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Time-resolved Characterization of Particle Associated Polycyclic Aromatic Hydrocarbons using a newly-developed Sequential Spot Sampler with Automated Extraction and Analysis

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Abstract

A versatile and compact sampling system, the Sequential Spot Sampler (S3) has been developed for pre-concentrated, time-resolved, dry collection of fine and ultrafine particles. Using a temperature-moderated laminar flow water condensation method, ambient particles as small as 6 nm are deposited within a dry, 1-mm diameter spot. Sequential samples are collected on a multiwell plate. Chemical analyses are laboratory-based, but automated. The sample preparation, extraction and chemical analysis steps are all handled through a commercially-available, needle-based autosampler coupled to a liquid chromatography system. This automation is enabled by the small deposition area of the collection. The entire sample is extracted into 50–100 µl volume of solvent, providing quantifiable samples with small collected air volumes. A pair of S3 units was deployed in Stockton (CA) from November 2011 to February 2012. PM_{2.5} samples were collected every 12 hrs, and analyzed for polycyclic aromatic hydrocarbons (PAHs). In parallel, conventional filter samples were collected for 48 hrs and used to assess the new system's performance. An automated sample preparation and extraction was developed for samples collected using the S3. Collocated data from the two sequential spot samplers were highly correlated for all measured compounds, with a regression slope of 1.1 and $r^2=0.9$ for all measured concentrations. S3/filter ratios for the mean concentration of each individual PAH vary between 0.82 and 1.33, with the larger variability observed for the semivolatile components. Ratio for total PAH concentrations was 1.08. Total PAH concentrations showed similar temporal trend as ambient PM_{2.5} concentrations. Source apportionment analysis estimated a significant contribution of biomass burning to ambient PAH concentrations during winter.

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Keywords

sequential spot sampler; time-resolved chemical speciation; ambient particulate matter; polycyclic aromatic hydrocarbons

1. INTRODUCTION

Time- and chemically-resolved data on airborne particles are critically important to understand particle emission sources, their role in global climate and their adverse effects on human health (Block and Calderon-Garciduenas, 2009; Hsu et al., 2011; Lin et al., 2011). On-going epidemiological studies show the importance of ambient particulate matter exposure in determining adverse outcomes. However complete, uninterrupted, time- and chemically-resolved data are not routinely supported.

To date, sample collection for chemical, toxicological and biological studies is conducted using filter-based samplers. These samplers, sturdy and simple to operate in the field, are heavy, bulky and noisy, limiting their deployment possibilities and their use in indoor, occupied locations. Sample handling and laboratory analyses are manually intensive and time-consuming, and results are not immediately available. Deployment and laboratory requirements limit routine measurements to 24hr samples collected every 6th day. The ability to routinely collect samples on daily basis, and with better time resolution, would facilitate the understanding of emission sources, photochemical transformations, human exposure and health effects of airborne particles.

To address the need for uninterrupted data, several instruments have been developed to measure particle chemical composition in near-real time. The Particle-Into-Liquid Sampler (PILS) quantifies inorganic ions and water soluble organics several times per hour (Duong et al., 2011; Maimone et al., 2011). The Aerosol Mass Spectrometer (AMS) provides time- and size-resolved data on particle constituents in the size range below 1 μm (anions, hydrocarbon-like organics, oxygenated organics) and is commonly used to characterize the contribution of emission sources to ambient particulate matter (Carbone et al., 2013; Ge et al., 2012). The thermal desorption aerosol gas chromatograph-MS (TAG-MS), provides hourly quantification of hundreds of semivolatile organic compounds (Kreisberg et al., 2009; Williams et al., 2010). These instruments do not require laboratory analyses, and report continuous data immediately. Although the information collected is substantial, their complexity, size and cost, limit their use for routine monitoring.

There remains a need for affordable methods for uninterrupted, time-resolved particle chemical characterization in ambient and micro-environments. Both routine monitoring and exposure assessment in epidemiological studies would benefit from a technique that combines the simplicity of filter sampling with the data completeness offered by in-situ automated systems. The recently developed sequential spot sampler (S3) (Eiguren Fernandez et al., 2014) addresses this need through the sequential collection of preconcentrated ambient particulate matter in a small and portable unit, combined with an interface for automated, laboratory-based extraction and analysis. Using a new, temperature-moderated water condensation approach (Hering et al, 2014), the S3 directly deposits

particulate matter samples as dry spots into a multiwell plate, providing sets of up to 23 sequential, time-resolved samples on a single plate. Once in the laboratory this multiwell plate is placed on an autosampler that handles automatically sample extraction and injection into the analytical system.

The S3 capitalizes on the approach of concentrated, “ready-to-analyze” particle collection used in many of the real-time analyzers, but keeps the bulky and expensive analytical equipment in the laboratory where their performance is more stable. This allows a common set of analytical instruments to be used for multiple sites, increasing analytical precision, reliability and data completeness among locations. A prior publication (Eiguren Fernandez et al., 2014) presents the S3 design and its laboratory evaluation for quantification of ambient concentrations of sulfate and nitrate. These tests showed collection efficiencies > 90% for particles as small as 6 nm for nitrate-sulfate mixtures, and 10 nm for oleic acid (highly hydrophobic). The S3 showed good retention of ammonium nitrate during sample collection, and precision of the order of $0.1\mu\text{g}/\text{m}^3$ for collocated sampling. Hecobian et al. (2012) evaluated the sampler in field tests conducted at the San Geronio National Park (San Bernardino, CA), and found that ambient concentrations of nitrate and sulfate collected with the S3 were similar to those obtained with a PILS (17 min), and with integrated collection using URG-denuder filter packs (24-hr).

In this study we extend the capabilities of the S3 for time-resolved measurement of ambient concentrations of particle-bound polycyclic aromatic hydrocarbons (p-PAHs). p-PAHs are important because of their known adverse health effects and their use as tracer of combustion sources (Corrêa and Arbilla, 2006; Tobiszewski and Namiełnik, 2012). They have been associated with oxidative stress and other adverse health outcomes (Li et al., 2003; Peiffer et al., 2013). PAH collection using conventional systems (filters) has proven challenging; positive and negative artifacts are common during collection, and extraction steps prior to chemical analyses are expensive and time consuming. With the S3 particles are deposited as a concentrated, dry spot which can be extracted with small solvent volumes. The small volume increases the concentration of compounds in the extract and allows shorter collection periods. The dry collection is expected to maintain the integrity of the sample while in the field, as it is not subjected to vapor uptake, water chemistry or biological interferences. The dry deposits can be stored in the freezer for long periods of time prior to analysis, while maintaining their chemical properties.

This manuscript describes the results of the first field deployment of the S3 for identification and quantification of p-PAHs. Data were collected with 12-hr time-resolution over a three month period, with only weekly visits to the site. An automated extraction and analysis system, compatible with the collection plate was developed, and validated using ambient samples. This procedure reduces extraction time and minimizes sample handling prior to laboratory analysis, thereby facilitating the measurement of a large number of samples. The S3 performance was evaluated through direct comparison with conventional filter based samplers.

2. MATERIAL AND METHODS

2.1. Sequential Spot Sampler (S3)

The S3 consists of a water condensation growth tube followed by a single-jet impactor collector, with collection onto a rotatable, multiwell collection plate. It may be operated at a flow rates between 1.0 and 1.5 L/min. The growth tube uses the three-stage, moderated laminar flow condensation approach described by Eiguren Fernandez et al (2014). This provides for sufficient supersaturation to activate particles in the nanometer size range, down to 6 nm (Hering et al., 2014; Lewis and Hering, 2013), but moderates the flow temperatures and exiting dew point such that the majority of the flow remains below 25°C and the exiting dew point is below 18°C. A detailed description of the purpose of each section was previously published (Hering et al., 2014). Briefly, the laminar flow passes from the cooler section into the warm-, wet-walled growth region where particle activation occurs. The third stage provides the distance needed for particle growth. Particles grow to form 1–3 μm droplets, and are collected by impaction as a 1-mm diameter spot within a well. Because the particles impact as droplets there is no loss from particle bounce, and because the dew point exiting the growth tube is low the droplets evaporate within a few minutes of being deposited forming a concentrated, dry deposit.

The three stages are the “conditioner”, “initiator” and “moderator”, and measure 154 mm, 73 mm and 100 mm long, respectively. With the collection chamber and control box, the system is around 550 mm tall and 150 mm wide (Figure 1), and weights 7kg.

Typical operating temperatures for the conditioner, initiator and moderator are 5°C, 35°C and 8°C respectively. As the flow enters the collection chamber it is slightly subsaturated at approximately 20°C, with each particle encapsulated within a supermicrometer size water droplet. The flow then accelerates through a single 1mm diameter nozzle centered above a collection well and the droplet-encapsulated ambient particles are deposited by impaction. The water content encapsulating the particles eliminates particle bounce and a small heater, positioned under the active well and kept between 25–30°C, evaporates the water as the droplets are deposited. A small heater on the nozzle mount prevents water condensation within the nozzle. A Teflon gasket mounted on the ceiling of the collection chamber covers all but the active well reducing contamination during sampling and storage.

The collection plate contains 24 evenly spaced wells, each measuring 6 mm diameter and 4 mm depth, and capable of holding 100 μL of solution. Individual samples are collected in each well, and a small stepper motor advances the plate to the next well at the end of the specified collection period. The S3 temperatures, sample collection time, and water fill are controlled through in-house electronics and software using a BD-Micro MAVRIC-IB microcontroller. The control system also monitors all system parameters and outputs a serial data stream. Operating temperatures and sample collection intervals are user-selectable.

Once collection ends, the plate is retrieved from the sampler and placed in a petri-dish, closed with Teflon tape and kept in the freezer until automated extraction and analysis in the laboratory. Plates are re-usable and easy to clean. The cleaning process consists of 15 min sonication with soap, manual cleaning of each well with a lab brush and cotton tipped

applicators, 15 min sonication with double distilled water (DDW), and a final rinse with DDW. No contamination from previous sampling was observed in laboratory controlled tests after cleaning.

2.2. Sample collection

Two S3 units and a filter sampling system were deployed at the California Air Resources Board (CARB) monitoring station in Stockton, CA, for collocated measurements from mid November 2011 to mid February 2012. Stockton is an inland, agricultural area located in the San Joaquin Valley. The San Joaquin Valley has some of the highest ambient particulate levels in the country; annual average PM_{10} concentration of $17.0 \mu\text{g}/\text{m}^3$ was measured between 2009–2011 (ALA, 2013) with over 40 days a year exceeding the National Standard of $35 \mu\text{g}/\text{m}^3$; in 2012, the highest 24-hr concentration measured for PM_{10} was $114 \mu\text{g}/\text{m}^3$ (SJVAPCD, 2013). This area has also high rates of childhood asthma compared to the rest of California (CHIS, 2001; McGeehin et al., 2004).

The sampling configuration, shown in Figure 2, used an AIHL cyclone (Reischl and John, 1985) operated at 20–25 L/min, to provide a common $PM_{2.5}$ precut. Two S3 units were run in parallel at a flow rate of 1.5 lpm (controlled by a needle valve), with 12-hr collection periods from 2:00am to 2:00pm local time. This collection schedule was selected to allow easy access to the site and convenience for field personnel. Particles were collected as dry deposits onto PEEK and aluminum multiwell plates. System operating parameters were logged continuously via computer. The samplers ran unattended with weekly servicing, except during holidays which extended the servicing interval to 10 days. Service visits involved checking flow rates, replenishing the water reservoir, retrieving the multiwell plates, and installing clean plates for the next sampling period. Upon return, multiwell plates were kept in the freezer prior to laboratory analysis. In parallel conventional filter based samples were collected on 25mm Teflon (Savilex) filters over 48-hr periods at a flow rate of 7 lpm.

Collected $PM_{2.5}$ samples were analyzed for 12 of the 16-EPA PAHs: phenanthrene (PHE); anthracene (ANT); fluoranthene (FLT); pyrene (PYR); benz(a)anthracene (BAA); chrysene (CRY); benzo(b)fluoranthene (BBF); benzo(k)fluoranthene (BKF); benz[a]pyrene (BAP); dibenz(a,h)anthracene (DBA); benzo(g,h,i)perylene (BGP); and indeno(1,2,3-cd)pyrene (IND). Samples collected during the first 2 weeks of the deployment were used for optimizing the extraction method, followed by 2 weeks for system reproducibility, and 5 weeks for comparison with filter collection.

During the nearly 3 months of field deployment, 168 consecutive 12-hr samples were collected from each S3, and a total of 48 filter samples.

2.3. Well plate analysis

For PAH analysis the plates containing the collected samples were placed directly in the autosampler where the automated extraction and analysis was conducted (Figure 3).

Individual PAH analysis and detection was done using a CTC-PAL autosampler coupled to an Agilent 1100 (Agilent, Santa Clara, CA) high performance liquid chromatograph

consisting of a quaternary pump, a degasser, a thermostated column compartment and a fluorescence detector with variable excitation and emission wavelengths. Retention times, codes and excitation and emission wavelengths for all 12-EPA PAHs are shown on Table 1. A detailed separation and detection method was published previously (Eiguren-Fernandez and Miguel, 2003). Briefly, the PAH separation was carried out using a supelcosil LC-PAH column (5 μ m, 15cm $\times$ 4.6mm) preceded by a Supelcoguard LC-18 pre-column. A mobile phase of acetonitrile and water was used for the separation in a gradient mode. The analysis time required for optimum separation of the PAHs was 20 min. Limit of detections for individual compounds are listed by Eiguren-Fernandez and Miguel (2003).

The CTC-PAL autosampler is capable of conducting all sample preparation, extraction and injection steps predetermined in the analytical method without user intervention. The autosampler dispenses a determined volume of solvent containing the internal standard d-perylene in an individual sample and conducts the necessary steps for the extraction. Sample extraction occurs while the system processes the previous sample. Once the sample is ready, the autosampler injects an aliquot of the extract into the HPLC for analysis. The procedure is repeated for each sample in sequence. This automated extraction reduces considerably the time required to identify and quantify PAHs present in ambient particulate matter. Moreover, it reduces cost of filters, vials, and personnel's time, and eliminates possible artifacts and mistakes during handling.

Several procedures were tested for the optimization of the extraction procedure: soaking, soaking with mechanical agitation for 1 minute, and soaking with 20 sec sonication. To minimize the time required to run a multi-well plate, the sample run time was established as the maximum time for sample preparation. For the soaking only, aliquots of the extract were dispensed onto the sample and no further steps were conducted prior to injection. The mechanical agitation device was custom built at ADI and consisted on a metal rod with a small vibrator at one end which was inserted manually in the well once the solvent was dispensed. The agitation lasted 1 min and the device was manually removed before injection. After this step the sample soaked for the remaining of the 20 min. Sonication was conducted using a custom made bath. After dispensing the solvent, sonication was conducted in 2 consecutive steps of 10 sec each, after which the sample was left soaking until injection. No personnel intervention was needed for this extraction method.

2.4. Filter analysis

Filters were extracted with 1mL acetonitrile and sonicated for 30 min following a previously published method. Briefly, 1 mL acetonitrile, containing the internal standard d-Perylene was added and filters extracted by sonication (2 periods of 15 min each, with bath water changed between periods). The extracts were filtered using a nylon syringe filter (0.2 μ m) and volume reduced to $\sim$ 100 μ L. The extract was analyzed following the same analytical program as for plate analysis. Extraction recoveries were not measured in this study as the procedure had been previously validated using NIST SRM 1649a (Eiguren-Fernandez and Miguel, 2003).

2.5. Source identification using the Chemical Mass Balance model

Northern California uses biomass burning as a source of heating during winter periods. In the Bay area, the contribution of biomass burning to ambient $PM_{2.5}$ varies between 15 and 35%. The $PM_{2.5}$ mass contributed by this source can increase up to 4 times in winter (Tanrikulu et al., 2009). To evaluate the contribution of this source in Stockton we used the Chemical Mass Balance (CMB) Model EPA-CMBv8.2.

The CMB8 is one of several receptor models used for quantitative assessment of the contribution of different sources to environmental pollutants over the last two decades. This is a quantitative approach over the total mass on a series of samples and over the chemical distribution on a specific sample. Results are calculated using an effective-variance least squares method (EVLS), and requires of speciated profiles of potentially contributing sources and the corresponding ambient data from analyzed samples collected at a single receptor site. The model has been applied successfully for assessing contribution of sources to air concentrations of trace elements, elemental and organic carbon, and organics (Eiguren-Fernandez and Miguel, 2009; Kavouras and Zielinska, 2012; Larsen et al., 2012).

The CMBv8.2 model was downloaded from the EPA's webpage. PAH signatures from three combustion sources: gasoline emissions, diesel engine emissions, and residential wood combustion were included in the model. Source profiles for gasoline and diesel engines were obtained from previous studies conducted in the Caldecott Tunnel (Berkeley, CA) (Eiguren-Fernandez and Miguel, 2005) and the biomass burning emission profile was obtained from Fine et al. (2004). Li and Kamens (1993) suggested that ratios among the measured p-PAHs could be stable in a given source, and that a stable source pattern in terms of a "normalized PAH concentration" could be more useful as a source signature than individual concentrations. Based on this, we used "normalized concentrations" (measured concentration of individual compounds divided by the sum of concentrations of all selected compounds) of a group of 7 PAHs with lower volatility and less affected by sampling artifacts: BAA, CRY, BBF, BKF, BAP, BGP and IND.

3. RESULTS and DISCUSSION

3.1. Field Operational Performance

Apart from weekly visits to the site for sample plate exchange, the S3 ran unattended. The frequency of site visits was determined by the sampling schedule (twice/day, 14/week) and the number of wells in the plate (23), rather than by the system requirements for maintenance and calibration. Sample retrieval and system preparation for a new collection was done in less than 30 min. Sampling flows were measured both at the beginning and end of each sampling period; variations in the flow rates were on average 2% for the S3. System operating temperatures were stable, within 1.5°C of their set points.

Overall, the samplers' performance was excellent and did not need regular attention, with minimum personnel time required when on site.

3.2. PAH extraction efficiency

Collocated samples collected with systems 1 and 2 during the first two weeks of the deployment were used to optimize the extraction process. Both systems were maintained at similar operational temperatures and sampling flows. As sonication is the most common method used for PAH extraction it was used as reference for comparison with simpler methods: soaking (as found effective for inorganic ions (Eiguren Fernandez et al, 2014) and mechanical stirring.

Differences between sonication and soaking are shown in Figure 4a. Soaking for 20 min alone was sufficient for low PAH concentrations, but more vigorous procedures were required for optimum extraction at higher concentrations. Mechanical agitation was better than soaking but still 30% lower than sonication (Figure 4b), and we observed that solvent displacement occurred often during agitation. In addition, personnel involvement was required during mechanical agitation. Considering the results, sonication was selected as a less troublesome, shorter and efficient extraction process.

To evaluate extraction efficiency of the sonication, extracted samples were subjected to a second sonication step. The measured concentrations on the second extraction were on average less than 10% of the initial extraction step. Based on this results, we decided to use the initial 20 sec sonication step for the automated extraction of PAHs.

The optimized, automated extraction method was as follows: 1) at $t=0$, 40 μL of acetonitrile containing the internal standard d-Perylene were added to the well followed by 2 consecutive sonication steps of 10 sec each; 2) at $t=10$ min, 20 μL of acetonitrile were added; 3) finally, at $t=20$ min, and prior to injection, another 20 μL of acetonitrile were dispensed into the sample well. The extraction and analysis method is fully automated and there is no need for any preparation steps prior to placing the collection plate in the autosampler. An example of a chromatogram obtained after the analysis of a sample collected with the S3 is shown on Figure 5.

Our method development included an examination of multiwell plate materials. One week of parallel samples were collected using a PEEK plate in one system and Aluminum in the other, and analyzed with the same protocol. No major differences were observed in the concentrations measured on samples collected on either material (data not shown). However, PEEK material was selected for future collections as these plates can be used for other chemical analyses such as inorganic ions.

3.3. System Precision

System reproducibility was evaluated on samples collected in parallel with System 1 and 2 for a three-week period, and extracted and analyzed using the optimized analytical method. Measured concentrations for each individual PAH were compared to assess system to system variability. Figure 6 shows the comparison for individual PAHs measured with both systems. For total PAH concentrations, the correlation between systems was within 10%, except for one sample (left side of the graph), where concentrations on System 1 were considerably lower for all measured compounds.

Linear correlation parameters and ratio of the mean concentrations for each individual PAH measured with System 1 and 2 are shown on Table 2. Good correlation was found for all measured compounds, except for IND, with system 2 measuring 50% lower than System 1. This discrepancy cannot be explained at this point as only this compound showed this considerable difference. Higher variability was observed for the semivolatile PAHs with System 2 measuring 15–30% higher than System 1.

3.4. Comparison with filter sampling

After the automated extraction was optimized and system reproducibility proven adequate, averaged PAH concentrations (4 samples accounting for 48-hrs) measured on the samples collected using the S3 were compared with the concentrations found on the filter samples. Correlation between individual concentrations measured on filters and averaged concentrations on the well plates for 5 weeks of sampling are shown in Figure 7.

In general, good correlation was observed between filters and S3. To better analyze the extent of the variability, differences between filter and S3 collection were determined for each individual p-PAH. Table 3 shows the minimum, maximum and average concentrations measured both methods (concentrations reported at ambient conditions).

Concentrations measured with both methods were similar for high molecular weight PAHs; however, larger variability was observed for semivolatiles. PHE and CHY showed consistently higher concentrations on the S3 samples than the filters. Although PAHs are hydrophobic and their solubility in water is small, gas-phase volatile and semivolatiles could be captured in the water during particle growth, resulting in the higher concentrations measured. However, as the water rapidly evaporates after deposition, these PAHs could also be lost to the vapor-phase in the process. Concentrations of the most volatile and hydrophilic PAHs, which correspond to naphthalene, acenaphthene and fluorene, were below the limit of detection of the analytical method, suggesting that the contribution of volatile PAHs capture during particle growth, if any, was minimal.

The low correlation observed for PYR may have resulted from one outlier, where the measured concentration on the filter was 10 times lower than the S3. The higher differences observed for the semivolatiles may have resulted from artifacts associated with long sampling periods on filters; semivolatiles can be blown off the filters or can react in the filter during collection. Adsorption of semivolatiles on samples collected using the S3 is assumed to be minimal. PEEK is an inert material with similar adsorption properties to Teflon, commonly used for p-PAH measurements to reduce artifacts. Adsorption onto the deposited particles could happen during sampling. The layer of particles collected with the S3 are exposed to the incoming flow for a period of time ranging from 20 min to 1 hr before a new layer of particles covers them. However, this artifact may occur in both systems; nevertheless, the effects may be specific to each sampling method as the particle collection mechanism is different (filtration vs. impaction). The lower recovery of BGP and IND in the S3 may be due to a lower efficiency of the automated extraction process used; however, an increase in recoveries using consecutive sonication steps was proven to be minimal.

3.5. Temporal variation on particle-bound PAHs in Stockton, CA

Sample collections of 12 hrs allowed assessing diurnal patterns of ambient PAH concentrations. Temporal variability of 6 individual PAHs measured in Stockton are shown in Figure 8.

Total p-PAH concentrations vary between 0.04 ng/m³ and 9.53 mg/m³, with an average concentration of 2.26 ng/m³. For individual PAHs, the highest averaged concentrations were measured for BBF (0.40 ng/m³) and BGP (0.38 ng/m³). Peak concentrations as high as 1.62 ng/m³ and 1.56 ng/m³ were observed for BBF and BAA, respectively. Among the semivolatiles, PHE concentrations were the highest, with a maximum of 1.12 ng/m³. These concentrations are similar to values observed for p-PAHs in Fresno by Gale et al. (2012) and by the California Air Resources Board (CARB, 2010), with average total concentrations of 6.84 ng/m³ and 2.82 ng/m³ respectively. However, these concentrations are considerably lower than levels reported in 1995–1996 by Schauer and Cass (2000).

Lower concentrations were measured at the beginning and end of the sampling period, while higher concentrations, and larger variability, were observed during December and beginning of January. To better understand the temporal variability of PAHs, Σ PAH concentrations were compared with PM_{2.5} levels (24-hr average) measured by CARB at the Stockton station. The averaged ($\pm$ STDEV) PM_{2.5} concentration measured for this period was 28.7 ($\pm$ 14.1) (μ g/m³). Ambient PM_{2.5} concentrations exceeded the national 24-hr standard (35 μ g/m³) on 22 days out of the 77 days of the study, with most of them occurring between December and mid January, which is consistent with values reported by previous studies (Tanrikulu et al., 2009). Temporal variability of Σ PAHs and PM_{2.5} concentrations are shown in Figure 9. Σ PAH concentrations were higher during the periods when PM_{2.5} levels were high ($r^2=0.7$). These results suggest that PM_{2.5} and PAHs have similar emission sources. A more detailed diurnal variability analysis showed that in general, higher p-PAH concentrations were found in the second half of the day, from 2:00pm to 2:00am (Figure 10).

Previous studies have shown that ambient concentrations increase during the periods when the height of the surface thermal inversion is lower, temperatures are low, prevailing winds are weak, and emissions from cold starts are important (Guzmán-Torres et al., 2009; Liu et al., 2013; Ringuet et al., 2012). In our study, these conditions are found during the evening sampling period (2:00pm to 2:00 am). In addition, during winter, emissions from biomass burning are higher during the evening when people get back from work.

Because concentrations in the morning period are systematically lower than the afternoon, the 24-hr averaged concentrations do not capture the peak concentrations observed during the afternoon period. On average, 12-hr peak concentrations were 20% higher than the 24-hr average, with one afternoon peak concentration twice the morning maximum level. Peak concentrations are important when conducting exposure assessment studies and evaluating acute and chronic health effects associated with exposure to ambient pollutants.

3.6. Source identification

Results from the CMBv8.2 model showed that p-PAH emissions were dominated by gasoline engines and biomass combustion, with contribution from diesel engines only estimated on few occasions. There is no significant diesel truck traffic in the area, but some days, road construction was observed on the main road adjacent to the monitoring station, which could have contributed to the estimated spikes.

CMB model estimated contribution of the three sources is shown in Figure 11. Biomass burning contributions were more significant in the afternoons (Figure 12), suggesting that emissions from this source could play an important role in ambient PAH concentrations observed during this period. The higher PAH concentrations observed in the afternoon (Figure 10) may have resulted from an increase in biomass burning emissions. Biomass contribution was higher during December and beginning of January, when lowest temperatures were recorded.

The source profile used in this study corresponded only to one type of wood common in California. However, several other types are available and contribution of biomass burning could be slightly different if emissions from other wood types were considered in the model.

4. CONCLUSIONS

We have evaluated the field performance of a new sampler for the identification and quantification of ambient p-PAHs. The sampler enables the sequential, uninterrupted, time-resolved collection of concentrated dry particles. As a result of the concentrated nature of the collection (1 mm spots) short collection times are possible allowing for 12-hr collection with minimum personnel intervention in the field. Personnel visits to the site were reduced to once per week. Once in the laboratory, the extraction and analysis of the samples was conducted in a fully automated manner. The automated procedure reduces the time and cost of chemical analyses, as well as artifacts that may result from sample handling, filtration and/or volume evaporation processes prior to analysis.

System reproducibility and precision were acceptable, although one system presented a bias towards the IND. Ambient levels of total p-PAHs measured with the S3 were within 15% of those measured on standard filter collection. Semivolatile PAHs showed higher difference between filter and S3 than high molecular weight PAHs. This higher discrepancy may have resulted from sampling artifacts that occurred during the 48-hr collection periods for the filters. Results from the sub-daily chemical characterization showed that concentrations in the afternoon were significantly higher than in the morning hours, with emissions from biomass burning contributing in some cases up to 80% of the measured PAH levels.

The S3 is a portable sampler that can run unattended for several weeks. The time-resolved collection capability and the variety of chemical analyses that can be conducted in an automated manner can improve the chemical speciation data base, resulting on a better understanding of the contribution of emission sources and photochemical transformations on ambient air pollution and possible adverse effects in climate and human health.

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HIGHLIGHTS

- a new sampler provides time-resolved speciation of polycyclic aromatic hydrocarbons
- ambient particulate matter is deposited as 1-mm spots within a multiwell plate
- laboratory-based analyses, including extraction and injection, are automated
- ambient levels of 12 PAH compounds are reported with 12-hr resolution for 90 days
- the method is compatible with several analytical techniques

Figure 1.
Sequential Spot Sampler

Figure 2. Sampling set up. F1: filter 1; F2: filter 2; F3: filter 3; F4: filter 4; S³-1: system 1; S³-2: system 2

Figure 3.
Automated extraction; a) plate location on autosampler; b) solvent dispensed by autosampler on sample-well.

Figure 4.
Extraction efficiencies; a) sonication vs. soaking; b) sonication vs. mechanical agitation.

Figure 5.

Chromatogram obtained after automated extraction and analysis of a PM_{2.5} sample collected on January 10, 2012, using the S3. Compounds: 1) PHE; 2) ANT; 3) FLT; 4) PYR; 5) BAA; 6) CRY; 7) d-PER; 8) BBF; 9) BKF; 10) BAP; 11) DBA; 12) BGP; 13) IND.

Figure 6.
Individual PAH concentrations measured on each sampling system (n=22).

Figure 7.

Comparison of individual p-PAH concentrations measured on filters and averaged samples on the new S3 (n=19).

Figure 8.
Time-resolved ambient concentrations of 6 PAHs in Stockton, CA

Figure 9. Temporal trend for PM_{2.5} (black) and Σ PAH (red) concentrations. Green line corresponds to the National Standard concentration.

Figure 10.
ΣPAH concentrations observed for the morning and afternoon periods.

Figure 11.
Estimated contribution of emission sources to p-PAH concentrations.

Figure 12.
Biomass burning contribution (%) estimated for morning and afternoon periods.

Table 1

Codes, retention times, and excitation and emission wavelengths for each PAH.

Compound	Code	Rt* (min)	λ_{ex} (nm)	λ_{em} (nm)
Phenanthrene	PHE	8.30	260	360
Anthracene	ANT	9.00	245	382
Fluoranthene	FLT	9.78	235	449
Pyrene	PYR	10.3	235	389
Benz[<i>a</i>]anthracene	BAA	12.1	265	381
Chrysene	CRY	12.5		
d-Perylene [#]	d-PER	13.4	260	460
Benzo[<i>b</i>]fluoranthene	BBF	13.7		
Benzo[<i>k</i>]fluoranthene	BKF	14.3	260	420
Benzo[<i>a</i>]pyrene	BAP	14.8		
Dibenz[<i>ah</i>]anthracene	DBA	16.2	295	420
Benzo[<i>ghi</i>]perylene	BGP	16.7		
Indeno[1,2,3- <i>cd</i>]pyrene	IND	17.3	300	500

*
Rt: retention time;[#]
internal standard

Table 2

Linear correlation parameters (slope and r²) and ratio of mean concentrations measured in each system for individual compounds

Compound	Slope	R ²	Ratio
PHE	1.19	0.94	1.07
ANT	1.26	0.83	1.27
FLT	1.19	0.95	1.16
PYR	0.98	0.86	1.33
BAA	0.76	0.88	0.82
CRY	1.12	0.96	1.17
BBF	1.05	0.96	1.10
BKF	0.99	0.86	1.07
BAP	1.01	0.96	1.05
DBA	0.78	0.80	1.03
BGP	1.11	0.90	1.09
IND	0.55	0.82	0.85
ΣPAHs	0.99	0.95	1.03

Table 3

PAH concentration (pg/m³) range and average measured on filter and S3 samples.

Compound	Filter			Sequential Spot Sampler			R ²
	Min	Max	Average	Min	Max	Average	
PHE	13.6	709	210	52.7	885	352	1.67
FLT	21.6	222	91.6	11.3	177	68.3	0.75
PYR	3.06	118	64.4	10.1	214	47.3	0.73
BAA	63.0	1,046	383	73.3	1,092	445	1.16
CRY	28.3	194	96.7	80.7	794	334	3.45
BBF	99.3	1,522	558	145	1,269	628	1.13
BKF	22.7	529	174	43.2	435	185	1.06
BAP	56.6	1,289	439	96.8	985	457	1.04
DBA	23.0	209	85.0	24.8	167	87.3	1.03
BGP	182	1,560	729	102	1,102	584	0.80
IND	119	1,179	528	63.0	1,067	440	0.83
ΣPAHs	648	7783	3359	773	7647	3267	0.97
							0.96