Environmental Pollution 157 (2009) 3290–3297

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Novel sampling methods for atmospheric semi-volatile organic compounds (SOCs) in a high altitude alpine environment

I. Offenthaler[a], G. Jakobi[b], A. Kaiser[c], M. Kirchner[b], N. Kräuchi[d], B. Niedermoser[c], K.-W. Schramm[b], I. Sedivy[d], M. Staudinger[c], G. Thanner[a], P. Weiss[a], W. Moche[a,*]

[a] Umweltbundesamt GmbH, Austria
[b] Helmholtz Zentrum München (German Research Centre for Environmental Health), Germany
[c] ZAMG–Zentralanstalt für Meteorologie und Geo-dynamik, Austria
[d] WSL–Swiss Federal Institute for Forest, Snow and Landscape Research, Switzerland

Equipment for direction-specific air sampling and bulk deposition sampling in mountains was developed and tested.

ARTICLE INFO

Article history:
Received 15 May 2009
Accepted 17 May 2009

Keywords:
Active air sampling
Bulk deposition
SOC
Atmosphere
Alps

ABSTRACT

High- and low-volume active air samplers as well as bulk deposition samplers were developed to sample atmospheric SOCs under the adverse conditions of a mountain environment. Active sampling employed separate filters for different European source regions. Filters were switched depending on daily trajectory forecasts, whose accuracy was evaluated *post hoc*. The sampling continued on three alpine summits over five periods of four months. The prevailing trajectories varied stronger between sampling periods than between stations. The sampling equipment (active and bulk deposition) proved dependable for operation in a mountain environment, with idle times being mainly due to non-routine manipulations and connectivity.

1. Introduction

Large mountain ranges are not only meteorological traps for airborne semi-volatile organic compounds (SOC; Daly and Wania, 2005; Daly et al., 2007) but also an adequate domain to monitor long-range atmospheric pollution transport: their summits rise sufficiently far off and beyond industrial/domestic activity to be regarded remote, i.e. representative for regions whose pollutant loads are imported over the atmosphere. Atmospheric concentrations of various SOC at such background sites are so low that active air samplers have to operate over several days to collect detectable amounts. Relevant sources for the captured pollutants are usually located by tracking back the travel paths of the incoming air masses (Cheng et al., 2007). However, the probability of overlaying trajectories blurring spatial definition increases with time. By relaying the incoming airflow among an array of filters, sampling can keep up with veering trajectories and, thus, maintain geographic information throughout the required long observation periods. However, the concept of filter rotation requires knowledge about the source direction. Using a vane to identify upwind regions on site seems a straightforward approach, but the usually turbulent and squally conditions up in the mountains will frequently uncouple direction and origin of the arriving gusts. Under such circumstances, meso- to large scale synoptic weather forecasts seem a much more accurate and reasonably dependable approach. Apart from the high wind speeds, large diurnal and seasonal temperature amplitudes and increased UV radiation pose additional challenges for instrumentation design and specification. For instance, samples have to be shielded from photolysis, flowpaths of liquid samples have to be kept above freezing temperature and temperature gradients along the flowpath of gaseous samples have to be levelled. Therefore, not only active air samplers but also deposition samplers had to be modified and tested for use in an alpine environment.

2. Materials and methods

2.1. Sampling sites

A full set of samplers (high- and low-volume active air samplers, deposition samplers) was installed at each of the following summits (Fig. 3): Weissfluhjoch (Switzerland: 2663 m a.s.l.), Zugspitze (Germany: 2650 m) and Sonnblick (Austria: 3106 m). These sites host research stations and provide year-round infrastructure and maintenance.

2.2. Design of active samplers

Conventional low volume samplers (flow rate: 3 m^3 h^{-1}; Digitel Enviro-Sense[1], Hegnau, Switzerland) were equipped with a carousel to mechanically switch

* Corresponding author.
E-mail address: wolfgang.moche@umweltbundesamt.at (W. Moche).

[1] http://www.digitel-ag.ch/envirosense.htm

0269-7491/$ – see front matter © 2009 Published by Elsevier Ltd.
doi:10.1016/j.envpol.2009.05.053

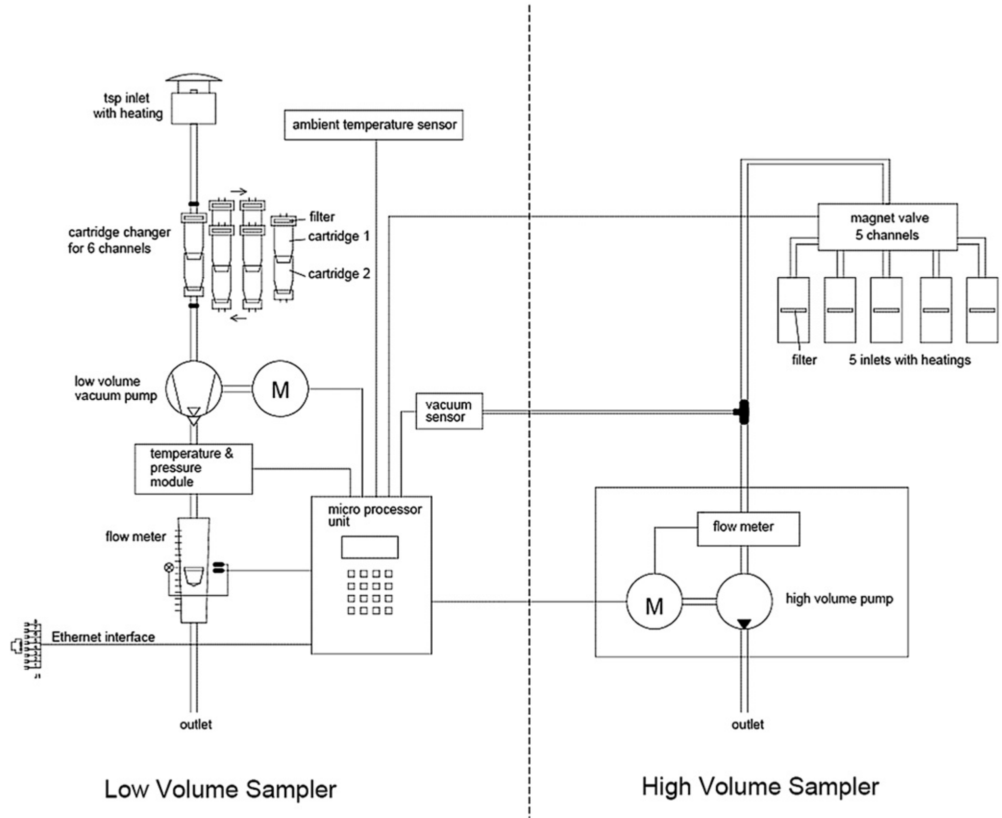

Fig. 1. Control cycle for high- and low-volume samplers.

between up to six filter cartridges, an ethernet interface and an extended control unit to forward and process control- and status-information. The control unit was also used as an interface to the valve-operated filter selection of the high-volume sampler (flow rate: 8 $m^3 h^{-1}$; MonitoringSystems GmbH[2], Kottingbrunn, Austria and Kroneis, Vienna, Austria[3]). Low volume filters consisted of a glass fibre layer and XAD-2 resin. They were cleaned before use by Soxhlet extraction with a 3:1 n-hexane/acetone mixture for 24 h. High-volume filters consisted of a glass fibre layer and two polyurethane foam (PUF) plugs, in agreement with standard methods (VDI, 1997, 2002a). Before deployment, the plugs were cleaned by Soxhlet extraction with toluene and subsequently acetone (24 h each solvent).

All filter housings were temperature controlled to prevent freezing. The air inlets of high- and low-volume samplers were heated to ca. 10 °C above ambient temperature to prevent excess condensation on the filter material (where gas temperature drops with aerodynamic pressure). Fig. 1 shows the details of flow control- and filter-rotation. Filters were replaced every four months, starting December 2005, and sampling continued over five consecutive periods until June 2007. Routine sampling is continuous, except short ($<$5 min d^{-1}) interruptions needed to switch between filters and the manipulation time ($<$2 h) for filter replacement and maintenance at the end of each sampling period.

High-volume samples were analysed for polychlorinated dibenzo–p–dioxins and dibenzofurans (PCDD and PCDF), polychlorinated biphenyls (PCB) and poly-brominated diphenylethers (PBDE). Low volume samplers were analysed for poly-cyclic aromatic hydrocarbons (PAH) and organochloropesticides (OCP).

2.3. Deposition

Standard funnel-adsorber bulk deposition samplers (VDI, 2002b) were insulated and equipped with internal temperature regulation to avoid clogging or bursting of the filter cartridges at subzero temperatures (Fig. 2; construction: Kroneis,[3] Vienna, Austria). XAD-2 resin was used as adsorber. During routine operation, deposition cartridges were exchanged every four months (synchronous to the active sampling periods). Unlike active sampling, deposition was not collected separately from different source regions. Each site hosted a rack of seven identical deposition samplers. Each of the seven filter extracts was reserved for one of the following analytes: PCDD/F and PCB, PBDE, PAH, OCP, chloroparaffines (CP), nitrophenols (NP) and trichloroacetic acid (TCA).

2.4. Identification of source regions

Air sampling was designed to distinguish between three sectors. These sectors had been defined *a priori*, on a European scale, as presumable agglomerates of different sources (industrial, agricultural, domestic): Fig. 3. A fourth region of nominally unspecified origin was defined for fast travelling air masses that had resided less than 2–3 days over any source region's terrestric surface before arrival at the sampling sites. Such air masses were typically of Atlantic or north polar origin or had descended rapidly from higher altitudes. As a corollary, this air would be hardly influenced by European emissions, compared to air from the three sectors described earlier.

2.5. Trajectory forecasts and evaluation

Meteorological services were provided by the Austrian Central Institute for Meteorology and Geodynamics. Trajectories were predicted daily at a resolution of 1 h. Forecasts combined expert meteorological prognosis with the predictions of two numerical trajectory models (global: ECMWF[4], alpine range: ALADIN-Austria[5]; Fig. 4).

The accuracy of forecasts was evaluated by *post hoc* inspection of the trajectories of air actually collected by each filter unit, i.e. air masses passing the site when the respective filter was operative (cf. Kaiser, 2009).

2.6. Sampler control- and filter-rotation

Daily trajectory forecasts were coded into a set of control files for Internet upload to the samplers. Similarly, status protocols could be retrieved from the samplers as required. High- and low-volume samplers were equipped with four identical filter units, each unit of a quadruple being loaded with air from one source region only. As illustrated with Fig. 1, filters were rotated physically

[2] http://www.dioxinmonitoring.com/
[3] http://www.kroneis.co.at

[4] ECMWF (European Centre for Medium-Range Weather Forecasts): http://www.ecmwf.int/.
[5] ALADIN (Numerical Weather Prediction Project): http://www.cnrm.meteo.fr/aladin