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METHODS FOR DETERMINATION OF  
PHOSPHATE AND TOTAL PHOSPHORUS  
IN PRECIPITATION AND PARTICULATE  
MATTER

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Tekijät  
Ulla Makkonen, Karri Saarnio, Tuija Ruoho-Airola  
ja Hannele HakolaProjektin nimi  
Ilmaperäisen fosforin kuormitus Itämereen  
(Maj ja Tor Nesslingin säätiö)Nimeke  
Määrittymenetelmät sadeveden ja ilmakehän hiukkasten sisältämälle fosfaatille ja kokonaisfosforille

## Tiivistelmä

Itämeren pahimpana ongelmana pidetään typpi- ja fosforikuormituksen aiheuttamaa rehevöitymistä. Typpeä ja fosforia joutuu Itämereen paitsi valumana rantavaltioista myös merkittävässä määrin ilman kautta. Ilmaperäisen typpilaskeuman määrää ja sen kehitystä on selvitetty mittauksin ja mallinnuksen avulla 1980-luvulta lähtien, mutta ilmaperäistä fosforikuormaa Itämereen on mitattu vain sateen mukana laskeutuvan märkälasseuman osalta muutamilla asemilla. Hiukkasiin sitoutuneesta kuivalaskeumasta ei mittatietoa ole julkaistu lainkaan, eikä Itämeren ympärysvaltioilla ole käytettävissään menetelmää ilmaperäisen fosforikuorman hiukkasosuuden seuraamiseksi.

Tässä työssä kehitettiin ja testattiin menetelmät ilmakehästä sadeveden mukana tulevan sekä ilmakehän hiukkasiin sitoutuneen fosfaatin sekä kokonaisfosforin määrittämiseksi. Menetelmäkehitys sisälsi näytteenkeruumenetelmät, näytteen esikäsittelymenetelmät sekä kemialliset analyysimenetelmät. Menetelmiä testattiin Utön saarella Saaristomeren ulkolaidalla vuosien 2013–2015 aikana. Utön saarella toimii Ilmatieteen laitoksen mittausasema, jonka mittaustulokset edustavat ilmanlaadun tausta-arvoja pohjoisella Itämerellä.

Testattuina fosforin ja fosfaatin kuiva- ja märkälasseuman näytteenkeruumenetelminä toimivat olemassa olevat ja laajasti käyttöönotetut EMEP-protokollaan perustuvat menetelmät. Näytteiden kokonaisfosforipitoisuuden määrittämiseen sovellettiin olemassa olevaa ISO-standardiin perustuvaa spektrometristä menetelmää. Vesiliukoisen fosfaatin pitoisuuden määrittämiseen hyödynnettiin käytössä olevaa ISO-standardiin perustuvaa ionikromatografista menetelmää, jota laajennettiin sisältämään fosfaatin määrittäminen muiden epäorgaanisten ionien kanssa samassa analyysissä. Havaittiin, että sekä märkä- että kuivalaskeumanäytteiden sisältämät kokonaisfosfori- ja fosfaattipitoisuudet olivat erittäin alhaisia, usein pitoisuudet olivat lähellä analyysimenetelmien määrittämissä rajoja tai niiden alle. Kuitenkin mittausjakson ajalta saatiin riittävä määrä määrittäytuloksia, joiden avulla voidaan laskea aiempaa luotettavampi arvio vuotuisesta ilmaperäisestä fosforikuormituksesta Itämereen.

Työssä tutkittiin Utön saaren mittausasemalla suoritetun intensiivikampanjan aikana mahdollisuutta määrittää hiukkasissa olevan fosfaatin pitoisuutta jatkuvatoimisella ionikromatografiilla. Menetelmän herkkyyden osoittautui kuitenkin riittämättömäksi ilmakehän hiukkasten fosfaattipitoisuuden määrittämiseen.

Käytetyt menetelmät on esitelty tässä raportissa siten, että menetelmät voidaan ottaa käyttöön muillakin mittausasemilla ja laboratorioissa sadeveden ja ilmakehän hiukkasten sisältämien fosfaatin ja kokonaisfosforin pitoisuuksien määrittämiseksi, ja siten ilmaperäisen fosforin kuormitusta voidaan arvioida luotettavammin ja laajemmin Itämeren alueella.

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Methods for determination of phosphate and total phosphorus in precipitation and particulate matter

## Abstract

Eutrophication caused by nitrogen and phosphorus load is generally thought as the most severe problem of the Baltic Sea. Nitrogen and phosphorus end up in the Baltic Sea not only by run-off from the coastal countries of the Baltic Sea but to an important extent also from the atmosphere. The amount of atmospheric nitrogen load and its development have been determined using measurements and models since the 1980's. The atmospheric phosphorus load to the Baltic Sea has been measured earlier only from the wet deposition from the collected rain water samples from a few sites around the Baltic Sea; no published data exists about the particle bound dry deposition of phosphorus. The coastal countries of the Baltic Sea haven't got any method in use to measure the particle bound phosphorus deposition.

In this work, methods for determining the concentrations of phosphate and total phosphorus in atmospheric precipitation and particulate matter were developed and tested. The method development included the sampling, sample pre-treatment, and chemical analysis techniques. The methods were tested onsite on the Utö Island in the outskirts of the Archipelago Sea during the years 2013–2015. The monitoring station on the Utö Island is operated by the Finnish Meteorological Institute. The measurements on the station represent the background air quality of the northern Baltic Sea area.

The existing and widely used sampling methods based on the EMEP protocols were tested for the sampling of dry and wet deposition of phosphorus and phosphate. A spectrometric method based on an ISO standard was applied for determination of the total phosphorus concentration of the samples. For the determination of dissolved phosphate, an ion chromatographic method based on an ISO standard was extended to include the analysis of phosphate with the main inorganic ions. It was discovered that the concentrations of total phosphorus and dissolved phosphate in the dry and wet deposition samples were very low; the concentrations were often close to the determination limits of the used analytical methods or even below those. Nevertheless, a sufficiency of samples were determined to be able to estimate the yearly atmospheric phosphorus load to the Baltic Sea more reliably than earlier.

In addition, feasibility of measuring the concentration of particle-bound phosphate using a semi-continuous ion chromatograph was tested in the Utö Island during an intensive campaign. However, the sensitivity of the analyser was not sufficient to measure the low atmospheric concentrations of phosphate.

The used methods are presented in this report so that they can be taken into use in other sampling sites and laboratories to determine the concentrations of phosphate and total phosphorus in the precipitation and in the atmospheric particulate matter. Thus, more reliable estimates of the atmospheric phosphorus load to the Baltic Sea could be calculated more widely.

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# **METHODS FOR THE DETERMINATION OF PHOSPHATE AND TOTAL PHOSPHORUS IN PRECIPITATION AND PARTICULATE MATTER**

## **1 Introduction**

The fulfilment of the HELCOM Baltic Sea Action Plan requires knowledge of the entire nutrient input to the Baltic Sea. The airborne phosphorus input is inadequately quantified, partly because of the low number of monitoring results. This report presents methods developed at the Finnish Meteorological Institute (FMI) for monitoring of phosphorus and water-soluble phosphate in precipitation and particulate matter. Documentation and distribution of these methods aim to promote the use of comparable methods for estimation of airborne phosphorus input in the HELCOM countries.

For the determination of the phosphorus and phosphate deposition, precipitation samples (bulk samples) were collected on the Utö Island (N 59° 46', E 21° 22') in the outskirts of the Archipelago Sea in the Baltic Sea in 2013–2015. Furthermore, as a part of the normal EMEP (European Monitoring and Evaluation Program) protocol of the station, particulate matter (cut-off at about 10 µm) was collected daily on EMEP 3-stage filters packs and PM<sub>2.5</sub> particles (particles with aerodynamic diameter smaller than 2.5 µm) were collected weekly. In addition to the samples collected on filters, phosphate was measured from the particles using an online ion chromatograph MARGA 2S (Monitor for AeRosols and Gases in Air) during an intensive measurement period in May–June 2015.

During the test periods, it appeared that it is quite demanding to measure the concentrations of phosphorus species in ambient background air because they are most of the time below or close to the detection limits of the analytical methods used in this work. In the following sections the used sampling and analytical methods are described. More detailed information of the methods can be found in the ISO standards and the EMEP Manual (EMEP, 2001).



## **2 Sampling**

### **2.1 Precipitation samples**

Weekly precipitation samples are collected according to the EMEP-protocol (EMEP, 2001) using the NILU-type bulk collectors (Norwegian Institute for Air Research). The collector opening is horizontal at 1.8 m height when placed in the mounting stand (Fig. 1). The precipitation collector is changed at pre-described time intervals to a clean one, e.g., every Monday at 8 a.m. in winter and at 9 a.m. summertime (i.e., both at 6 a.m. UTC), even though there wouldn't be any rain during the sampling period. Touching barehanded inside the collector must be avoided in order to protect the sample from contamination. Therefore clean disposable gloves are to be always used when handling the precipitation collector.

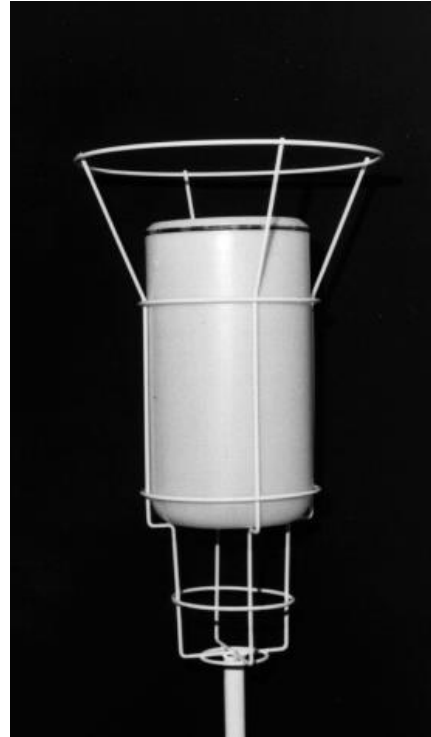
The summer bulk precipitation collector consists of a funnel connected to a bottle (Fig.1). There is a net in the throat of the funnel preventing, e.g., insects to end up into the sample. A new funnel is screwed on a new bottle and the net is mounted into the throat of the funnel using clean disposable plastic gloves. The new collector is placed on the mounting stand and the start and end times and possible remarks are written on the sample form. After sampling, the funnel is unscrewed from the bottle and the bottle is corked tightly. The start and the end dates are marked also on the bottle tape. The funnel and the enclosed bottle are placed in a plastic bag and sent to the laboratory for the sample analysis and cleaning. The sampling form, where the start and end times and possible remarks have been recorded, must be included in the post package.

During the cold period, a cylinder winter precipitation collector is used (Fig. 1). After sampling, the possible snow sample inside the collector is melted in a clean place at room temperature, then poured to a clean polyethylene bottle, and sent to the laboratory. The start and the end dates are marked on the bottle tape. In other respects, the operating instructions are similar to those of summer samples.

In the laboratory precipitation samples are weighted. The total amount of phosphorus is determined from an aliquot of an unfiltered sample using the method described in Section 2.2 and the concentration of phosphate with the main inorganic ions in the sample using the method described in Section 2.3. Conductivity and pH can also be measured from a filtered aliquot (not described in this report).



Summer collector



Winter collector



Summer collector

**Figure 1.** Precipitation collectors (NILU-type).

## 2.2 Sampling of particulate matter, daily samples

Daily samples of particulate matter (PM<sub>10</sub>) are collected using the three-stage EMEP filter pack (filter holder: NILU Products, Kjeller, Norway) that has a Teflon front filter for particles (e.g., PTFE Ø 47 mm, 3.0 µm, FS, Fluoropore TM, Millipore), a Whatman 40 filter (cellulose filter Ø 47 mm, Whatman International Ltd) impregnated with sodium hydroxide or potassium hydroxide for collecting acidic gases (i.e., sulphur dioxide and nitric acid), and finally a cellulose filter impregnated with oxalic acid for trapping gaseous ammonia from the sample air (flow rate about 16 l min<sup>-1</sup>). The sample air intake has a 15-cm wide and 25-cm high plastic cylindrical section to reduce the sampling efficiency for particles larger than 10 µm. The open-face filter pack is installed in outside air and connected to the sampling line with an airtight seal. The sampling line connects the air intake and the filter pack to a membrane pump and a gas flow meter, which are kept at room temperature to get the sample air volume at 20 °C. The system must be leak proof to get a reliable air volume measurement (EMEP, 2001).

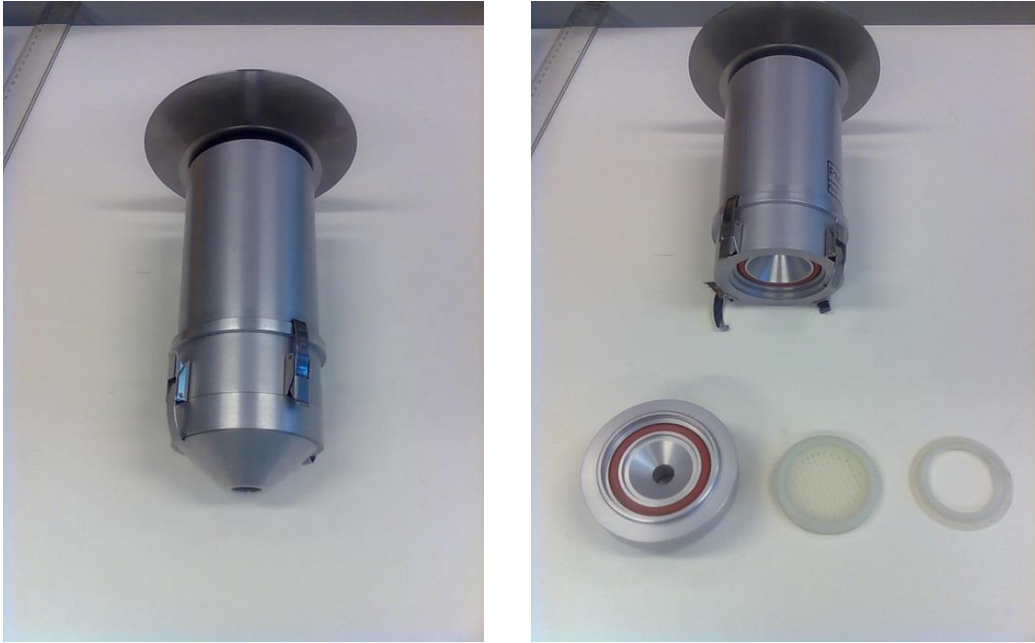
The filter pack samples (Fig. 2) are changed every morning at 6 a.m. UTC. New disposable gloves must be used when handling the filter packs in order to avoid sample contamination. Touching the filter must be avoided at the sampling site. The exposed filter pack is unscrewed and the new unexposed filter pack is mounted at the air intake. Start and end times are marked on the filter packs. Start and end times, air volumes, pressure values and remarks on exceptional events are recorded on the sampling form. There is a blank filter pack with every one-week set of filter packs in the plastic transport container. During sampling the blank filter is kept in the transport box. Once a week, the used set of filter packs is posted to the laboratory, where the filter packs are dismounted for the analysis. After pre-treatment (see Section 3.1), the total amount of phosphorus in the sample is determined using the spectrophotometric method (see Section 3.2) and the concentration of water-soluble phosphate using an ion chromatographic method (see Section 3.3).



**Figure 2.** EMEP 3-stage filter packs (NILU Products, Norway).

### **2.3 Sampling of fine particles, weekly samples**

Particulate matter in fine particle ( $PM_{2.5}$ ) fraction is collected on Teflon membrane filters (PTFE 47 mm, 3.0  $\mu m$ , FS, Fluoropore TM, Millipore) using a size-selective inlet (e.g., Micro-PNS, MCZ Umwelttechnik, flow rate 17 l  $min^{-1}$ ). New disposable gloves are used when handling the filters in order to avoid sample contamination. The filter is changed every Monday morning at 6 a.m. UTC. After sampling, the exposed filter is removed to a petri dish and a new Teflon filter is mounted in the collector using tweezers. Start and end times are marked on the exterior of the petri dish. Start and end times, air volumes, pressure values and remarks on exceptional events are recorded on the sampling form. A blank filter in a petri dish is included in every set of filters. The blank filter is kept in the transport box during sampling. After sampling the filters, including the blank filter, are posted to the laboratory for the analysis. Similarly as for the daily  $PM_{10}$  samples described in the previous section, the same pre-treatment and analysis methods are used to determine the concentrations of total phosphorus and dissolved phosphate in the weekly  $PM_{2.5}$  samples.



**Figure 3.** PM<sub>2.5</sub>-sampling head (Micro-PNS, MCZ Umwelttechnik, flow rate 17 l min<sup>-1</sup>).

### **3 Chemical analysis methods**

If several analyses (both total phosphorus and the water-soluble phosphate concentrations as well as conductivity and pH of the sample) are to be performed for a sample, the liquid sample must be divided into aliquots.

#### **3.1 Pre-treatment of particulate filter samples**

Water-soluble phosphate can be determined both from the filtered water sample, i.e., precipitation sample, and from the water extract of the particles collected on the filter material (both PM<sub>10</sub> and PM<sub>2.5</sub>).

For the ion chromatographic analysis (see Section 3.3), the filters are preferably extracted on the same day as they are removed from the filter pack, otherwise, the sample solution must be kept in a refrigerator after the extraction. The exposed filter is put in a clean plastic test tube and 10 ml ultrapure water is added on the filter. The rack of test tubes is kept in the ultrasonic bath for 30 minutes. The water sample is filtered directly to the sampling vial of the ion chromatograph using a disposable syringe (Gelman Sciences and Discardit II 10 ml, Becton Dickinson) and a syringe filter (e.g., Acrodisc 13, Ø 13 mm, porosity 0.45 µm) and the analysis is carried on as soon as possible.

### **3.2 Determination of total phosphorus by the spectrometric method**

Total amount of phosphorus is determined from the unfiltered sample using the ammonium molybdate spectrometric method. The standard ISO 6878:2004 specifies methods for the determination of orthophosphate, orthophosphate after solvent extraction, hydrolysable phosphate plus orthophosphate, and total phosphorus after decomposition. The methods can be used without dilution to water samples, in which phosphorus concentrations are within the range of 0.005 mg l<sup>-1</sup> to 0.8 mg l<sup>-1</sup>.

The method can be used both for the precipitation samples and the extracted filter samples of particles. The collected water samples and extracts are made acidic by adding sulfuric acid (1.0 ml 4 M H<sub>2</sub>SO<sub>4</sub> per 100 ml sample solution) and stored in a refrigerator.

For the determination of total phosphorous, polyphosphates are first hydrolysed to orthophosphate with sulfuric acid. Sulfuric acid and potassium persulphate are added to the samples before the samples are treated in an autoclave to complete the oxidation. After oxidation, ascorbic acid and molybdate reagent are added to the sample. In the solution, orthophosphate ions form a blue complex with molybdate and antimony(III), which enables the absorbance measurement by a spectrophotometer at the wavelength of 880 nm. Calibration solutions should be prepared for concentrations of 2.5–100 µg l<sup>-1</sup>.

The detection limit of the method for precipitation samples and other water solutions is 2 µg l<sup>-1</sup>. For the daily particle samples collected on EMEP-filters (sample volume about 23 m<sup>3</sup>) the detection limit is 0.9 ng m<sup>-3</sup> and for the weekly fine particle samples (171 m<sup>3</sup>) the detection limit is 0.12 ng m<sup>-3</sup>.

### **3.3 Determination of dissolved phosphate by ion chromatography**

The method for the determination of dissolved bromide, chloride, fluoride, nitrate, nitrite, orthophosphate, and sulphate in water by liquid chromatography of ions is specified in the standard ISO 10304-1:2007. According to the ISO standard, the lower limit of the application is 0.1 mg l<sup>-1</sup> for orthophosphate depending on the matrix and the interferences encountered. However, the working range is expanded to lower concentrations, if an appropriate pre-treatment of the sample (e.g., conditions for trace analyses, pre-concentration technique) or bigger sampling loop is applied. For the analysis, an ion chromatographic system with an anion column capable to measure phosphate can be used.

Prior to the ion chromatographic analysis, the samples must be filtered as described in Section 3.1 to remove particles. The Waters ion chromatograph used at laboratory of FMI, consists of a separation module (Alliance 2695: an autosampler, an injector, and a pump), a conductivity detector (Waters Model 432), and a computer with Empower 2 software for controlling the ion chromatograph, running the analysis, and handling the data. Phosphate standards and samples are injected (injection volume 200 µl) through the guard column (Waters Anion Guard Pak, WAT 010551, Waters Oy) to the analytical column (Waters IC-Pak A HR; 4,6 x 75 mm, WAT 026765, Waters Oy) using borate gluconate eluent. The instrument is used according to the manufacturer's instructions. For the quantitative determination, six calibration solutions are used within the concentration range of 0.06–6 mg l<sup>-1</sup> as phosphate (PO<sub>4</sub><sup>3-</sup>). The detection limit of PO<sub>4</sub><sup>3-</sup> is 0.02 mg l<sup>-1</sup> (= 20 µg l<sup>-1</sup>) and the quantification limit 0.06 mg l<sup>-1</sup> (= 60 µg l<sup>-1</sup>). The detection limit for a daily EMEP filter sample is 9 ng m<sup>-3</sup> and for the weekly fine particle filter sample 1.2 ng m<sup>-3</sup>.



## 4 Calculation of deposition

### 4.1 Calculation of wet deposition

The wet deposition of total phosphorus or phosphate at the sampling station of the Utö Island is calculated by multiplying the determined concentration in the bulk deposition sample with the precipitation amount. The precipitation amount from a meteorological rain gauge located in the immediate neighbourhood of the bulk precipitation sampler is used because of the weak sampling efficiency of the bulk precipitation sampler in the windy conditions of the rocky island.

The influence of sea spray on the phosphorus concentration in the bulk samples is estimated by assuming that all chlorine in the bulk samples originates from sea spray. Monthly observation data of phosphorus and chlorine in the upper layer of sea water at a Finnish marine monitoring site in the Utö area is used. The concentration of phosphorus in the bulk sample which originates from sea spray  $C_{P,ss}$  is

$$C_{P,ss} = \frac{C_P(\text{sea water, month of precipitation sample}) \times C_{Cl}(\text{precipitation sample})}{C_{Cl}(\text{sea water, month of precipitation sample})} \quad (1)$$

where  $C_P(\text{sea water, month of precipitation sample})$  is concentration of phosphorus in sea water during the same month as the bulk sample;  
 $C_{Cl}(\text{precipitation sample})$  is concentration of chlorine in the bulk sample under calculation;  
 $C_{Cl}(\text{sea water, month of precipitation sample})$  is concentration of chlorine in sea water during the same month as the bulk sample.

For the sea spray correction, the phosphorus and chlorine concentration in sea water should represent the same month as the precipitation sample because of the strong seasonal variability in the sea water concentration. The corrected phosphorus concentration ( $C_{P,precipitation}$ ) in the bulk deposition sample is obtained by

$$C_{P,precipitation} = C_{P,analysed} - C_{P,ss} \quad (2)$$

## 4.2 Calculation of dry deposition

The effect of the sampling material and sampling procedure to the phosphorus concentration in the particle samples is corrected with help of field blanks, one complete filter pack not used for sampling should follow the other filter packs every week. The field blanks should be analysed as the normally exposed samples and their phosphorus concentration subtracted from the phosphorus concentration in the real samples of the corresponding week according to the EMEP Manual (EMEP 2001).

The concentration of total phosphorus or phosphate in atmospheric particles ( $C_{P,air}$ ) is calculated by

$$C_{P,air} = \frac{C_{P,extraction} \times Vol_{extraction}}{Vol_{air}} \quad (3)$$

where  $C_{P,extraction}$  is the concentration of phosphorus in the extracted aerosol sample;

$Vol_{extraction}$  is the extraction volume of the aerosol sample;

$Vol_{air}$  is the volume of the sample air through the filter sample.

The sea spray correction is done with the same method as in Section 4.1.

The dry deposition of total phosphorus or phosphate  $DD_P$  at Utö, is calculated by

$$DD_P = C_{P,air} \times V_d \times t \quad (4)$$

where  $C_{P,air}$  is the concentration of phosphorus in atmospheric particles;

$V_d$  is deposition velocity;

$t$  is time in seconds.

The term  $V_d$  is dependent on particle size distribution and local meteorological conditions, and thus very difficult to determine for atmospheric aerosols in the sampling situation. The  $DD_P$  at Utö is therefore calculated using  $V_d$  values found in the literature. The  $V_d$  value has to be estimated separately to both aerosol fractions  $PM_{2.5}$  and  $PM_{10}$ . For Utö, constant  $V_d$  values through the year are used.

$V_d$  values  $0.5 \text{ cm s}^{-1}$  and  $2.0 \text{ cm s}^{-1}$  for the  $\text{PM}_{2.5}$  and the  $\text{PM}_{10}$  samples, respectively, are used for the Utö dry deposition calculation based on studies in Vicars et al. (2010) and the  $V_d$  review by Sehmel (1980). The  $V_d$  values used contain a large uncertainty and should be studied further.

## 5 Special case: Semi-continuous measurement of phosphate

Water soluble fraction of phosphate in  $\text{PM}_{10}$  or in  $\text{PM}_{2.5}$  is measured semi-continuously using an online ion chromatograph, MARGA (Fig. 4). The MARGA 2S ADI 2080 instrument (Applikon Analytical BV, The Netherlands) consists of two identical sampling boxes and one analytical box. A  $\text{PM}_{10}$  inlet (Teflon coated, URG-2000-30DBQ) draws in ambient air through the high density polyethylene tube ( $\text{Ø } 1''$ ), which is divided into two equal polyethylene tubes ( $\text{Ø } 0.5''$ ): one leading into the  $\text{PM}_{10}$  sample box ( $1 \text{ m}^3 \text{ h}^{-1}$ ) and the other into the  $\text{PM}_{2.5}$  sample box through a  $\text{PM}_{2.5}$  cyclone ( $1 \text{ m}^3 \text{ h}^{-1}$ , Teflon-coated inlet, URG-2000-30ENB). In the sample box, the sample air first enters the Wet Rotating Denuder (WRD), where water-soluble gases are diffused into the absorption solution; then a Steam Jet Aerosol Collector (SJAC) collects the particles. Diluted hydrogen peroxide (10 ppm) serves as the absorption solution to prevent microbiological growth. Absorption solutions are drawn from the WRD and the SJAC into syringes (25 ml) in the analytical box.

Each hour after filling the syringes, samples are injected into the Metrohm cation and anion chromatographs with the internal standard (LiBr). A Metrosep C4 (100/4.0) cation column uses  $3.2 \text{ mmol l}^{-1}$  MSA eluent to separate cations, whereas a Metrosep A Supp 10 (75/4.0) column with  $\text{Na}_2\text{CO}_3 - \text{NaHCO}_3$  ( $7 \text{ mmol l}^{-1}/8 \text{ mmol l}^{-1}$ ) eluent serves to separate anions. To get lower detection limits, the normal sample loop of cation analysis is replaced by a cation concentration column (Metrosep C PCC 1 VHC/4.0) and that of anion analysis by an anion concentration column (Metrosep A PCC 1 HC/4.0). After injecting the sample into the concentration column, it is eluted from the column using counter flow and it is transported through the analytical column to the conductivity detector. In the MARGA instrument, a chemical suppressor is used in the anion chromatograph. The suppressor is frequently regenerated with acid and after that rinsed with ultrapure water. In the suppressor, the counter ions of anions (like  $\text{Na}^+$  in  $\text{NaCl}$ ) are replaced by protons ( $\text{H}^+$ ) to increase the conductivity of the sample solution and therefore also the signal strength.

During the MARGA measurements in Utö, phosphoric acid ( $\text{H}_3\text{PO}_4$ ) was used for the regeneration of the suppressor, but to be sure to avoid contamination in the system, it would be better to use methanesulphonic acid (MSA) instead. Normally there is not any contamination from the regenerator,

but if the sample inline filter is blocked, then vacuum may appear in the syringes. On the moment when the syringes change direction, the vacuum may be filled with the content of the waste line, i.e., the old sample and the used  $\text{H}_3\text{PO}_4$  from the suppressor (discussion with Rob Proost, Metrohm Applikom).

The detection limit for phosphate ( $\text{PO}_4^{3-}$ ) is about  $0.01\text{--}0.02 \mu\text{g m}^{-3}$  ( $= 10\text{--}20 \text{ ng m}^{-3}$ ) with a concentration column, but the detection limit is dependent on the conditions used (e.g., column aging, and possible temperature variations in the column oven). However, during the measurement period in Utö, the concentrations were generally below the detection limit and the method should be further developed to measure low concentrations of phosphate in ambient air (e.g., by using a longer sampling time).



**Figure 4.** MARGA 1S (Monitor for AeRosols and Gases in Air).

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## References

EMEP (2001). *Manual for sampling and chemical analysis*. Norwegian Institute for Air Research, Kjeller. EMEP/CCC-Report 1/95, Rev. 2001, EMEP Manual for Sampling and Analysis <http://www.nilu.no/projects/ccc/manual/>

ISO 6878:2004. Water quality – Determination of phosphorus – Ammonium molybdate spectrometric method.

ISO 10304-1:2007. Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate.

Sehmel G.A. (1980). Particle and gas dry deposition – a review. *Atmospheric Environment* 14: 983-1011.

Vicars W.C., Sickman J.O. and Ziemann P.J. (2010). Atmospheric phosphorus deposition at a montane site: Size distribution, effects of wildfire, and ecological implications. *Atmospheric Environment* 44: 2813-2821.

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