain in melting snow and can undergo photochemical transformations, which can result in more persistent substances. Seasonal melting can cause the release of POPs from the old snow into the atmosphere and river basin (Landlová 2006). Monitoring of the snow cover in terms of impacts of solutions produced by its melting, on the chemical composition of surface and groundwater, geological conditions and on the environment, is done by a hydro-geochemical approach. This monitoring is carried out in several areas of Slovakia within the scope of monitoring geological factors. Actual results confirmed the greatest mineralization (2.96 to 5.95 $mg.l^{-1}$) in the populated industrial areas. Maximum levels are also linked to point pollution sources. The highest values of the anion composition reached monitored indicators including CO_3^-, subsequently NO_3^-, SO_4^{2-} and Cl^-. The representations of cations and anions were unstable and varied in all localities. The level of indicators is also closely related to the pH and effects of SO_X and NO_X. Moreover, past monitoring showed a smaller burden of environment by these indicators in comparison with previous years. Apparently, it is related to the shorter duration of the continuous snow cover due to which was snow less exposed to dry deposition. Thus, the total average mineralisation of snow sample solutions was lower (Kordík *et al.* 2013).

Organic pollutants

A number of recent studies have revealed the potential negative impact of organic substances which are accumulated in natural environment. Groups such as PAHs, PCBs, PCDD, PCDF, OCP, MTBE, 4 - NP belong to POPs that are suspected for environmental risks and became the part of priority pollutants. Their resistance against biological and chemical degradation tend to be very high. They are removed through the process of deposition from the atmosphere into water, soil and organisms. After deposition, a semi - volatile compounds can undergo a number of processes, such as repartitioning and translocation within the snowpack, volatilisation and drainage at the time of snowmelt (Wania *et al.* 1998).

VOCs, PM_{10} dust particles and the ground level ozone

As it was mentioned in the introduction, the high level of PM_{10} concentrations of dust particles in air poses a potential problem in Slovakia. PM_{10} particles refer to the suspended particulates that are allowed through a device with the entrance vent, which is defined by a reference method for sampling and measuring, and which selects particles with an aerodynamic diameter 10 μm with a 50% efficiency (NRSR 2010). A variety of substances can bind on these types of particles, especially pyrenes, heavy metals and dioxins or PAHs. Many of these substances are highly persistent (POPs) and are accumulated in the environment. PM_{10} dust particles are trapped in the upper respiratory tract and can cause health problems because of the substances which are carried on it (Envitech 2015).

The measurements of these particles is carried out at the monitoring stations of SHMÚ. In 2014 the limit level of PM_{10} was also exceeded in the town of Ružomberok, however, an average annual level was slightly decreasing at every station (SHMÚ 2015).

Another potential environmental risk is represented by the amounts of ground level ozone. Its formation is a very difficult process in which local effects (O_3 production and titration in the town centres) interact with effects from larger distances. A slow recovery of the ozone layer, which has been destroyed mainly by the production of CFC is expected in the middle of this century. The growing of O_3 concentrations is also associated with the increasing emission of ozone precursors (NO_X, VOCs, CO) from car transport, power generation and industry. The ground level ozone threshold limit to the public was not exceeded at any of the stations. The national ozone level reduction potential is very small (SHMÚ 2015).

Although the subject of this study is mainly about the proportion of organic substances in the snow from the town of Ružomberok, we are briefly going to mention the relationship between the occurrence of VOCs, which are also produced by the pulp mill, and the formation of ozone in the atmosphere, which currently represents an increasing risk of environmental pollution (SHMÚ 2015).

In general, the ozone creation process in Europe might be largely conditioned by biogenic emissions of volatile organic compounds (BVOC) and NO_X from natural sources. BVOC are also produced by forests that cover a substantial part of Slovakia, although their values remain yet unspecified. In the period from May to August they emit a greater extent, for example, isoprene and terpenes. On warm and sunny days BVOC, as well as NO_X emissions from land (an estimated 15% of total NO_X emissions in Europe), contribute significantly to increases in ground-level ozone. Based on measurements, SHMÚ found that the local production of ozone is very small, the maximum level of about several percent increases in the summer followed by approximately the same decrease in winter. However, it is important to continue in the monitoring of this situation (SHMÚ 2015).

Our research area was situated in Ružomberok surroundings that belong among the highly polluted regions of Slovak Republic. This pollution is caused primarily by the paper and pulp producer Mondi SCP, Inc. In case of the combination of negative meteorological conditions (temperature inversion, depression and wind direction), the town and its near localities are characterised by specific malodour. It is caused by the presence of sulphur compounds in the atmosphere as a result of the cellulose production by using sodium hydroxide (NaOH) and sodium sulphide (Na_2S) as basic compounds (Drímal *et al.* 2013). However, the spectrum of monitored potential pollutants from the cellulose production needs to be widen. This is one of the reasons why we have decided to determine the potential pollutants from snow, air humidity, frost deposit and fog samples concentrated in this area. We also monitored the level of ions in water samples that can be used to compare them with annual reports, and state potential environmental pollution and risks. Additionally, we concentrated on the monitoring of average day levels of carbon dioxide (CO_2), air humidity, temperature, ozone and PM_{10} during the whole period of sampling.

Aims of the study were:

- to collect air humidity (air water), rain water, snow and frost deposit (solid water) samples from the Lisková village
- to detect and describe potential organic pollutants in the samples using gas chromatography/mass selective detection
- to measure the level of ions dissolved in the samples (Cl^-, SO_4^{2-}, CO_3^{2-}, $N\text{-}NH_4$, NO_3^-, PO_4^{3-}) using photometry
- to monitor the daily levels of CO_2, O_3, PM_{10}, relative humidity and calculate their averages for further statistical analyses together with ions dissolved in water samples

Material and Methods

Sampling

The study area was situated in an immediate vicinity of the paper and pulp mill Mondi SCP, Inc. in the town of Ružomberok.

During approximately one-year long period, we collected several types of samples. The type of a collected sample was related to the atmospheric and weather condition at the time of collecting. Altogether we collected the following samples: air humidity (119 samples), frost deposit (8 samples), snow (20 samples), rainfall (50 samples), fog (1 sample), dew (1 sample).

The first sample of air humidity was collected in March 2015, and we continued up to the end of March 2016. The air humidity samples were collected daily using the dehumidifier Delonghi DEM 8.5.

Rain water samples were collected into the 15 jam glasses with the volume of 700 ml. These glasses were placed on the ground during raining at the Lisková sampling site with the coordinates - latitude 49° 05’27.93” N and longitude 19° 21’00.45” E.

The number of days with favourable conditions for collecting the frost deposit was 8 - in November, December, January, February and also one day in March 2016. The temperature was between -9 and +4° C. Sampling was always carried out at 7 o´ clock in the morning from two glass plates with the size 55x55 cm, and one bigger glass plate with the size 55x120 cm while using an ice scraper. The samples were put into glass vials and left to thaw at room temperature.

Snow samples were collected on the sampling coordinates for the Lisková village - latitude 49° 05’27.93” N and longitude 19° 21’00.45” E. The collection of snow samples was carried out mainly in January and February, which were the months with the highest frequency of snowing. The first snow sample was collected in November and the last in March. Totally, we collected 20 samples. Every effort was made to collect fresh, well -preserved surface snow not affected by post-depositional processes and without any soil particles, even the snow layer was small. Snow was collected at a different time of a day, between 7:00 - 14:00, but mostly in the morning at ten o´ clock. It was placed into a graduated glass of a greater volume, and was left to be melted at room temperature. It was necessary to collect a big amount of snow because at least 1 litre of meltwater was needed to provide further analyses. Taking large amounts of snow guarantees a greater homogeneity and thus the reproducibility of the results of chemical analysis. Then, the molten snow was poured into a dark reagent bottle and stored in a laboratory refrigerator. We also monitored weat-her conditions at the time of sampling.

The measurement of PM_{10} dust particles, ozone and carbon dioxide was carried out simultaneously 24 hours per day while using specialised devices.

Laboratory analysis of samples

The detection of components present in the samples was carried out by using two different analytic methods. The photometric analysis was used to determine concentrations of ions dissolved in water. Organic pollutants were identified via the chromatographic analysis.

Colorimetry is one of the most important optical - analytical methods. In colorimetry, the solution concentration is related to the colour of a coloured substance solution (Szabadváry 1966). Colorimetry belongs to the methods of photometric analysis in which the visible light is used. A radiation intensity that passes through the analysed sample is compared to an initial intensity of a blank sample. Concentrations of ions in our samples were determined by the YSI 9500 photometer (YSI inc., Ohio, USA). For every parameter, a different test procedure was used which requires a specific reagent. We used Ammonia PHOT.4., Chloride (Chloridol) PHOT.46., Nitrate PHOT.23., Phosphate PHOT.28.and Sulphate PHOT.32. The results were processed in Microsoft Excel.

Before our chromatographic analysis, the extraction technique was done using 1l of water sample which was mixed with 3 ml of hexane. The sample was being shaken manually for three minutes and subsequently the hexane layer was isolated on the upper part of the sample solution. Sodium sulphate powder was added to remove the excess of air. The volume of this isolated extract ranged between 1.2 - 2.1 ml. The extract was then evaporated and after that refilled with 0.3 ml (300 µml) of hexane. After that the samples were analysed in the gas chromatograph.

To detect organic compounds in our samples, we used the GC - MSD method. A mass- selective detection (MSD) system means the simple mass spectrometry (MS). The analyses were carried out by the Agilent Technologies 5977A stand-alone capillary GC detector (Agilent Technologies 2013) and Agilent 7890B mass selective detector (MSD) with the MassHunter software. The automatic liquid sampler (ALS) was used to inject 2 µl (injection volume). The injector (inlets) was with the Agilent 5190 - 2293: 900 µl liner (splitless, single taper, ultra-inert). Technologies use helium as a carrier gas, which has the ability to help the vacuum system, and also to increase the separation efficiency (Vékey 2001). Capillary columns from Agilent Technologies (19091S - 431UI: 1 HP - 5ms Ultra inert) had 15 m x 250 µm x 0.25 µm with the following temperature program: the initial temperature of the column oven was 70° C, after that 150° C - 25 min./200° C - 3 min./300° C - 8 min. The conditions of MSD were the following: a detection method was in the mode of the selected ion monitoring scan, abbreviated as SIM. The MS source temperature was 230 ° C, the temperature of MS quadrupole was 150° C. The evaluation of chromatograms was performed while using the software Agilent Technologies (2013), Mass Hunter Quantitative Analysis Version B.06.00, in combination with the mass spectral library of selected compounds (NIST14.L).

Results

Chromatographic analysis

Compounds among all the analysed samples, which were found in the selected samples for the gas - chromatography analysis, belong to the chemical groups of phosphoric acid esters (including chlorinated organophosphates), phthalates, carboxylic acid esters, carbonyl compounds (mainly aldehydes and ketones), ethers of various compounds, alcohols, PAHs, carboxylic acids, aromatic hydrocarbons (including terpenes), alkanes, derivates of ammonia, biphenyl, mercaptan and a number of other (see Appendix).

Colorimetric analysis

The results of colorimetry were processed while using the PCA - principal component analysis on a correlation matrix in combination with ANOVA. Individual variables were tested for a type of precipitation (air, rain or solid water) as well as for the whole sampling period expressed in months. Table 1 displays eigenvectors from the correlation matrix of 14 variables to the first seven factors (principal components) from the samples of different sources (type of water).

Factor 1

The correlations on PC1 are of almost uniformly high values of the same sign at Cl^-, CO_3^{2-} and NO_3, and describe their mutual variability in dependence on the type of samples (Fig. 1a) and potentially seasons (Fig. 1b). The high values of these ions occurred in rain and solid water, and in winter and mid-summer. In the months when the air water was collected, the ions occurred at a lower level than in the summer or winter.

Factor 2

The correlations on the PC2 of Factor 2 displays that the values of rH are negative in opposite to the positive values of CO_2 and O_3. This effect describes that with increasing temperature there is an increase of CO_2, O_3, mainly air and rain water (Fig. 2a). It is evident according to the fact that solid precipitation takes place when the temperatures are low, especially in winter months, when air water is not present. The ground level ozone and CO_2 values occurred to be high especially in summer months that contributes to their decreasing tendency in winter, because of increasing relative humidity in summer (Fig. 2b).

Factor 3

The amount of $N\text{-}NH_4$ and PO_4^{3-} dependent on dust (PM_{10}) did not differ among different types of precipitation, but their values were high, mainly in some months of the second half of the calendar year and January (Fig. 3).

Factor 4

Factor 4 was characterised by the correlation values on the PC4 of the positive sign at NO_3^- and $N\text{-}NO_3$ and negative sign at $N\text{-}NH_4$ and PO_4^{3-} which describes their dependency between each other with respect to the precipitation type. The observed effect is probably related to the nitrogen transformations in the atmosphere. During this process the ammoniac substances are either formed or not. $N\text{-}NH_4$ and PO_4^{3-} are most abundant in air water,

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7
pH	0,007052	-0,150702	0,107027	-0,185998	-0,056655	0,832180	0,330849
Cl^-	0,460433	0,026160	-0,287895	-0,143825	-0,039603	0,049867	-0,094673
NaCl	0,454210	0,017796	-0,300080	-0,163369	-0,038259	0,056053	-0,103802
$CaCO_3$	0,460433	0,026160	-0,287894	-0,143825	-0,039603	0,049866	-0,094673
SO_4^{2-}	0,199285	-0,007600	0,015070	0,032683	-0,401120	-0,335919	0,820352
$N\text{-}NH_4$	0,219996	0,066252	0,531505	-0,369752	0,108338	-0,027280	0,048431
NO_3^-	0,348750	0,035972	0,285637	0,517202	0,078067	0,052227	-0,047350
$N\text{-}NO_3$	0,348750	0,035972	0,285637	0,517202	0,078067	0,052227	-0,047350
PO_4^{3-}	0,181060	-0,057507	0,376391	-0,426293	0,425429	-0,234711	0,033242
CO_2	-0,008131	0,436579	0,154281	-0,162680	-0,372170	-0,056300	-0,190040
rH	0,005697	-0,461830	-0,040288	-0,035648	-0,151278	-0,310006	-0,112374
t	-0,043226	0,543929	0,026746	-0,081998	-0,154172	-0,066754	-0,078678
O_3	-0,049466	0,495656	-0,104222	0,075059	0,180077	0,078600	0,196093
PM_{10}	0,032925	-0,140854	0,328870	-0,052392	-0,639363	0,123786	-0,295871

Table 1. Eigenvectors of correlation matrix.

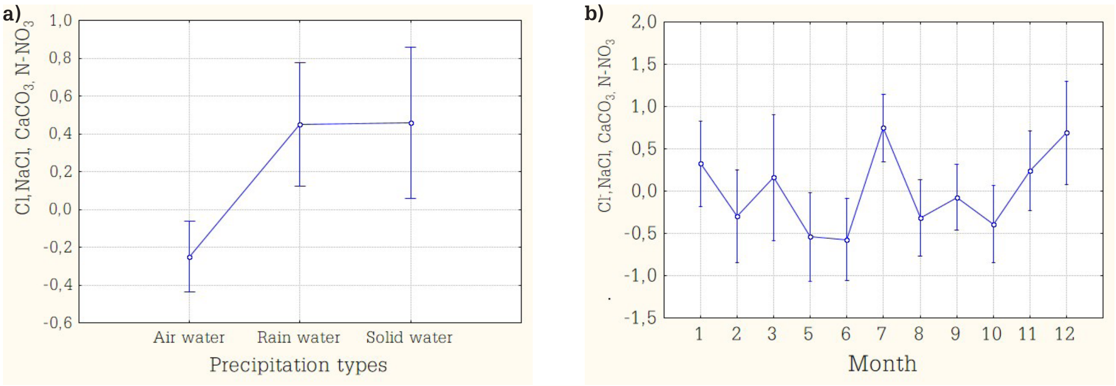

Fig. 1. Occurrence of Cl^-, NaCl, $CaCO_3$, NO_3, $N\text{-}NO_3$. **a)** In relation to the precipitation types [F (2, 152) =9.776, p=0.001]. **b)** In relation to months [F (10, 144) =3.738, p=0.001].

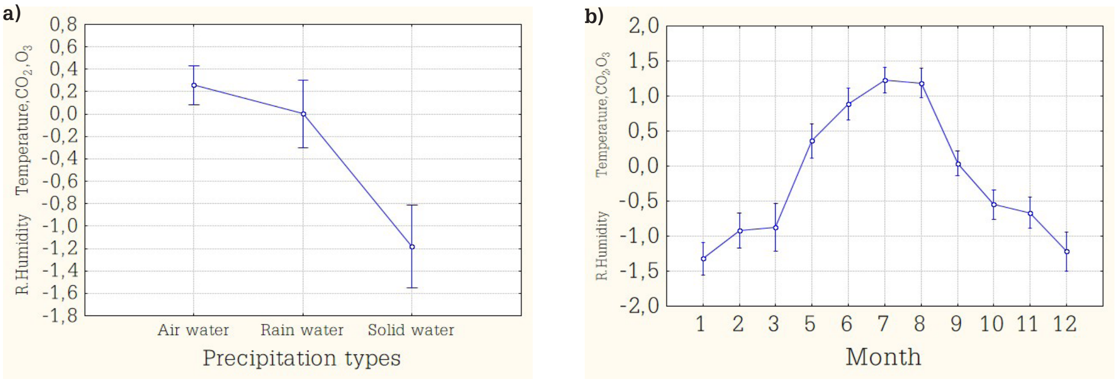

Fig. 2. Inverse relationship between relative humidity and temperature and the O_3, CO_2 increase. **a)** In relation to precipitation types [F (2, 152) =24.286, p=0.001]. **b)** In relation to months [F (10, 144) =70.625, p=0.001].

and $N\text{-}NH_4$ are converted to the $N\text{-}NO_3$. Subsequently, its nitrate phase is getting on the ground through the rain or solid precipitation. The effect takes place in all months identically, irrespective of the season (Fig. 4).

Factor 5

According to the correlations of PC5, Fig. 5a describes high values of PM_{10}, SO_4^{2-}, CO_2 in air water while the level of PO_4^{3-} is more increased in rain and solid water. SO_4^{2-} and CO_2 fixed to the large dust particles are reduced, and at their expense, at that moment, are more phosphate salts in rain water and partially in solid water. The effect proves especially the binding of SO_4^{2-} to the PM_{10} in humid atmosphere.

At the beginning of the calendar year the level of PO_4^{3-} was higher but it was gradually decreasing, followed by the increasing PM_{10} and

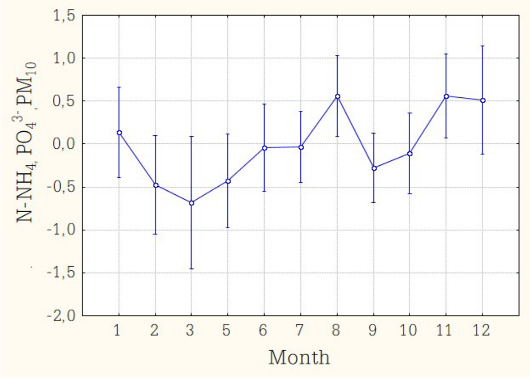

Fig. 3. Ammonia, phosphates and dust in relation to months [F (10, 144) =2.368, p=0.013].

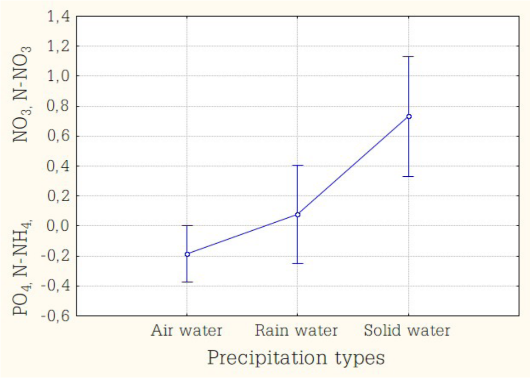

Fig. 4. Inverse relationship between phosphate and ammonia ions and nitrates in relation to the precipitation types [F (2, 152) =8.447, p=0.001].

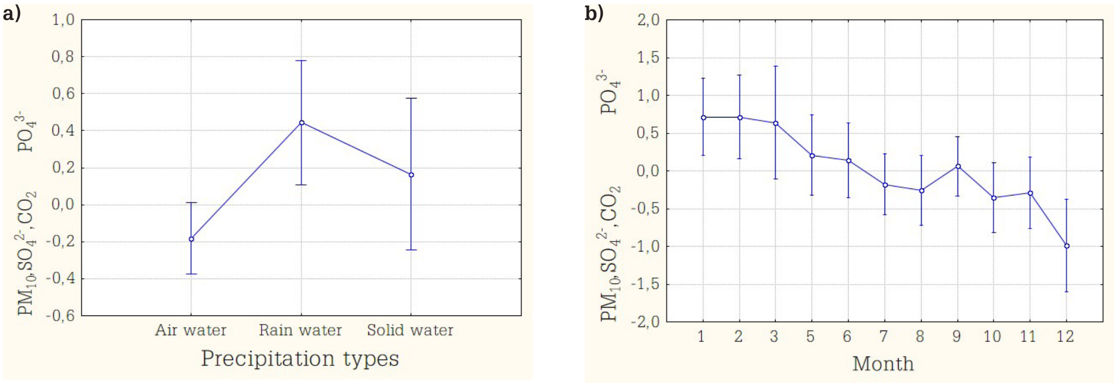

Fig. 5. Inverse relationship in the dusty precipitation with more CO_2/SO_4 ions and PO_4. **a)** In relation to precipitation types [F (2, 152) =5.501, p=0.005]. **b)** In relation to months [F (10, 144) =3.369, p=0.001].

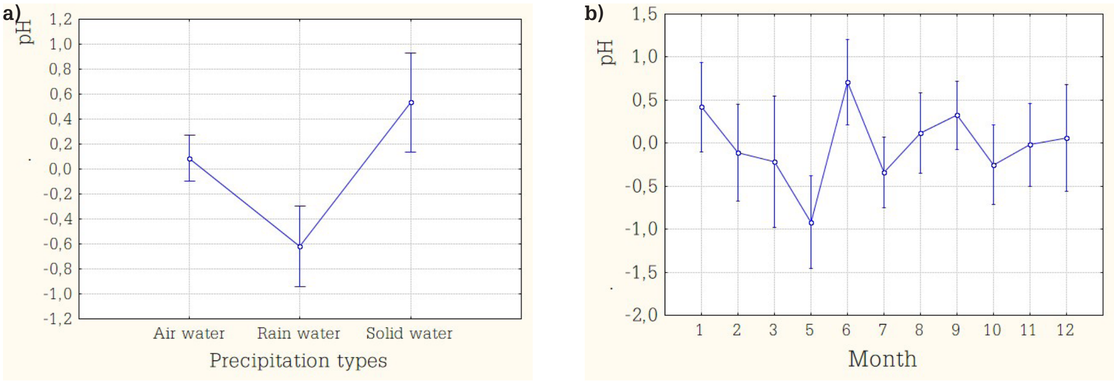

Fig. 6. Acid water. **a)** In relation to precipitation types [F (2, 152) =11.120, p=0.003]. **b)** In relation to months [F (10, 144) =2.909, p=0.002].

SO_4^{2-}. Monthly trends of the downward decrease of PO_4^{3-} and upward trend of SO_4^{2-} and PM_{10} suggests that phosphorus or PO_4^{3-} dominate in rain water in the first half of the year, while the second half is characterised by the increasing amount of PM_{10}, SO_4^{2-} and CO_2 that fluctuate mainly in air water (Fig. 5b).

Factor 6

The correlations on PC6 showed a significantly high value of the positive sign at pH variable. Effects of pH were highly demonstrable and strongly associated with the type of samples. Rain water was characterised as the most acidic, followed by less acidic air water and the most alkaline solid water (Fig. 6a). More acidic water was found mainly during rainy days in spring and autumn (Fig. 6b).

Factor 7

The separate accumulation of sulphur describes a unipolar vector, which refers to the variability of SO_4^{2-} in the air, and is independent of the other monitored variables as well as of the types of the precipitation in different seasons, in which it has the same course. Sulphur compounds are stored primarily in the water of a solid state and partly in the humid air. Proportionally less sulphate salts are present in the liquid state (Fig. 7).

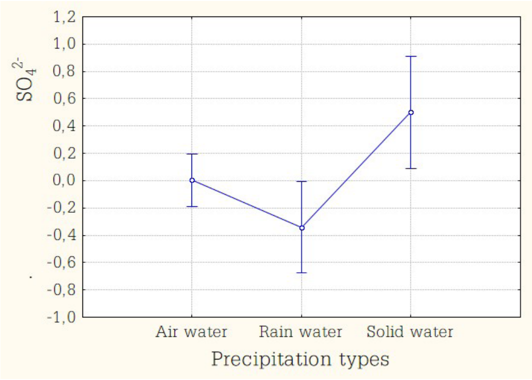

Fig. 7. Sulphates in relation to precipitation types [F (2, 152) =4.921, p=0.009].

Discussion

The results confirmed some of the potential organic pollutants or their derivatives which were discussed in the literature review. The main chemical groups of investigated organics were: alcohols, alkenes, aromatic hydrocarbons (including terpenes), carbonyl compounds (aldehydes and ketones), carboxylic acid esters, carboxylic acids, derivatives of ammonia, biphenyl or mercaptan, ethers, PAHs (including pyrenes), phosphoric acid esters (including chlorinated organophosphates) and phthalates. There were also two compounds that contain sulphur and iodine in their molecule. All the selected samples for analyses were collected in 2015, from May to November. Great variations of organics were found in each season and the type of a precipitation event, which can be explained by the different sources of pollution and moving air masses that influence the distribution of pollutants (Czuczwa 1988).

Organic compounds, especially the PAHs are similar or resemble one another in different types of precipitation (snow, winter and summer rain) which indicate their similar sources and scavenging mechanisms (Leuenberger *et al.* 1988). In our research, there was also a group of completely the same or similar organics which were found in each type of precipitation. A large proportion from the results confirmed diacids that exist as particles and are more efficiently scavenged from the atmosphere than other water soluble organic compounds (Sempére and Kawamura 1994).

Organics have a tendency to vary among seasons and between the type of precipitation, which can be explained by the size of hydrometeors - rain or fog droplets, snowflakes) and their scavenging efficiencies (Leuenberger *et al.* 1988). Snowfall samples collected during winter should have higher concentrations of organics because snow is better for scavenging and atmospheric circulation during winter (Krawczyk and Skret 2005). That might be the reason why certain compounds that were present only in solid water were not found in air or rain water and vice versa.

Rain acts as an effective scavenger of the different types of pollutants and can effectively trap all types of oxidized and non - oxidized organics. Their properties can vary depending upon location and season of the year. Organic aerosol is dominated by oxidized organic fragments (aldehyde/acid/ketone etc.). Rainwater residues also contain organo sulphates. They indicate that some part of the dissolved aerosols has undergone aqueous processing, possibly inside the cloud (Chakraborty *et al.* 2016). We indicated aldehyde and ketones in all the types of precipitation, especially in rain water. One of them also belongs to organo sulphates [2-(5-Hydroxypent-2-ynyl)-3-oxocyclopentyl] thioacetic acid, S-t-butyl ester). None of them was indicated in the solid water, which can be explained by a smaller surface area of hydrometeors.

Risk compounds found in the organic detection include especially PAHs or TCPP. PAHs have the ability to form carcinogenic and mutagenic diols and epoxides that react with DNA (Macdonald *et al.* 2000). They are formed in the atmosphere primarily from the incomplete combustion of fossil fuels, vehicular exhaust, forest fires and industrial activities. Less volatile PAHs tend to be attached to atmospheric particles or return to the atmosphere after deposition. Phenenthrene, fluorene, acenaphthene and pyrene were found with the highest values in air (Macdonald *et al.* 2000). TCPP, whose presence was very common in our samples, belongs to chlorinated organophosphate retardants which are added to polymeric material and have toxic effects (Lehner *et al.* 2010).

Phthalates belonging among the priority pollutants are used in the production of plastics and are spread globally, present in every environmental sample.

Benzophenone, which belongs to the priority pollutants according to the US EPA list, was detected in the rainwater sample from July. Other organics containing benzyl functional groups were found in rain water as well, however, in October. Widely used phthalates include dibutyl- and bis-(2-ethylhexyl) (Poliakova *et al.* 2000). The results of our chromatographic analyses were not an exception. Dibutyl phthalate was found in all the samples, however, bis-(2-ethylhexyl) only in the sample of the air water from October.

Alkanes belong among the most common environmental polluters (Poliakova *et al.* 2000). We detected hexadecane, 2, 6, 11, 15-tetramethyl in the solid water sample from November 2015. When hydrocarbons undergo degradation, other groups of organic compounds are formed. They are known as fatty acids and their source is also connected to the hydrolysis of fats (Poliakova *et al.* 2000). We confirmed one ester of fatty acids, methyl 5, 9-heptadecadienoate, in the air water from July.

Another group of priority pollutants are phenols (Poliakova *et al.* 2000). We found 2,4-Di-tert-butylphenol and 1,4-Methanoazulen-3-ol, decahydro-1,5,5,8a-tetramethyl-, [1S- (1.alpha.,3.beta.,3a.beta.,4.alpha.,8a.beta.)] in the rain water sample from November. The second one was also present in the air water sample from August.

Finally, the gas chromatography analysis is able to detect many miscellaneous organic compounds from different classes such as alcohols, amides, aldehydes, ketones, esters, etc. These compounds are not included in the lists of priority pollutants since they have low or unknown toxicities, and they are less spread over the world (Poliakova *et al.* 2000). Different members of these groups were found in every sample from our analysis.

The colorimetric analysis results of the samples collected at the sampling site Lisková in an immediate vicinity of the town of Ružomberok, in which Mondi SCP, Inc. is located, showed a number of evidential effects. Kraft paper mills are sources which can affect the atmospheric composition up to the distance of at least 20 km (Boyce and Butcher 1976). The variables pH, Cl^-, $CaCO_3$, SO_4^{2-}, N-NH_4, NO_3^-, N-NO_3, PO_4^{3-}, CO_2, rH, t, O_3 and PM_{10} were tested using PCA in two ways - based on the type of water and based on the months in which samples were collected. According to the obtained graphs for 7 different factors we assumed the following:

A higher amount of precipitation in summer and winter in the town of Ružomberok is in the form of rain water and solid water, which fall mostly in July and winter months. It refers to the higher presence of Cl^-, CO_2 and NO_3^- in these types of precipitation, however, according to the recent studies, an increase in the atmospheric concentration of carbon dioxide tends to suppress precipitation. Similarly, a decrease in the atmospheric concentration of carbon dioxide tends to increase precipitation (Cao *et al.* 2012). The presence of these ions depends on the type of water as well as on the season. The amount of ions found in precipitation is usually dependent on the type of water, however, it is also associated with the amount of precipitation (Boyce and Butcher 1976). Cl^- together with the NO_3^- belong to the group of the most significant anions in the ambient air. In evaluating the precipitation composition, it is important to mention that Cl- has its origin in the compounds containing sodium chloride, which are spread globally. For example, in the vicinity of power plants, there may be the source of Cl^- from HCl local (Radojevic and Harrison 1992).

With increasing temperature in summer months, the amount of CO_2 and O_3 increases in air water and rain water, while the relative humidity is decreasing. Generally, the high levels of ozone usually occur in summer, in the warm months from May to September. The formation of ozone during warm sunny days depends on the presence of precursor pollutants (EEA 2013).

N-NH_4, PO_4^{3-} tend to have the highest occurrence in August and winter months, and are related to a high level of PM_{10} dust particles in these seasons. In most cases, the concentration of PM_{10} is significantly higher in the winter season than in summer (Envitech 2015). The Envitech study in the town of Ružomberok, provided last year, confirmed the concentration of dust particles PM_{10} to be 1.5 times higher in winter than in summer.

Due to the effect of nitrogen transformations in different precipitation types, N-NH_4 are highest in air water at the beginning, after that they are sequentially changed into N-NO_3, and fall from the atmosphere mainly in rain water and snow water according to the weather conditions of a season. NO_3^- and NH_4^+ are formed in air if atmospheric aerosols are not removed by atmospheric deposition. The formed acidic droplets are growing rapidly in the air by coagulation because they have a high concentration, but a smaller size (Radojevic and Harrison 1992). The cycle of any compound in the air has its residence time which refers to the average time spent by its molecules in air. Nitrogen transformation depends on the nitrogen cycle and also plays an important role of pathways of other substances in the atmosphere (Radojevic and Harrison 1992).

While the proportion of PM_{10}, SO_4^{2-} and CO_2 is the most significant in air water, rain water is characterised by a lower proportion of PO_4^{3-}. On the other hand, when the proportion of PO_4^{3-} is the most significant in rain water, PM_{10}, SO_4^{2-} and CO_2 are lower in air water. This effect probably relates to the binding of SO_4^{2-} and CO_2 to PM_{10} in air water, and PO_4^{3-} to PM_{10} in rain and snow water. Based on month in which the samples were obtained, we can observe a downward trend during the year. PO_4^{3-} are higher in the first half, followed by a decrease until they hit increasing PM_{10}, SO42- and CO_2 at the end of the year. PO_4^{3-} dominate in rain water in the first half of the year, and in the second half there is a higher proportion of CO_2, SO_4^{2-} and PM_{10} in air water.

Cloud processing is an important source of atmospheric sulphate (Moore *et al.* 2004), so, it is possible that the additional sulphate is produced inside the cloud and then comes down with the precipitation, thus increasing its net concentration.

The most acidic precipitation type is the rain water in summer months, especially in May, while the most alkaline is the solid precipitation in winter. Air water is less acidic among all the types. The acidity of precipitation is largely influenced by the precursor gases, acids in aerosol and vapor phases incorporated into atmospheric waters. Together, they determine the pH of clouds, fog and other precipitation elements (Radojevic and Harrison 1992). The source of the acidity is probably derived from the sulphur compounds in the atmosphere that provide hydrogen ions during oxidation in air and form sulfuric acids (Fisher 1968).

SO_4^{2-} are present mainly in solid water with a partial occurrence in air water and proportionally less in rain water. To state the exact reason of the distribution of sulphates in snow is very difficult with respect to the fact that every snowfall during winter has its own characteristics, which are probably related to the amount of pollutants from the meltwater. For example, according to the Babiakova and Bodiš (1986) study, the concentration of sulphates is higher in precipitation than in snow.

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APPENDIX

List of detected organic compounds in the analysed samples of air water (AW), rain water (RW) and solid water (SW) during May – November 2015 from the Lisková sampling area 1.

wather				**Type of**
Organic compound / Chemical group	**AW**	**RW**	**SW**	**Month**
(-)-Isolongifolol / ethers	X			July
(1S-(1Alpha,2alpha,4beta))-1-isopropenyl-4-methyl-1,2-cyclohexanediol /alcohols	X			July
(Z)1-Aflyl-2-methylcyclohexanol/derivates of alcohols	X			August
1,1´ -Bipheny, 3,4-diethyl / aromatic hydrocarbons		X		October, November
1,2-15,16-Diepoxyhexadecane / derivates of oxirane	X			July
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester / phthalates	X	X	X	May - November
1,3-di-iso-propybaphthalene / PAHs		X		July, November
1,7-di-iso-propylnaphthalene / PAHs		X		October
11-Hexadecyn-1-ol / pheromones	X			July. August
13-Tetradecenal / aldehydes	X			August September
1-Heptatriacotanol / alcohols		X		October
2-((4aS, 8R, 8aR)-4a,8-Dimethyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-2-yl) propan-2-ol / alclohols	X			October
2,4,7, 14-Telramethyl-4-vinyl-tricyclo[5.4.3.0(1,8)] tetradecan-6-ol / alcohols	X			July
2,4-Di-tert-butylphenol / phenols		X		November
2,6-Diisopropylnaphthalene / PAHs		X		July, October
2-Benzyloxyphenylacetic acid / carboxylic acids		X		July, November
2-Methoxybenzoic acid, benzyl ester / benzyl esters		X		October
2-Propanol, 1-chloro, phosphate (3:1) /phosphoric acid esters	X	X	X	May - November
4,6-di-tert-Butyl-m-cresol / alcohols		X		October
5,8,11,14-Eicosatetraynoic acid / carbon unsaturated fatty acids		X		October
6-Nonenal, 3,7-dimethyl- / aldehydes	X			August
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione / ketones		X		November
7-Acetyl-6-ethyl-1,1,4,4-tetramethyltetralin / PAHs		X		November
Ascaridole / terpenes	X			August
Benzene, 1,2-dimethoxy-4-(1-propenyl)- / ethers	X			August
Benzophenone / ketones		X		July. October. November
Bis(1-chloro-2-propyl)(3-chloro-1-propyl)phosphate / phosphoric acid esters			X	November
Bis(1-chloro-2-propyl)(3-chloro-1-propyl)phosphate / phosphoric acid esters	x	X	X	May - November
Bis(2-ethylhexyl) phthalate/ PAHs	X			October
Bis(3-chloro-1-propyl)(1-chloro-2-propyl)phosphate/ phosphoric acid esters	X			July. August
Carbonic acid, eicosyl vinyl ester / carboxylic acids			X	November
Cis-bicyclo[4.4.0]decan-1-ol-3-one/ ketones	X			August
Cyclopenta(def)phenanthrenone / ketones		X		July
Dibenzo[b,e]7,8-diazabicyclo[2.2.2]octa-2,5-diene / amines		X		October
Dibutyl phthalate / phthalates	X	X	X	May - November
Didodecyl phthalate / PAHs			X	November
Disulfide, di-tert-dodecyl/ disulfides	X	X		November
Dotriacontane, 1-iodo-/ alkanes			X	November
Eicosyloctyl ether/ ethers			X	November
Fenretinide/ retinoids		X		October
Hexadecane, 2,6,11,15-tetramethyl/ alkanes			1 x	November
Isolongifolol / alcohols	X			July, August

Longifolenaldehyde / aldehydes	X			August
Methanone / ketones		X		October
Methyl 5,9-heptadecadienoate / esters of fatty acids	x			July
Naphthalene, l-(phenylmethoxy)- ’ PAHs		X		October, November
Phosphoric acid, bis[2-chloro-1-(chloromethyl)ethyl] 2,3-dichloropropyl ester / phosphoric acid esters	X	X	X	May - November
Propiolic acid, 3-(1-hydroxy-2-isopropyl-5-methylcyclohexyl)-, ethyl ester / carboxylic acid esters		X		October
Pyrene / PAHs		X		July, September, October
Selin-6-en-4.alpha.-ol / alcohols		X		October
tert-Hexadecanethiol / derivates of mercaptane		X		November
Tributyl phosphate / organophosphorus compounds		X		November
Tributylacetylcitrate / carboxylic acid esters	X	X	X	May - November
Tributylacetylcitrate / PVCs			X	November
Tricyclo[7.4.0.0(3,8)]tridec-12-en-2-one, 5,6-epoxy-4-methyl-1-(2-propynyl)- / carbonyl compounds		X		November
Tris(1,3-dichloroisopropyl)phosphate /chlorinated organophosphates	X	X	X	May - November