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Long-term monitoring of black carbon across Germany

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ABSTRACT

Lately, black carbon (BC) has received significant attention due to its climate-warming properties and adverse health effects. Nevertheless, long-term observations in urban areas are scarce, most likely because BC monitoring is not required by environmental legislation. This, however, handicaps the evaluation of air quality models which can be used to assess the effectiveness of policy measures which aim to reduce BC concentrations.

Here, we present a new dataset of atmospheric BC measurements from Germany constructed from over six million measurements at over 170 stations. Data covering the period between 1994 and 2014 were collected from twelve German Federal States and the Federal Environment Agency, quality checked and harmonized into a database with comprehensive metadata. The final data in original time resolution are available for download (https://doi.org/10.1594/PANGAEA.881173). Though assembled in a consistent way, the dataset is characterized by differences in (a) measurement methodologies for determining evolved carbon and optical absorption, (b) covered time periods, and (c) temporal resolutions that ranged from half hourly to measurements every 6th day. Usage and interpretation of this dataset thus requires a careful consideration of these differences.

Our analysis focuses on 2009, the year with the largest data coverage with one single methodology, as well as on the relative changes in long-term trends over ten years. For 2009, we find that BC concentrations at traffic sites were at least twice as high as at urban background, industrial and rural sites. Weekly cycles are most prominent at traffic stations, however, the presence of differences in concentrations during the week and on weekends at other station types suggests that traffic plays an important role throughout the full network. Generally higher concentrations and weaker weekly cycles during the winter months point towards the influence of other sources such as domestic heating. Regarding the long-term trends, advanced statistical techniques allow us to account for instrumentation changes and to separate seasonal and long-term changes in our dataset. Analysis shows a downward trend in BC at nearly all locations and in all conditions, with a high level of confidence for the period of 2005–2014. In depth analysis indicates that background BC is decreasing slowly, while the occurrences of high concentrations are decreasing more rapidly.

In summary, legislation – both in Europe and locally – to reduce particulate emissions and indirectly BC appear to be working, based on this analysis. Adverse human health and climate impacts are likely to be diminished because of the improvements in air quality.

1. Introduction

Black carbon (BC), a component of particulate matter (PM), has an impact on climate and human health. Several studies have pointed out the importance of BC for adverse health effects (Janssen et al., 2011; Rohr and Wyzga, 2012) and that the relationship between short-term (daily) health effects and BC is more robust than the relationship with PM_{10} and $PM_{2.5}$ (particulate matter with a diameter below 10 and 2.5 μm, respectively) (WHO, 2012). BC is also among the most significant contributors to global warming with predominantly short-term effects. This is due to its light-absorbing characteristics (Bond et al., 2013).

Black carbon forms during incomplete combustion from sources such as transport (on-road, shipping, aviation), residential solid fuel burning, open biomass burning or coal-fired power plants (Bond et al., 2013). Sources of BC can vary widely across regions. For example, the

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main sources in Kathmandu, Nepal, one of the world's hot-spots in terms of air pollution, are brick kilns, traffic and open garbage burning (Putero et al., 2015). In comparison, the main sources in Europe are on-road diesel vehicles, non-road transport, and residential combustion (Kuenen et al., 2014). In European cities, BC typically originates from traffic or wood combustion. Healy et al. (2012) found for Paris in winter 2010 that more than 80% of BC came from fossil fuel sources and the remainder from biomass burning. Zotter et al. (2017) found for Zurich that contributions to BC from fossil fuel are dominant in the warmer seasons with > 80% while in winter contributions from biomass burning and fossil fuel combustion are approximately equal. Traffic restrictions or low emission zones (LEZ) have been introduced as measures of air quality management in several European cities that frequently exceeded air pollution limit values. While the effect of LEZ has been debated as they do not necessarily reduce the concentrations of bulk PM or trace gases such as NO_x, it has been shown that they are effective in reducing BC (Holman et al., 2015) indicating that traffic is an important source of BC across European cities.

Among the few observation-based European studies on BC that are not short term campaigns, are two projects, CARBOSOL (Legrand and Puxbaum, 2007) and the EMEP EC/OC campaign (Yttri et al., 2007) that investigated the elemental (EC) and organic carbon (OC) concentrations across Europe at several remote and two urban background sites in 2002–2003. General results included higher concentrations of EC during winter, likely due to higher energy consumption and unfavorable meteorological conditions, and the occasional but significant influence of fires at specific locations during spring and summer. More recent observational efforts have focused on detection method harmonization for EC within the framework of the European Supersites for Atmospheric Aerosol Research Project (EUSAAR) (Cavalli et al., 2010), and a European BC optical property phenomenology (Zanatta et al., 2016) in the framework of the European Aerosols, Clouds, and Trace gases Research InfraStructure (ACTRIS). These efforts, however, concentrate on regionally representative sites rather than urban areas where citizens are primarily exposed to air pollution. To date, only few long-term studies on urban BC in the context of air quality evaluation exist, one example is the city of London (Font and Fuller, 2016).

The scarcity of long-term urban BC observations is primarily due to the fact that monitoring of BC has generally not been and is currently not required. In Germany in 1995, an annual mean limit value of 14 $\mu g\,m^{-3}$ for “black smoke”, a surrogate for BC was introduced. From 1998 the limit was reduced to 8 $\mu g\,m^{-3}$. In 2005, with the introduction of mandatory monitoring of PM_{10} in the European Union the “black smoke” limit was abolished. T Even though “black smoke” measurements have not been required anymore in Germany since 2004, a number of monitoring stations continued their measurements of BC. In addition, new networks have recently been launched such as the Germany Ultrafine Aerosol Network (GUAN) (Birmili et al., 2016), providing quality assured equivalent BC (EBC) data. Also the number of sites in the European Monitoring and Evaluation Programme (EMEP) and ACTRIS networks measuring BC is growing due to the increasing interest in the substance (Genberg et al., 2013). However, while data from the GUAN, EMEP and ACTRIS networks are easily accessible through databases (e.g. EBAS, http://ebas.nilu.no/), urban monitoring data remains largely in the archives of local environment authorities from where it is difficult to access. Hence, what is known for Germany, for example, is that the PM_{10} annual mean concentrations between 2000 and 2016 decreased from > 35 $\mu g\,m^{-3}$ to < 25 $\mu g\,m^{-3}$ for traffic, urban background and rural background stations (Minkos, 2017). It is, however, unclear how BC concentrations evolved during that period, only relative emission trend information is available, i.e. between 2000 and 2015 a 60% reduction was found (UBA, 2018a).

Comprehensive datasets of BC could contribute to understanding changes in BC concentrations and their relation to air quality policy measures. Evaluating the effectiveness of policy measures is a crucial step towards reducing the adverse effects of BC on health and climate. One means of doing so is through air quality modeling, which needs to be verified by comprehensive measurement data. In particular, the simulation of total particulate matter with air quality models is often challenging (Giordano et al., 2015; Im et al., 2015; Kuik et al., 2016; Pan et al., 2004). More detailed information on the observed composition of PM, including BC, can help to pinpoint the sources of model bias when comparing simulated with observed concentrations, and thus improve the air quality models. Furthermore, the simulation of BC itself is still challenging. For example, several model studies have aimed at reproducing the above-mentioned EMEP EC/OC data set. Simpson et al. (2007), using the EMEP Meteorological Synthesizing Centre-West model (MSC-W), found that emissions from residential wood combustion were especially uncertain. Koch et al. (2009) evaluated BC simulations from 17 global models against the data set and found that most models produced higher BC concentrations than observed, whereas the spread of ratios of model versus observation ranged from 0.5 to 10. These studies also highlight the need of further improvements in emission inventories, which can be supported by detailed observations of the different components of PM, including BC (Kuenen et al., 2014).

In this work we present a comprehensive BC data set collected from 12 German federal states and the German Environment Agency (UBA), covering a period from the mid-90s to 2014. We describe how the data were obtained and organized into a database. The dataset is publicly available (https://doi.org/10.1594/PANGAEA.881173). To highlight some of the information contained in the dataset, we analyze variations in BC concentrations derived with the same measurement method for the year with the highest coverage of observations (2009), and derive long-term trends (2005–2014) for a subset of stations.

2. Methods

2.1. Data sources and measurement methods

Data from 213 stations were provided by the German Federal States (12 out of 16 federal states provided data for 131 stations) and the Federal Environment Agency (UBA, for 130 stations) upon request by the authors; whereby some data were reported by multiple sources. Locations are shown in Fig. 1.

In absence of a standardized method for BC determination, a variety of different methods were applied on four different sample matrices (total suspended particles, TSP; PM_{10}, $PM_{2.5}$ and PM_1, see Table 1 for details). The terminology for methods used across the different federal states was not harmonized. For consistency, we group each station's method into an evolved carbon or optical detection method category at a general level. Table 1 names the specific protocols applied for the evolved carbon detection. Table S1 in the supplementary material Section 1 (hereafter, SM Sec1) links the terminology used by the federal states to the terminology introduced in Table 1, and Table S2 (SM Sec2) connects each station with one particular measurement method or several if methods changed over time. In the following, brief descriptions of each method are provided.

2.1.1. Evolved carbon measurements

‘Evolved carbon’ detection methods are characterized by heating the sample following a temperature protocol and then detecting the formed CO_2 by varying methods. The largest number of stations (49) detected elemental carbon (EC) with a thermal-optical method following the VDI 2465, Sheet 2 procedure (e.g., Schmid et al., 2001). At some stations a different protocol for the thermal evolution was used, following the European Supersites for Atmospheric Aerosol Research 2 (EUSAAR2) protocol (Cavalli et al., 2010).

Some stations worked with the Ambient Carbon Particulate Monitor RP 5400 by Rupprecht and Patashnik (Lim et al., 2003; Rupprecht et al., 1995; RWTÜV, 1997). The RP 5400 instrument collects PM on a stainless steel impactor plate. The sample is heated in air to 275 °C to evaporate organic carbon. Subsequently the temperature is increased to

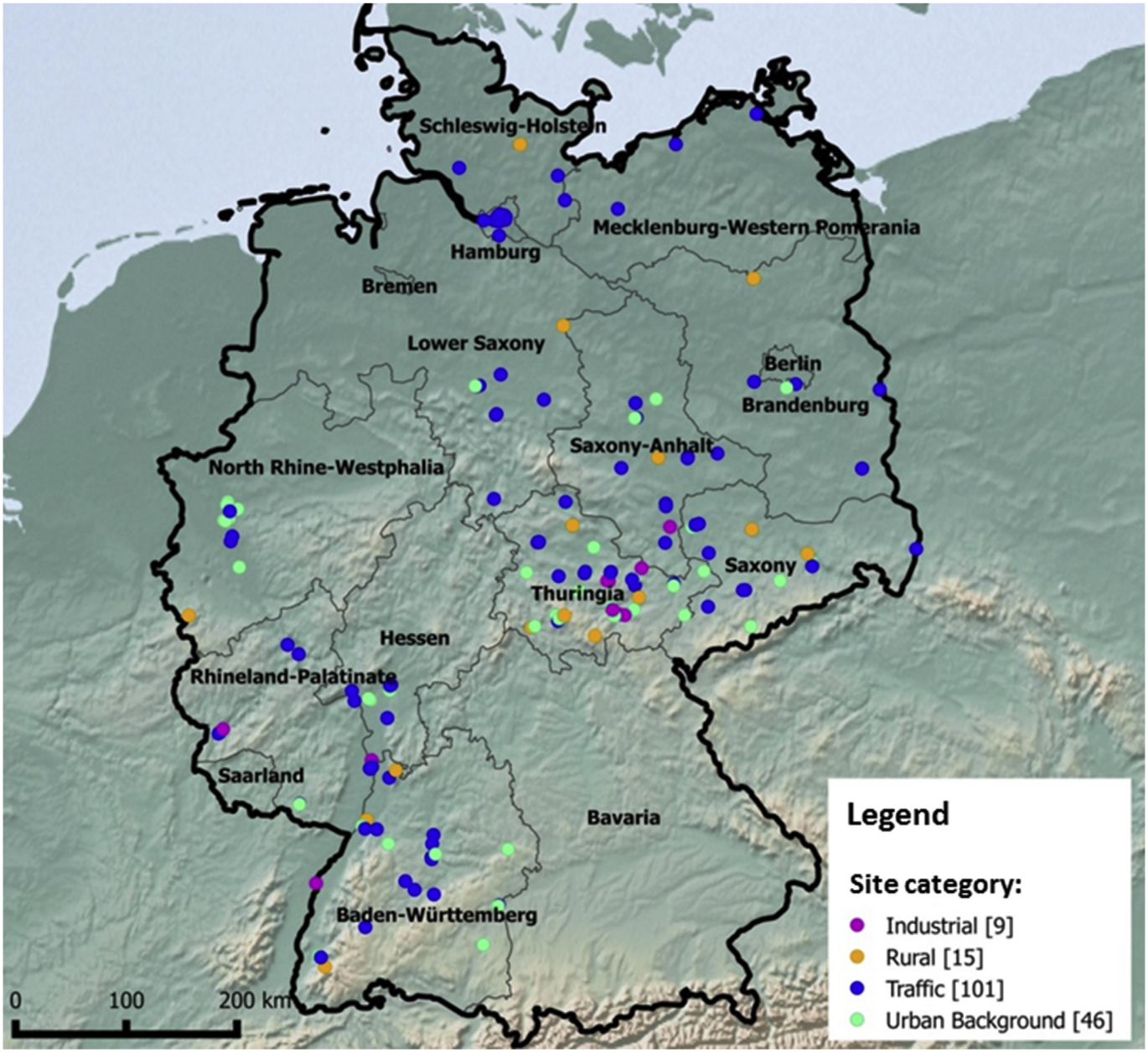

Fig. 1. Map of BC monitoring stations in Germany represented in this data set. The number of stations in each category is listed in the legend. The background map was plotted with QGIS version2.18.2 using Natural Earth version Cross Blended Hypso with Shaded Relief and Water, large size version 3.2.0.

750 °C to measure EC from the resulting CO_2 by infrared absorption.

Thirty-four sites followed the guideline VDI 2465, Sheet 1, see Schmid et al. (2001). The method relies on sample extraction with solvents. EC is oxidized to CO_2 in an oxygen atmosphere and quantified by coulometric titration using bariumhydroxide

2.1.2. Optical detection

Stations applying a light absorption method used either an aethalometer or the Multi Angle Absorption Photometer (MAAP) or followed the 'black smoke' method. The aethalometer (Hansen et al., 1984) collects PM on a quartz fiber filter tape and measures the absorption of light at one or multiple wavelengths. To convert the light absorption coefficient (σ_{ap}) signal into an equivalent black carbon (EBC) concentration a mass absorption cross section (MAC, units in $m^2\ g^{-1}$) needs to be applied. None of the stations reported the MAC which can vary substantially over time due to different source contributions and particle transformation in the atmosphere during transport (Petzold et al., 2013; Zanatta et al., 2016). However, the respective stations used the VDI 2465, Sheet 2, method to determine their local MAC value.

'Black smoke' (BS) measurements, commonly denoted as 'reflectometry' by the federal states, followed the national air pollution control regulation (23. Bundesimmissionsschutz Verordnung in Germany) until the early 2000s. The method involved collecting particulate matter on a filter and deriving its reflectance with a standardized reflectometer (ISO 9835:1993). The reflectance was then transformed into 'black smoke' mass concentrations using a standard curve (WHO, 2012). Comparison of the BS method with thermal-optical EC determination showed that while correlation coefficients can be high, the slope can vary considerably (WHO, 2012). BS concentrations vary strongly with the composition of particulate matter and are hence to be interpreted with caution.

The MAAP determines the aerosol light absorption coefficient by the simultaneous measurement of radiation at 637 nm passing through a particle-loaded filter and the back-scattered fraction at two angles

Table 1
Overview of BC detection methods.

Method	Terminology in this work[a]	Matrix	No. of stations[b]
Evolved Carbon			
Detection by coulometry (after VDI 2465, Sheet 1)	EC	PM_{10}	32
		$PM_{2.5}$	2
Detection by infrared spectrophotometry (after VDI 2465, Blatt 2)	EC	PM_{10}	46
		$PM_{2.5}$	3
Detection by infrared spectrophotometry (RP 5400)	EC	PM_{10}	15
EUSAAR 2 protocol	EC	$PM_{2.5}$	4
Optical Absorption			
Light Absorption	EBC	TSP	25
		PM_{10}	10
		PM_1	3
'black smoke' method	black smoke (BS)	TSP	7
		PM_{10}	40

[a] The terminology follows Petzold et al. (2013) except for 'black smoke' which is not covered in this reference. EC = elemental carbon, EBC = equivalent black carbon.

[b] The sum of methods applied at all stations amounts to 186, not including 42 submitted unusable data sets. The actual number of stations with usable data is 171. The larger number of applied methods reflects detection method changes at several stations.

(Petzold and Schönlinner, 2004). With a radiative transfer model the absorption coefficient is determined whereby the reflectance signals provide information on scattering and shadowing effects. The respective stations used the VDI 2465, Sheet 2, method to determine the MAC.

It has not been possible to obtain information about accuracy and precision of the data for each individual station. However, given that each federal state and the UBA followed standardized protocols or applied then state of the art instrumentation, the data are apt to provide information on the temporal evolution of BC concentrations or differences between station types (e.g., traffic vs rural). Section 2.3 elaborates on the data quality checks that were possible to be performed. Also, given the large spread of BC measurement techniques, it is difficult to compare absolute concentrations from this data set across methods. A number of studies exist that have investigated the comparability and found discrepancies of up to a factor of seven (Petzold et al., 2013) even though correlations were usually high (statistical significance level of $P \leq 0.05$). For that reason we do not compare absolute concentration between methods in this work and do not recommend doing it to future users.

2.2. Data collection and harmonization

All station information listed subsequently is provided in the SM Sec2 Table S2, a table showing some of the metadata. A column named 'data origin' indicates the data provider with 'BL' (for federal state) or 'UBA'. Data were accepted in all available formats and populated into a relational database (PostgreSQL 9.4). The minimal amount of metadata required for a station to be considered in this work included: station code, measurement method (e.g., light absorption, coulometry, see Table S1), and matrix (PM_{10}, $PM_{2.5}$, PM_1, TSP). Additional metadata such as federal state, station name, coordinates, altitude, type of area, and type of station were added based on the UBA database (http://www.env-it.de/stationen/public/open.do) if not provided. Cases of inconsistent information or datasets covering less than one year were not considered for this study. 171 stations out of 213 submitted usable data.

Data and metadata were processed by 'extract, transform and load' tools (ETL) such as Talend Open Studio, R and PERL and then uploaded into the relational database. Plausibility checks were used in the harmonization process to check for errors prior to – or as a result of – integration into the database, following the following steps: The station code, timestamp and data provider (Federal States, UBA or GUAN) were used to form a unique ID to identify each data point independently. Further, a time correction was carried out where necessary to ensure all data were local winter time (CET). Since the temporal resolution of the data ranged from half hourly values to measurements every 6 days, daily values were assigned a timestamp of 00:00:00. For stations with lower time resolution missing values were filled with NA values. The original time resolution was retained in the database for each station.

The final harmonized data set contains unique BC concentration time series in $\mu g\ m^{-3}$ for each station, including attributes specifying the measurement method, and the sample matrix among others. Based on the factor of 'data origin', only the data from the provider which submitted highest resolution and best coverage were used from the database in this paper in cases of duplicate submissions by a Federal State and UBA. Data can be downloaded from here: https://doi.org/10.1594/PANGAEA.881173

2.3. Data quality checks

Once the data were uploaded into the database, logical conjunctions between and within uploaded data (with station code, date stamp, and measurement and-methodology information) and metadata (with station code, methodology information, type of area, type of station as well as coordinates and origin (provider)) were checked. Any missing metadata were added. Furthermore, a consistency check for the completeness of metadata was conducted focusing on method and matrix. Then data from each station were plotted as a simple time series grouped by 'data origin' and methodology. Histograms and boxplots for visual inspection of the data, data coverage, extreme values and the general data range were created. Further, for each station concentration minimum, maximum, mean, 25th and 75th percentile, median, as well as the amount of data points per station were calculated. This approach allowed for identifying possible large shifts in the baseline likely linked to changes in instrumentation conditions or type, or changes in the measurement location, or other conditions that might result in inconsistencies in the time series. Stations, where reported BC concentrations were rounded to values without digits were excluded (e.g., a concentration of $4.2\ \mu g\ m^{-3}$ was reported as $4\ \mu g\ m^{-3}$). Cases, where significant differences in the baseline were found, were investigated for changes in instrumentation, and if this was the case, the associated metadata were updated. All outliers were kept in the data set. Data coverage for the 2009 and trend analysis was greater than 90% per year, with the exception of 8 years for a number of sites included in the trend analysis, where data coverage ranged between 44.2 and 88.5%.

2.4. Data analysis methods

All data were extracted from the database and analyzed with RStudio (Version 0.99.489 – © 2009–2015 RStudio, Inc.).

2009 was identified as the year with the greatest data coverage based on any one methodology, i.e. EC determination after VDI 2465, Sheet 2, in PM_{10}. A more in depth analysis was carried out to evaluate intra-annual characteristics of EC concentrations between these sites in 2009 (Section 3.1). The analysis focuses on monthly averages, as well as seasonal and weekly cycles of daily averages. Since there were only two stations classified as 'suburban background', and two as 'suburban traffic', we re-classified these stations to 'urban background' and 'urban traffic', respectively, in order to avoid splitting the 27 sites into too many sub-categories. In the SM Sec3 (Fig. S2) we show that there are no significant difference between the suburban and urban station types.

Data were also evaluated with the goal of identifying the longest uninterrupted time series for the largest amount of sites, independently of their methodology (Section 3.2). 12 stations were identified with at

least daily resolved BC concentrations applying four different methodologies that covered the years 2005–2014. In this case, it was possible to compare results of annual BC concentration trends between different measurement methods because only the relative change is considered as opposed to absolute concentrations. First, the data were tested for their distribution by plotting the concentrations in histograms. Quantile-Quantile plots were used to test data distribution for Gaussian or near-Gaussian behavior and to decide whether a parametric or non-parametric trend analysis was appropriate. In all cases, an autoregressive integrated moving average (ARIMA) model was applied for the trend analysis. The long-term time series were deseasonalized within the process of performing the trend analysis. By applying a deseasonalization patterns in the data influenced by e.g., meteorological parameters or cycles in emissions can be removed. For consistency, the data were averaged to the lowest available resolution (daily values). Trend analysis was based on daily means and fed into the ARIMA model which uses monthly means to calculate a change per year value.

Monthly averaged data from the twelve sites were fitted with an additive linear model:

$$BC = mean + seasonal + trend + N(1,0) \quad (1)$$

Where BC is the BC monthly concentration data for an individual station, the mean is derived as a single value, seasonality was derived assuming a smooth approximation from two sine and two cosine functions that do not change over time, and the trend is fitted with the approximation of a linear change over time. The unexplained portion of the data, N(1,0), was fitted as an ARIMA (1,0,0), or AR(1) process because the analysis of the residuals with both autocorrelation functions and partial autocorrelation functions supported this decision (Box et al., 2015). The known autocorrelation for these monthly data is apparent in visual inspection of the time series and is most likely related to both location or sources and local meteorological conditions, both of which have persistence on a multi-month timescale (Weatherhead et al., 1998). The results were generated for the 12 stations using the same model, allowing the data to be fitted for their individual mean, seasonality and trend components.

For two stations, a change in instrumentation resulted in a noticeable change in the BC levels recorded. This was approximated as an offset which was derived from the data by using an adjustment to the statistical trend model above. For these two stations, the trends were derived using:

$$BC = mean + seasonal + trend + offset + N(1,0) \quad (2)$$

Where the parameters are described as above, and the offset was derived by using a 'dummy variable' of c(0, 0, 0, …0, 1, 1, 1, ….1, 1) as an explanatory variable (Hardy, 1993). The set of zeros were used for the first eighteen months of data, when the original measuring methodology was in place, and the remainder of the data was represented by ones. This method allows a single trend to be derived for the entire time period, with an offset used to approximate the differences in the monthly data before and after instrument change. This method was applied to all trends derived for these two stations including the trends in means and quantile levels. For readers that may want to employ this method, further details, including R code, are given in SM Sec4.

3. Results and discussion

Data from 171 stations cover most German federal states. The highest density of measurements was found in Thuringia with 42 Stations, followed by Baden-Württemberg with 27 stations. The data cover the years from 1994 to 2014, with the greatest number of stations measuring in 2009. The largest amount of data comes from traffic (101), followed by urban background (46), rural (15) and industrial stations (9).

Figure S1 summarizes the data coverage available by station. The total number of BC measurements represented as data points in the database is 6,412,300. Of the 171 stations, the most common measurement methods were the thermal-optical method following the VDI 2465, Sheet 2, (49 stations) and the 'black smoke' method (47 stations), and the most common matrix was PM_{10}. The maximum measured concentration was recorded at a traffic station (DETH043) in 1998 with 90 μg m^{-3} by the 'black smoke' method. The greatest annual mean concentration was 11.3 μg m^{-3} in 1998 at an urban traffic station (DENI008, 'black smoke' method), compared to the lowest annual mean concentration which was observed in 2013 at a rural station (DEUB004, MAAP) with < 0.1 μg m^{-3}.

3.1. Focus 2009: comparing BC concentrations at various station types in Baden-Württemberg

The largest amount of data with the same methodology (VDI 2465, Sheet 2, procedure on PM_{10} filter samples) was identified for 2009 in Baden-Württemberg. EC measured with the same methodology is available for two more stations from different states for 2009. However, these data are excluded from our analysis because of the geographical focus on Baden-Württemberg that guarantees the same sample handling for all stations. The data coverage for the single stations included here was at least 90% (Table 2).

The annual mean (standard deviation) concentrations for urban background, traffic, rural and industrial sites in 2009 are 2.07 (± 1.14) μg m^{-3}, 5.36 (± 2.64) μg m^{-3}, 1.58 (± 1.20) μg m^{-3}, and 2.20 (± 1.33) μg m^{-3}, respectively. Seasonally averaged mean concentrations are provided in Table 3 by site type.

Traffic stations show a relatively flat seasonal cycle, indicating that traffic emissions are roughly constant throughout the year. However, as is shown in Fig. 2, some of the winter months (January) show higher concentrations, which indicates the influence of other sources such as potentially residential wood burning (domestic heating). At all other station types, concentrations tend to be higher in fall and winter. The

Table 2
Data coverage for all sites using the VDI 2465, Sheet 2, procedure to measure EC from PM_{10} in 2009.

Station code	Temporal resolution	Data coverage (%)
DEBW004	every 3 days	98.4
DEBW005	every 3 days	100.0
DEBW013	daily	98.4
DEBW019	every 3 days	97.5
DEBW022	every 3 days	99.2
DEBW029	every 3 days	98.4
DEBW033	every 3 days	97.5
DEBW046	daily	94.8
DEBW080	every 2 days	100.0
DEBW081	every 3 days	98.4
DEBW084	every 3 days	100.0
DEBW098	every 2 days	98.4
DEBW099	every 2 days	97.3
DEBW103	daily	92.3
DEBW116	every 3 days	100.0
DEBW118	daily	99.5
DEBW121	every 3 days	100.8[a]
DEBW122	every 2 days	99.5
DEBW125	every 3 days	100.8*
DEBW135	every 3 days	100.0
DEBW137	daily	98.1
DEBW147	every 3 days	100.0
DEBW151	every 3 days	99.2
DEBW153	every 3 days	100.0
DENW038	every 2 days	98.4
DEST002	every 2 days	91.3
DEST092	every 3 days	98.4

[a] In the two cases where data exceed 100% data covered one extra day in January. The base to derive the data coverage was calculated as 'every 3 days' in one year, but the actual number of measurement days was every three days plus one.

Table 3
Overview of seasonal 2009 data mean values and standard deviations based on daily data in Baden-Württemberg derived from applying the VDI 2465, Sheet 2, procedure on PM_{10}. Seasons are indicated by three letters: 'MAM' means March, April, May, for example.

	n	Mean (MAM)	Std (MAM)	Mean (JJA)	Std (JJA)	Mean (SON)	Std (SON)	Mean (JFD)[a]	Std (JFD)[a]
Industrial	2	1.98	0.87	1.68	0.50	2.16	1.25	2.99	1.90
Rural	2	1.42	0.95	1.20	0.49	1.49	0.89	2.19	1.80
Traffic	13	5.01	2.30	4.93	2.36	5.93	3.04	5.55	2.68
Urban Background	7	1.87	0.86	1.62	0.55	2.19	1.14	2.60	1.52

[a] Includes data from Jan, Feb and Dec of 2009

elevated concentrations during the cold season are likely related to domestic heating (Fuller et al., 2014; Genberg et al., 2013). Higher BC concentrations measured in January compared to those of the remaining winter months, suggest that besides general differences in emissions between winter and summer, the meteorological conditions might have influenced BC concentrations in January in particular, which will be discussed further below. Industrial sites also show higher concentrations in fall and winter; note, however, that there are only two stations in this category. The parallel in the elevated concentrations at the industrial sites to those of the other site types seems to suggest that domestic heating emissions also contribute to BC concentrations measured at these industrial sites, and that it is not linked to changes in industrial emissions. A flatter seasonal cycle would be expected if industrial emissions dominated BC concentrations at these stations, because the specific industrial activities at the two sites (a paper factory, and an industrial park including various types of businesses) are not expected to have a seasonal cycles.

The interquartile range (IQR) of the monthly statistics at traffic stations is relatively large all year around especially in comparison to other station types. To a certain degree this larger variability is due to the higher amount of available data points (13 traffic stations versus e.g., 2 stations for rural or industrial station types). However, some of the variation likely stems from the rapidly changing conditions in terms of emissions sources (e.g., number of cars, speed, etc.) in highly trafficked areas.

In 2009 two months, January and April, stand out with higher concentrations compared to their seasonal averages (Fig. 2). Beyond seasonally-dependent variations in emissions, there are other aspects that could be responsible for the elevated concentrations in these months: meteorology (including boundary layer height, and particularly low temperatures that induce increased heating), and/or forest fires. January was characterized by very cold and dry weather conditions (DWD, 2010). This supports the likelihood of increased emissions from heating due to cold weather conditions. In addition, ERA-Interim reanalysis data of the planetary boundary layer (PBL) height (http://apps.ecmwf.int/datasets/data/interim-full-daily), which are assembled using a combination of model results and observations, suggest that the median PBL was noticeably lower in January and April than the neighboring months in 2009. Comparing the median values for January and April of 2009 to the long term values of a 30 year period (1984–2014) also show that these were distinctly lower than typical (SM Sec5, Fig. S15). This indicates that a combination of a shallower boundary layer and thus a smaller mixing volume, as well as potentially increased emissions could have led to the observed increase in concentrations.

Also, the largest monthly number of fires in Germany in 2009 were recorded in April with a total of 286 ignitions, followed by August with 185 and May with 136 ignitions (JRC, 2010). The total burned area in

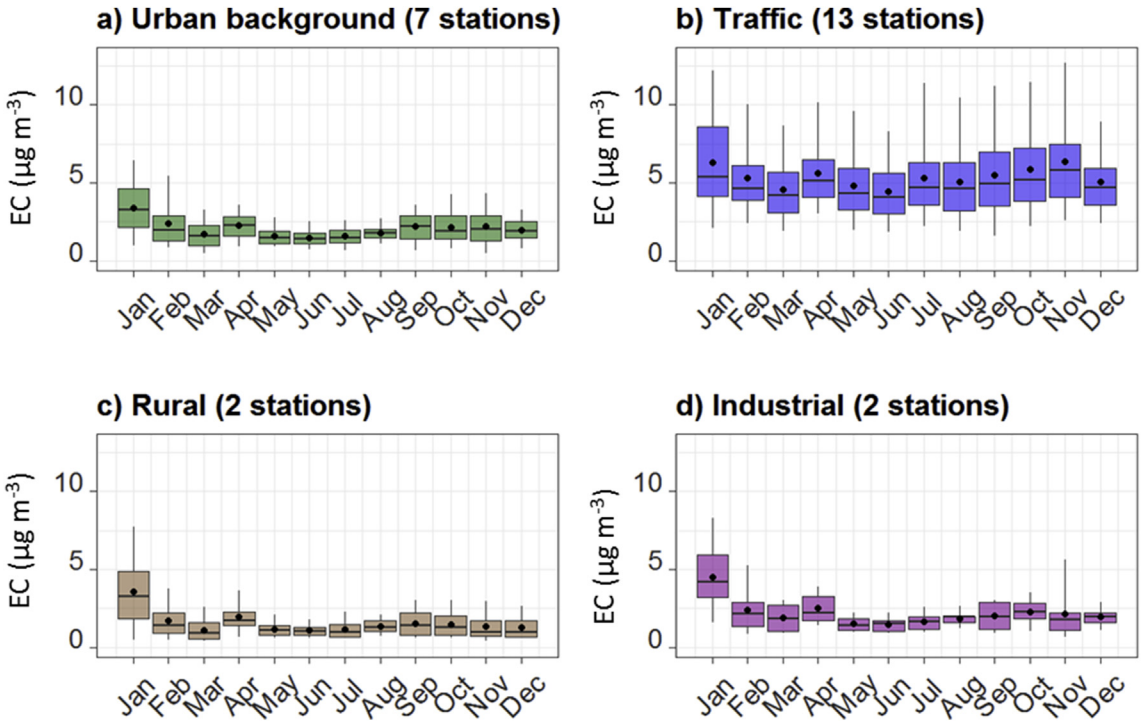

Fig. 2. Monthly concentration boxplot for all sites using the VDI 2465, Sheet 2, procedure on PM_{10} for 2009 in Baden-Württemberg grouped by site category (A – urban background [n = 7], B – traffic [n = 13], C – rural [n = 2], D industrial [n = 2]). The boxes indicate the 25th and 75th percentiles; the horizontal line in the box indicates the median, the dot the mean value, and the vertical lines the 5th and 95th percentiles.

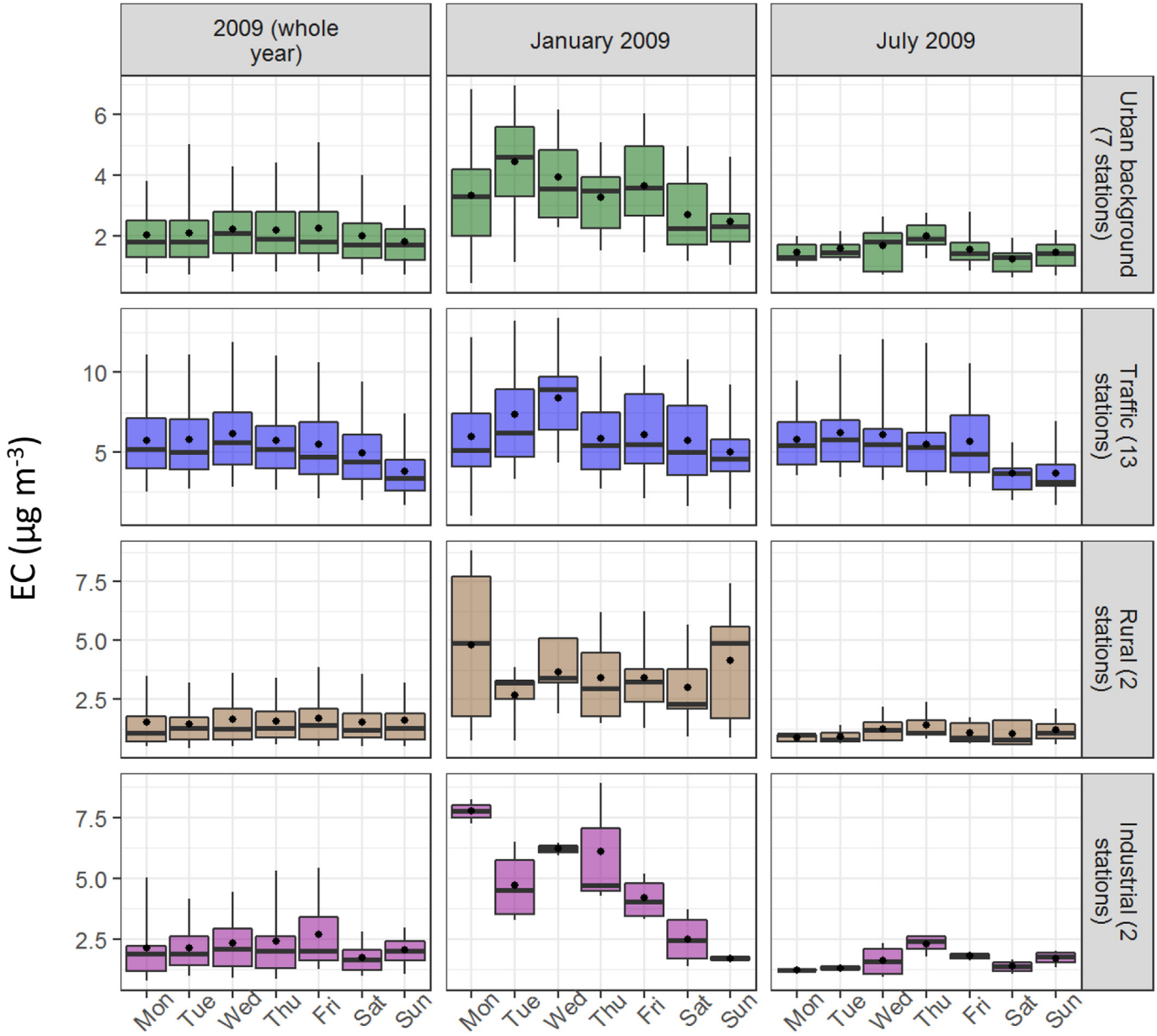

Fig. 3. Weekly cycle for all sites using the VDI 2465, Sheet 2, procedure on PM_{10} for 2009 in Baden-Württemberg grouped by site category for the whole year of 2009 as well as January and July. The boxes indicate the 25th and 75th percentiles; the horizontal line in the box indicates the median, the dot the mean value, and the vertical lines the 5th and 95th percentiles.

Baden-Württemberg during the year 2009 was 8.4 ha with 31 fires, which is more than in the northerly bordering federal states Hessen and Rhineland-Palatinate with 2.4 ha burned area (28 fires) and 6.8 ha burned area (25 fires), respectively. However those burned areas are relative small compared to the eastern neighboring federal state Bavaria with 505.8 ha burned with 116 fires, which might also impact measurements in Baden-Württemberg. The data associated with the wildfires however are not sufficient for a more in depth assessment, so no conclusion can be drawn as to the amount of influence this may have had.

For broader context, in comparison to other European cities, Beekmann et al. (2015) reported concentrations of urban background EBC (MAAP and aethalometer) in Paris of 1.8 µg m^{-3} (from September 2009 to September 2010) and about 2 µg m^{-3} in London (January to December 2009). A further study reported urban background average EBC concentrations (standard deviation) for 2009 for Barcelona, Spain, and Lugano, Switzerland, of 1.7 (± 0.6) µg m^{-3} and 1.8 (± 0.9) µg m^{-3}, respectively (Reche et al., 2011). The EC concentration for the urban background stations in Baden-Württemberg was 2.1 µg m^{-3} (January to December 2009). Note, however, that an evolved carbon method was applied. Mean (standard deviation) roadside EBC concentrations from a site in Bern (MAAP), Switzerland, and the Marylebone Road site in London (aethalometer), England, were reported to be 3.5 (± 1.3) µg m^{-3} and 7.8 (± 2.7) µg m^{-3} for 2009, respectively (Reche et al., 2011). The annual mean of traffic sites in this study falls in between with 5.36 (± 2.64) µg m^{-3} for 2009.

The left column in Fig. 3 shows the weekly cycle of BC concentrations for each station type in 2009. Generally, traffic site BC concentrations are a factor two or more higher than at all other station types The difference between weekday and weekend at the traffic sites is by far the most pronounced with only small differences at the urban background or industrial sites. Similar weekday concentrations were found for urban background, industrial, and rural sites. Lower concentrations on weekends compared to weekdays can be observed at

most site types, with the exception of rural sites. The fact that a weekend-effect is visible at the non-traffic stations suggests that traffic emissions are an important source of BC throughout.

To compare differences in the seasonality, the weekly cycle for January and July are shown in the middle and right column in Fig. 3. The weekly cycle with lower concentrations at the weekend is much less clear in January, whereas the weekly cycle for July shows a distinct pattern with higher concentrations during the weekdays at traffic sites. Overall, the weekly cycles for the remaining months (not shown) are more similar to July. Industrial, rural and urban background concentrations are much higher in January than in July. The lack of a clear weekly cycle in January, combined with the higher concentrations, supports the conclusion of the strong influence of a non-traffic source, such as domestic heating. These results are in agreement with previous work in Europe by e.g., Reche et al. (2011) where much higher weekday concentrations at traffic sites in Bern, Switzerland, and London, England, and far smaller, in some cases negligible weekday-weekend differences at urban background sites were found. Zotter et al. (2017) as well observed higher concentrations on weekdays at traffic sites in Zurich, Switzerland.

3.2. Comparison of BC trends from 2005 to 2014

Twelve stations were identified with a 10-year time series covering the period from 2005 through 2014. Those stations applied four different measurement methods on various matrices (optical absorption measured by a MAAP or an aethalometer, TSP and PM_{10}; black smoke on TSP and PM_{10}; evolved carbon measured by VDI 2465, Sheet 1, PM_{10}), see Table 4 and Table S2. While absolute BC concentrations obtained with different methodologies (EC, EBC and BS) are not directly comparable, the relative change can be compared. Trends in the monthly data were derived for each of the twelve stations using an ARIMA model that accounted for seasonality and assumed a linear trend (section 2.4). In addition to trends in the mean concentrations per station type trends for the 5th and 95th percentiles (indicators for changes in peak and background concentrations) for each individual station were also calculated (Fig. 4).

Within the ten years there were no changes to the methodology at the chosen sites, with the exception of two stations in Rhineland-Palatinate (RP041, RP042). At these two stations, a change in methodology occurred (from 'black smoke' measurements to EBC determination with a MAAP) in July 2006. To understand the importance of the consistency in measurement methodology an analysis was done to compare the trends neglecting the methodology change, as well as a test limiting the data to after the methodology change. The trend results discussed in the following do not include the two sites where a change in measurement methodology took place. Those two sites are addressed specifically later. Numbers in square brackets indicate the 95% confidence interval.

Trends from 2005 to 2014 show a decrease in BC concentrations for traffic stations ranging from -0.31 [-0.25; -0.37] μg m^{-3} y^{-1} to -0.15 [-0.11; -0.19] μg m^{-3} y^{-1} (six stations), for urban background between -0.07 [-0.05; -0.10] μg m^{-3} y^{-1} and -0.02 [0.00; -0.05] μg m^{-3} y^{-1} (three stations) and at the one rural station -0.00 [0.01; -0.02] μg m^{-3} y^{-1}. The trends at traffic sites show the greatest decrease in concentrations of BC over time. The uncertainty of the trends at traffic sites is larger than at the other site types, as indicated by the confidence intervals, because of the high variability observed at traffic sites. The trend values at urban background stations are generally smaller than the trends at traffic sites, but overall concentrations were also lower (compare Fig. 4). The trends in the 5th percentile at traffic stations ranged from -0.17 [-0.12; -0.21] μg m^{-3} y^{-1} to -0.03 [-0.01; -0.06] μg m^{-3} y^{-1}, at urban background stations from -0.03 [-0.02; -0.04] μg m^{-3} y^{-1} to -0.02 [-0.01; -0.03] μg m^{-3} y^{-1}, and was -0.0084 [-0.0048; -0.011] μg m^{-3} y^{-1} at the one rural station. These trends indicate that the background concentrations in BC are decreasing less strongly than the mean concentrations. On the other hand the trend of the 95th percentile at traffic stations range from -0.45 [-0.33; -0.57] μg m^{-3} y^{-1} to -0.20 [-0.08; -0.32 μg m^{-3} y^{-1}, at urban background stations from -0.12 [-0.06; -0.17] μg m^{-3} y^{-1} to -0.03 [0.04; -0.11] μg m^{-3} y^{-1} and the rural station has a trend of 0.01 μg m^{-3} y^{-1} [0.04; -0.02]. There is a much more evident decrease in the trend of the 95th percentile of the traffic stations than the trend in the mean levels. This indicates a stronger decrease in the peak concentrations than in the mean. Together, the trends in the mean, 5th percentile and 95th percentile levels show that the overall decrease observed is occurring for both background and local sources. The extreme high values are changing the most and thus strongly influencing the trends in the monthly and annual mean values.

Looking at the stations where a change in methodology took place, we find that the trend of the Rhineland-Palatinate traffic station (RP041), considering the change in methodology as described by Eq. (2), from 2005 to 2014 is -0.20 [-0.16; -0.24] μg m^{-3} yr^{-1} with an offset (standard error) of 1.44 (0.16) μg m^{-3}. This trend is stronger than determined for the whole 10 year period, based on Eq. 1, -0.09 [-0.03;-0.14] μg m^{-3} y^{-1} neglecting the change in methodology (Fig. 4). A similar result can be seen when comparing the Rhineland-Palatinate urban background station (RP042) mean trend by Eq. (2) (-0.10 μg m^{-3} [-0.07;-0.13] with an offset of 0.61 (0.13)) versus Eq. (1) which neglects the methodology change (-0.06 μg m^{-3} [-0.02; -0.09]). The same is true for the 5th and 95th percentiles trends at both sites. These differences demonstrate that it is crucial to account for changes that may have affected a (step) change in the measurements, such as measurement methodology or site re-location, as these can have a substantial effect on the trend.

A review and comparison of emission inventories showed that for Western Europe (which includes Germany) emissions of BC have been reported to be slightly decreasing since ca. 2000, with some stronger decreases being shown after 2005 (Granier et al., 2011). Other sources report that emissions of BC have declined by about one-third in the past two decades in Europe and North America, with up to 70% of the BC emissions in some European countries originating from diesel vehicles (Amann et al., 2013). National estimates for Germany from the German Environment Agency report a 60% reduction of total BC emissions in 2015 relative to 2000 (UBA, 2018a). In the context of emissions, estimates for BC are still associated with greater uncertainties relative to estimates for NO_x and SO_2, because of poor knowledge of emission factors and omission of some sources, such as flaring, in some regions (Amann et al., 2013). Another study by Wang et al. (2014) showed that emissions of BC were estimated to be relatively flat from 1990 to 2010 in the residential sector, while the authors show a minor increase in the industrial sector, and a substantial decrease in emissions from motor vehicles in developed countries. These reported decreases in emissions are in line with the trend results presented in this work.

The decreasing trends in BC are likely owing largely to mitigation measures in the traffic sector, as reflected in the emissions estimates. This is supported by ambient measurements. For example, a study showed that the introduction of a low emission zones (LEZ) in 2011 in Leipzig led to reductions of EBC concentrations between 18 and 36% (Rasch et al., 2013). The results were however obtained at other stations than the two traffic stations SN025 and SN077 included here. In Berlin, traffic-related BC concentrations were reduced by 52% along major roads in Berlin from 2007 to 2010 (Cyrys et al., 2014). However, no data from Berlin was made available for this study. The stations TH020 (urban background) and TH043 (traffic) from this study are also located in a LEZ that was introduced in 2012 in Erfurt.

Furthermore, on the national level, while reported emissions do not explicitly include BC, the reported PM_{10} and $PM_{2.5}$ emissions for road transport in Germany decreased by 44% and 55%, respectively, between 2000 and 2014 (UBA, 2018b). These reductions were much larger than those reported for PM_{10} and $PM_{2.5}$ for industry, which were 22% and 35%, respectively, for the same time period, with an increase

Table 4
Trends of BC concentrations for 12 stations covering the time period from 2005 to 2014. Full years (e.g., 2005) under the header 'Period' means that measurements were conducted between 1 January and 31 December. For trend plots, see Figures S3-S14.

Station[a]	mean annual trend ($\mu g\ m^{-3}\ year^{-1}$)	5th and 95th percentile confidence intervals ($\mu g\ m^{-3}\ year^{-1}$)		p-value	method	Period	Original time resolution	Data coverage range
RP041 – Traffic[b]	−0.20	−0.16	−0.24	< 0.00001	'Black Smoke' method, TSP	2005–03.07.2006	half-hourly	99.0–99.7
					Optical Absorption: use of a MAAP, TSP	03.07.2006–2014	hourly	98.1–100.0
RP042 - Urban Background[b]	−0.10	−0.07	−0.13	< 0.00001	'Black Smoke' method, TSP	2005–27.06.2006	hourly	44.2–94.8
					Optical Absorption: use of a MAAP, TSP	27.06.2006–2014	half-hourly	99.5–100
SN020 - Traffic	−0.17	−0.11	−0.24	< 0.00001	VDI 2465, Sheet 1, PM_{10}	2005–2014	every 6 days	96.2–100
SN025 - Traffic	−0.29	−0.23	−0.35	< 0.00001	VDI 2465, Sheet 1, PM_{10}	2005–2014	every 6 days	83.6–100
SN077 - Traffic	−0.22	−0.15	−0.29	< 0.00001	VDI 2465, Sheet 1, PM_{10}	2005–2014	every 6 days	75.4–100
SN083 - Traffic	−0.31	−0.25	−0.37	< 0.00001	VDI 2465, Sheet 1, PM_{10}	2005–2014	every 6 days	96.7–103.3[c]
SN084 - Traffic	−0.19	−0.14	−0.25	< 0.00001	VDI 2465, Sheet 1, PM_{10}	2005–2014	every 6 days	93.4–100
TH011 - Urban Background	−0.04	−0.01	−0.06	0.0016	'Black Smoke' method, PM_{10}	2005, 2006, 2008–2010	half-hourly	97.9–99.3
					'Black Smoke' method, PM_{10}	2007, 2011–2014	hourly	94.0–98.24
TH020 - Urban Background	−0.07	−0.05	−0.09	< 0.00001	'Black Smoke' method, PM_{10}	2005, 2006, 2008–2010	half-hourly	98.5–99.6
					'Black Smoke' method, PM_{10}	2007, 2011–2014	hourly	96.9–98.7
TH027 - Rural	0.00	0.01	−0.02	0.46	'Black Smoke' method, PM_{10}	2005, 2006, 2008–2010	half-hourly	97.2–99.3
					'Black Smoke' method, PM_{10}	2007, 2011–2014	hourly	95.5–97.9
TH036 - Urban Background	−0.02	0.01	−0.05	0.12	'Black Smoke' method, PM_{10}	2005, 2006, 2008–2010	half-hourly	97.7–99.4
					'Black Smoke' method, PM_{10}	2007, 2011–2014	hourly	96.4–98.8
TH043 - Traffic	−0.15	−0.11	−0.19	< 0.00001	'Black Smoke' method, PM_{10}	2005, 2006, 2008–2010	half-hourly	97.8–99.1
					'Black Smoke' method, PM_{10}	2007, 2011–2014	hourly	92.8–98.8

[a] The first two letters of the station code abbreviation indicate the federal state in which these monitoring stations are located. (RP = Rhineland-Palatinate; SN = Saxony; TH = Thuringia).
[b] Indicates that the trend values include an offset at the point of methodology change in early 2006; 1.44 for RP041 and 0.61 for RP042, as discussed in the text below.
[c] Data coverage exceeds 100% due to including two extra days in January.

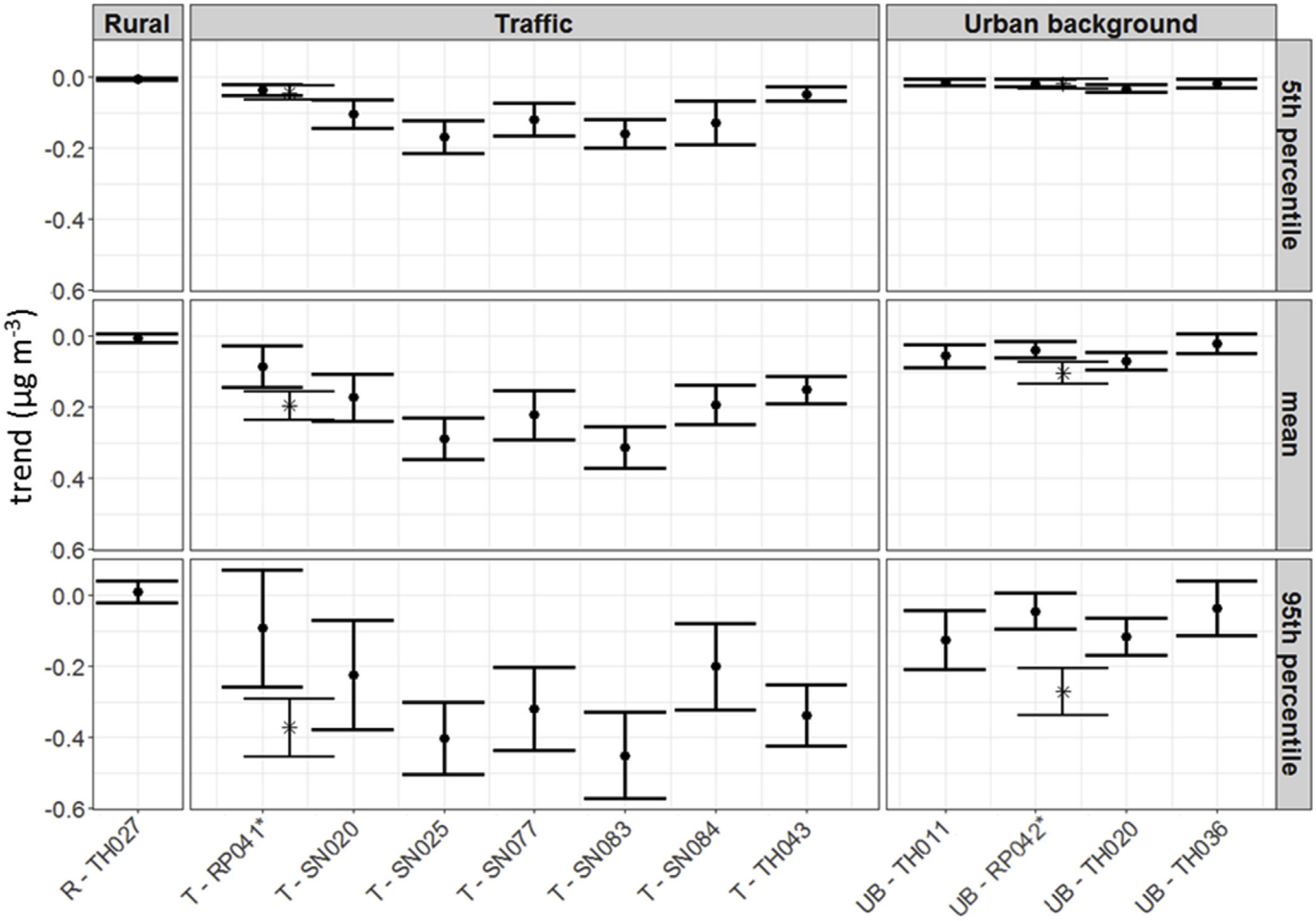

Fig. 4. Top panels show the 5th percentile trend, middle panels the mean trends and the bottom panels the 95th percentile trend of 12 stations with data coverage from 2005 to 2014. The point markers represent the trends with their confidence intervalls in the time period 2005 to 2014 (based on Eq. (1)), and the star symbol (*) with its confidence intervals the trends calculated with Eq. (2). Station codes marked with a star symbol are stations with a change in methodology after the first one and a half years. The station category is displayed over each of the three columns.

in emissions between 2009 and 2011 and no reduction since then (see also SM Sec6). In addition to traffic restriction measures, end of pipe technology, such as diesel particulate filters has also been increasingly implemented, and has been shown to be effective at reducing not only PM, but also BC emissions (Louis et al., 2016; Robinson et al., 2015). Since 2010, the contribution of Euro 5 passenger cars in Germany has increased from 5 to 27%. The contribution of Euro 6 cars was 1.5% in 2014 but is on the rise, while all other categories are decreasing, with Euro 4 accounting for 46% in 2014 (Knörr et al., 2016). The growing implementation of such measures is reflected in the trends shown here, specifically with the greatest decreases observed for traffic stations, as these measures have been most focused on reducing emissions from vehicles.

Data from this study support the reductions in BC owing to traffic measures, as traffic stations with higher mean BC concentrations show stronger decreasing trends, as shown in Fig. 5. Stations with lower mean values for the year 2005 showed a lower decrease in the BC trends for 2005–2014.

4. Conclusion

This work presents a large dataset of BC observations in Germany created from measurements conducted by the German Federal States and the Federal Environment Agency. More than six million data points were assembled and harmonized, introducing a consistent description of the different measurement methodologies as well as of the different types of measurement stations represented by the data. Though assembled in a consistent way, the dataset is characterized by differences in measurement methodologies, measurement time periods and time resolutions. An analysis of this dataset thus necessarily requires a careful consideration of these differences.

We focused our analysis on 2009, the year with the largest coverage of data obtained with one single methodology, as well as on the relative changes in long-term trends from 2005 to 2014. The analysis for 2009, conducted solely on the basis of data from one federal state, shows that traffic stations are characterized by a smaller seasonal cycle than other station types (urban background, rural, industrial). This suggests that traffic stations are least influenced by sources other than traffic, such as residential combustion, as residential combustion emissions are usually highest in the winter months. The analysis also shows that observed BC concentrations in 2009 were likely influenced by episodes of particular meteorological conditions and emissions in January and April. January of 2009 was characterized by very low temperatures and a lower than usual average boundary layer height, suggesting that the meteorological situation probably led to both increased emissions and reduced mixing of BC concentrations in the atmosphere. In April, the number of forest fire events was higher than in the other spring months, which may have caused higher BC concentrations in this particular month.

Relative changes in long-term trends can be compared even though differing measurement methodologies were used at stations where a

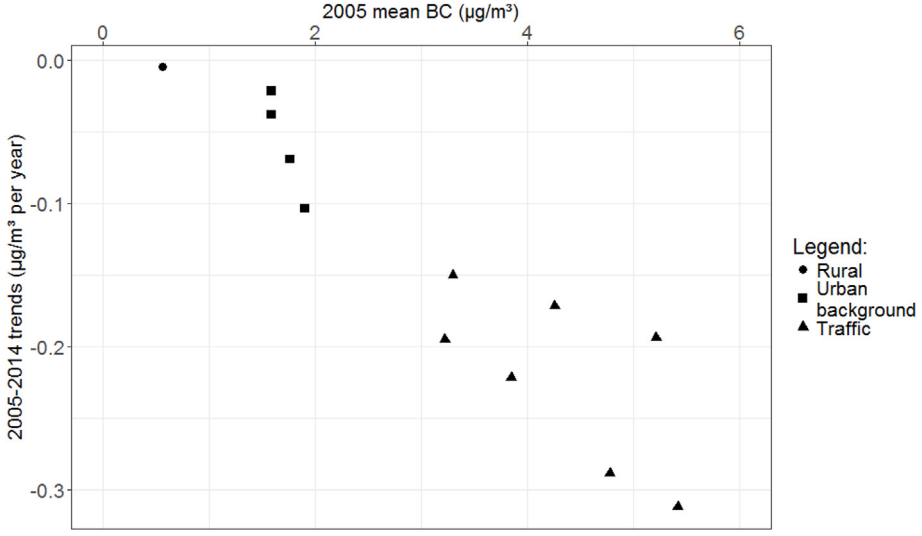

Fig. 5. Trends calculated for 12 stations for 2005–2014 plotted against their 2005 annual mean values. The circle, triangle and squares represent the categories rural, traffic and urban background, respectively.

long time series of BC observations is available. To this end, an auto-regressive integrated moving average (ARIMA) model is used. Between 2005 and 2014, the trend in observed BC concentrations is negative at nearly all locations and in all conditions. Stronger reductions were observed for traffic stations which generally exhibit higher BC concentration levels compared to rural and urban stations (Fig. 5). This is consistent with reported changes in BC emissions, which can largely be attributed to a reduction in BC emissions from traffic. Also, the downward trend in the 95th percentile concentrations is much higher than in the mean on 5th percentile, indicating that situations with high concentrations were mitigated more successfully.

The flexibility offered by the ARIMA function allows for a trend analysis that can account for not only the auto-correlation and seasonality in the data, but also a possible step change in the measurement data, as we demonstrated with two stations. Accounting for such characteristics in the data is crucial for reliable data analysis and interpretation. Future efforts to evaluate BC concentrations on a national or European level would be particularly valuable when taking this into account. In addition harmonization of monitoring methods for BC measurement would provide consistency to better compare concentrations across monitoring sites throughout Germany and/or Europe. We reiterate that the differences in measurement methods and the lack of intercomparisons impose constraints on the interpretation of this particular dataset. Furthermore, while this dataset already covers 12 out of 16 German Federal States, a more complete spatial coverage of future observations would additionally enhance the quality and applicability of such a dataset. Following the recommendations of the Directive (EU) 2016/2284, BC monitoring might become more important in the European policy arena in the near future.

In summary, air quality legislation to reduce particulate matter emissions and indirectly BC appear to be working in Germany based on this analysis. Hence policy in the last two decades has most likely contributed to mitigating human health and climate impacts of BC. Despite the challenge of a breadth in measurement methodologies used and incomplete spatial coverage, this work presents the first comprehensive compilation of BC observations in Germany. With the consent of the providers of the original data, the dataset has been made available online for further analysis (https://doi.org/10.1594/PANGAEA.881173). It can build the basis for further policy analysis of BC in Germany and Europe, as well as support air quality modelling activities, ultimately contributing to reducing the adverse effects of BC on health and climate.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2018.04.039.

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