

Accepted Manuscript

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A. Šoštarić, S. Stanišić Stojić, G. Vuković, Z. Mijić, A. Stojić, I. Gržetić



PII: S1352-2310(17)30558-7

DOI: [10.1016/j.atmosenv.2017.08.045](https://doi.org/10.1016/j.atmosenv.2017.08.045)

Reference: AEA 15515

To appear in: *Atmospheric Environment*

Received Date: 14 March 2017

Revised Date: 15 August 2017

Accepted Date: 18 August 2017

Please cite this article as: Šoštarić, A., Stanišić Stojić, S., Vuković, G., Mijić, Z., Stojić, A., Gržetić, I., Rainwater capacities for BTEX scavenging from ambient air, *Atmospheric Environment* (2017), doi: 10.1016/j.atmosenv.2017.08.045.

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1 Rainwater capacities for BTEX scavenging from ambient air

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3 A. Šoštarić^{1*}, S. Stanišić Stojić², G. Vuković³, Z. Mijić³, A. Stojić³ and I. Gržetić⁴

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5 *1 Institute of Public Health Belgrade, Bulevar Despota Stefana 54a, 11000 Belgrade, Serbia*6 *2 Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia*7 *3 Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia*8 *4 Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia*9 *Corresponding author: andrej.sostaric@zdravlje.org.rs; Phone: +381 64 13 94 185; Fax: +381 11 32 35 080;
10 Bulevar Despota Stefana 54a, 11000 Belgrade, Serbia.

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37 Abstract

38 The contribution of atmospheric precipitation to volatile organic compound (VOC) removal from the
39 atmosphere remains a matter of scientific debate. The aim of this study was to examine the potential
40 of rainwater for benzene, toluene, ethylbenzene and xylene (BTEX) scavenging from ambient air. To
41 that end, air and rainwater samples were collected simultaneously during several rain events that
42 occurred over two distinct time periods in the summer and autumn of 2015. BTEX concentrations in
43 the gaseous and aqueous phases were determined using proton transfer reaction mass
44 spectrometry. The results reveal that the registered amounts of BTEX in rainwater samples were
45 higher than those predicted by Henry's law. Additional analysis, including physico-chemical
46 characterization and source apportionment, was performed and a possible mechanism underlying
47 the BTEX adsorption to the aqueous phase was considered and discussed herein. Finally, regression
48 multivariate methods (MVA) were successfully applied (with relative errors from 20%) to examine
49 the functional dependency of BTEX enrichment factor on gaseous concentrations, physico-chemical
50 properties of rainwater and meteorological parameters.

51 **Keywords:** BTEX, wet deposition, rain, PTR-MS, multivariate methods, Unmix.

52

53 1. Introduction

54 Benzene, toluene, ethylbenzene and the three xylene isomers, frequently referred to as BTEX,
55 constitute a group of aromatic hydrocarbon species of particular environmental interest, commonly
56 associated with the petrochemical industry and incomplete fossil fuel oxidation (Stojić et al. 2015a;
57 Stojić et al., 2015b). Besides being important photochemical precursors for tropospheric ozone and
58 secondary organic aerosols (SOA) (Chatani et al., 2015), these hazardous air pollutants cause chronic
59 toxicity even in small concentrations (Stojić et al., 2015c). According to the IARC data, benzene is
60 recognized as a significant public health threat and classified as group I carcinogen, ethylbenzene is a
61 suspected IIB carcinogen, while both toluene and the xylene isomers belong to group III neurotoxins
62 (WHO, 1986, 1993, 1997; Durmusoglu et al., 2010).

63 In the atmosphere, volatile species are distributed between the gaseous, aqueous and particle phase
64 (Matsumoto et al., 2010). In their biogeochemical cycle, it is believed that the role of atmospheric
65 water is quite prominent, but this issue is still subject to continuous scientific debate (McNeill et al.,
66 2012). The concentrations of BTEX in various forms of atmospheric water depend on various factors
67 including their ambient gas mixing ratios, water solubility and Henry's law constant, frequency and
68 intensity of precipitation events (Balla et al., 2014), gas-water surface interactions (Raja and Valsaraj,
69 2004), content and concentrations of other species in atmospheric water (Okochi et al., 2005; Sato et
70 al., 2006; Allou et al., 2011), as well as the origin of air masses (Mullaugh et al., 2015). Previous
71 studies, which primarily focused on wet deposition of BTEX and their partition between gaseous and
72 aqueous phases, were relatively scarce and provided contradictory conclusions.

73 In the study aimed at investigating the capacity of rainwater for wet scavenging of BTEX, Okochi et al.
74 (2004) reported that the concentrations of species detected in rain samples were higher than those
75 predicted by Henry's law, and concluded that atmospheric precipitation might play significantly
76 greater role in removing BTEX from ambient air than previously thought. Thereby, the observed
77 supersaturation was assumed to be associated with the presence of surface-active agents in rain
78 droplets, whereas the rainfall intensity appeared to be of negligible importance. Accordingly, our
79 previous study confirmed a significant enrichment of BTEX in the aqueous phase in a dynamic
80 equilibrium system designed to resemble the interactions between the gaseous and water phase
81 during rainfall (Šoštarić et al., 2016). Conversely, recent findings of Mullaugh et al. (2015) indicate
82 that BTEX were not efficiently scavenged from the atmosphere by wet deposition processes.
83 Furthermore, the authors concluded that light-mediated reactions with OH· or nitrogen radicals
84 remain the major atmospheric sink for BTEX. Nonetheless, it should be noted that this research was

85 not based on the ambient air measurements, but it mainly relied on the previously published BTEX
86 data from similar locations.

87 In order to better understand the fate of volatile species in atmospheric, terrestrial and aquatic
88 systems, the present study examines the contribution of rainwater to wet scavenging of atmospheric
89 BTEX, as well as the mechanisms related to their air-water distribution transfer.

90

91 **2. Materials and methods**

92 A total of 53 sample pairs of air and rainwater samples were collected simultaneously during several
93 rain events that occurred over two distinct time periods in the summer and autumn season of 2015.
94 The sampling was performed at the Institute of Physics (Belgrade, Serbia; 44°49' N, 20°28' E), located
95 in the vicinity of the Danube river, in the suburban residential area, with a number of local fireboxes
96 active during the heating season.

97 Rainwater sampling was performed using a custom-built precipitation collector with the effective
98 sampling area of 9 m². The steep collecting panels (45°) were designed to reduce rainfall retention
99 time and minimize possible BTEX volatilization. Such large sampling area enabled collecting a vast
100 number of samples per each rain event. The panels were thoroughly rinsed with 18 MΩ ultrapure
101 water (ELGA PURELAB maxima system) prior to each sampling campaign, and the rinsing water was
102 collected and analyzed as a field blank control sample. No target compounds were detected in the
103 field blank control samples. The samples were collected and stored directly into brown glass bottles
104 of 1300 mL. All bottles were washed with detergent, thoroughly rinsed with ultrapure water and
105 dried in an oven for two hours at 105°C to remove any trace of contamination. During the sampling,
106 the bottles were filled to the top to avoid headspace, and the sampling duration and sample
107 temperature were recorded. Since sampling equipment enables collection of large volumes of
108 rainwater within a short period, the last sample in each sampling campaign was collected in the
109 bottle of 2,600 mL and was split into two standard aliquots. The first aliquot was analyzed
110 immediately, whereas the other one was examined after all other samples to determine whether the
111 BTEX levels changed over time. No difference could be observed in the obtained quantity of double
112 samples (Table S1, Supplementary material).

113 BTEX concentrations in both gas and water phases were measured using proton transfer reaction
114 mass spectrometer (Standard PTR-quad-MS, Ionicon Analytik, GmbH, Austria), whose detailed
115 description is given elsewhere (Lindinger et al., 1998). Since PTR-quad-MS is not capable of
116 distinguishing isobaric ions, the signal detected at m/z 107 referred to C₈ aromatic hydrocarbons,
117 ethylbenzene, o-, m-, and p-xylene. Signals detected at m/z 79 and m/z 93 referred to benzene and
118 toluene, respectively (Warneke et al., 2003).

119 The air samples were collected as a side flow from a 1/8-inch teflon tube sampling line through which
120 ambient air was drawn at the flow rate of about 50 L min⁻¹ to ensure short residence. The sample
121 inlet was located 6 m above ground level with a sampling angle of 360°. Drift tube parameters
122 included: pressure, ranging from 2.04 to 2.14 mbar; temperature, 60 °C; voltage, 600 V; E/N
123 parameter, 145 Td providing reaction time of 90 μs. The count rate of H₃O⁺H₂O was 3 to 8% of the
124 9.2·10⁶ counts s⁻¹ count rate of primary H₃O⁺ ions. PTR-MS calibration was performed before and
125 after each sampling campaign using an external standard five-point calibration, ranging from
126 0-26 ppbV, 0-25 ppbV and 0-80 ppbV for B, T and EX, respectively. For this purpose, 2.5 ppmV
127 mixture of BTEX (BTEX in nitrogen, Messer Group GmbH) was diluted with high-purity synthetic air
128 (CH free, Messer Group GmbH) by means of HORIBA ASGU 370-P system.

129 Determination of BTEX concentrations in rainwater was performed immediately after each sampling
130 campaign. A liter of each unfiltered rainwater sample was transferred to the gas washing bottle
131 (GWB) and purged out with synthetic air at a flow rate of 1 L min⁻¹. Rainwater filtration was avoided
132 due to potential adsorption of species on the filter. The GWB output was connected with PTR-MS

133 inlet via T-piece, and further analytical procedure, calibration and data processing were conducted as
 134 described in Šoštarić et al. (2016). In brief, PTR-MS signal obtained during exsufflation was subject to
 135 baseline fitting. The exsufflation time was determined for each sample as the interval required for
 136 equilibrium to be achieved (t_{eq}). The obtained exsufflation time was used for determining the
 137 amounts of target compounds retained in the analyzed rainwater samples. The aqueous
 138 concentrations of analyzed species were calculated by multiplying the obtained amounts by the
 139 conversion factor (3.25; 3.83 and 4.41 for B, T and EX, respectively). The detection limits (DL) in
 140 rainwater were determined using HC free air and calculated as 10 nM, 10 nM and 20 nM for B, T and
 141 EX, respectively. The remaining portion of each rainwater sample was transferred to a 300-mL bottle
 142 and stored at 4°C until further analysis, which included determination of the major inorganic anions
 143 (F^- , Cl^- , SO_4^{2-} , NO_2^- and NO_3^-), dissolved cations (Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}), total organic carbon,
 144 electrical conductivity, UV extinction, turbidity and pH, in accordance with the standard methods (US
 145 EPA 300.1:1993, EN ISO 14911:1998, ISO 8245:1999, EN 27888:1993, SMEWW 19th method 5910 B,
 146 US EPA 180.1:1993, EN ISO 10523:2008, respectively). More details of the methods and equipment
 147 applied for physico-chemical analysis conducted on rainwater samples are presented in
 148 Supplementary material.

149 In order to determine the extent to which Henry's law constant (K_H) describes BTEX distribution
 150 between the gaseous and aqueous phase, distribution coefficients (D_{OBS}) were calculated for each
 151 sample pair and each species, as the ratio of the corresponding experimentally derived rainwater
 152 concentrations in nM (C_R) and ambient gas phase mixing ratios in ppbV (p_g):

$$153 \quad D_{OBS} = C_R / p_g \quad (M \text{ atm}^{-1}) \quad (1)$$

154 Furthermore, the enrichment factors (EF) were calculated as the ratio of D_{OBS} and K_H .

155 Considering the K_H temperature dependence, EF were calculated using temperature corrected $K_H T$
 156 for each rain sample by means of the following equation (Sander, 2015):

$$157 \quad K_H T = K_H(298.15) \exp \left\{ \frac{-\Delta H}{R} \left(\frac{1}{298.15} - \frac{1}{T} \right) \right\} \quad (2)$$

158 where K_H is the Henry's law constant at 298.15 K for pure water, ΔH is the enthalpy change of air-
 159 water transfer, T is the rainwater temperature, and R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).
 160 Furthermore, to assess the representativeness of ground level conditions for the atmospheric
 161 conditions during rainfall, $K_H T$ and EF altitude profiles were calculated using the temperature profiles
 162 obtained from GDAS1 (Global Data Assimilation System, 2015), by replacing the rainwater
 163 temperature value by the temperature at the corresponding altitude.

164 Meteorological parameters during rain events (precipitation (accumulated rainfall, rain current and
 165 peak intensity, and the duration of a rain event), wind speed and direction, pressure, humidity and
 166 temperature) were measured by Vaisala Weather Transmitter WXT530 Series. Cloud information,
 167 including cloud height and type, was obtained from the airport "Nikola Tesla", Belgrade, ICAO code
 168 LYBE, located 8.9 km SSW from the sampling site.

169 The relationships between enrichment factors (EF), physico-chemical characteristics and wind
 170 characteristics (wind speed and direction) were examined using the bivariate polar plot analyses
 171 (Carslaw and Beevers, 2013) implemented in the Openair package (Carslaw and Ropkins, 2012)
 172 within the statistical software environment R (Team, 2012).

173 The neutralization factors (NF) were calculated based on the study of Moreda-Piñeiro et al. (2014),
 174 Tiwari et al. (2016) and references therein in order to examine the potential of the cations to balance
 175 the rainwater acidic components:

$$176 \quad [NF_{Ca^{2+}}] = \frac{[nssCa^{2+}]}{NO_3^- + [nssSO_4^{2-}]} \quad (3)$$

$$177 \quad [NF_{Mg^{2+}}] = \frac{[nssMg^{2+}]}{NO_3^- + [nssSO_4^{2-}]} \quad (4)$$

$$178 \quad [NF_{NH_4^+}] = \frac{[NH_4^+]}{NO_3^- + [nssSO_4^{2-}]} \quad (5)$$

$$179 \quad [NF_{K^+}] = \frac{[nssK^+]}{NO_3^- + [nssSO_4^{2-}]} \quad (6)$$

180 To calculate the non-sea salt fraction of any particular ion (*nss*), we assumed that all Na originated
181 from marine sources, and used it as a referent element. The *nss* contribution is given as:

$$182 \quad [nss - X]_i = [X]_i - [Na^+]_i \left[\frac{[X]}{[Na^+]} \right]_{sea\ salt} \quad (7)$$

183 where $[nss - X]_i$ is the *nss* concentration of the selected ion in the sample *i*, $[X]_i$ is the total
184 concentration of the ion X measured in the rainwater sample *i*, $[Na^+]_i$ is the total concentration of Na^+
185 measured in the rainwater sample, and $\left[\frac{[X]}{[Na^+]} \right]_{seasalt}$ is the reference ratio determined in the
186 seawater.

187 Potential remote source regions that might affect the observed BTEX mixing ratios were identified
188 using HYSPLIT-derived 72-h back trajectories (Draxler and Rolph, 2014). The trajectories were
189 computed for each hour UTC a day before and during each rain event, above the sampling location at
190 the half of the planetary boundary layer height calculated from GDAS1 using Meteoinfo (Wang,
191 2014), as described in Stojić et al. (2016) and Stojić and Stanišić Stojić (2017).

192 Rainwater source apportionment was performed using Unmix (USEPA, 2007). The maximum number
193 of species selected as input variables was chosen using the trial and error with the overall aim of
194 yielding the most physically meaningful results. For concentrations below the DL, a value equal to the
195 half of the DL was used.

196 Guided regularized random forest (GRRF) was applied (Deng and Runger, 2013) for the selection of
197 features that are most relevant for EF. Random forest (RF) consists of a number of decision trees
198 which every node represents a condition on a single variable designed to split the dataset in two
199 parts so that similar response values end up in the same set. Variable importance measures how
200 much each variable decreases the weighted impurity across all trees, a measure based on which the
201 optimal condition is chosen. GRFF uses the importance scores from a preliminary RF to guide the
202 feature selection of regularized random forest (RRF), and has several advantages as follows: it is
203 more robust and computationally efficient than RRF, varSelRF and LASSO logistic regression; it can
204 select compact feature subsets moderating the curse of dimensionality; it avoids the effort to analyze
205 irrelevant or redundant features; and it has competitive accuracy performance. Variable importance
206 presented herein was obtained by calculating the average value of 2000 GRRF runs. The appropriate
207 number of trees was determined to assure out-of-bag error convergence. Method performance was
208 tested by 100 times replicated 10-fold cross validation.

209 To analyze the relationship between EF and features that are considered most relevant for EF
210 prediction, the following 24 regression MVA methods implemented in Weka 3.8 (Hall et al., 2009)
211 were applied: Alternating Model Tree, Conjunctive Rule, Decision Stump, Decision Table, Elastic Net,
212 Gaussian Processes, IBk, IBkLG, Isotonic Regression, K*, Least Median Squared, Linear Regression,
213 Locally Weighted Learning, M5P, M5 Rules, Multilayer Perceptron, Pace Regression, Random Forest,
214 Random Tree, Radial Base Function (RBF) Network, RBF Regressor, REP Tree, Simple Linear
215 Regression and SMOreg Support Vector Machine. A brief description of the methods, including
216 functions (neural network, support vector machine, etc.), clustering techniques, rules and trees, is
217 provided in Supplementary material. Method performance was tested by 10 times replicated 10-fold
218 cross-validation.

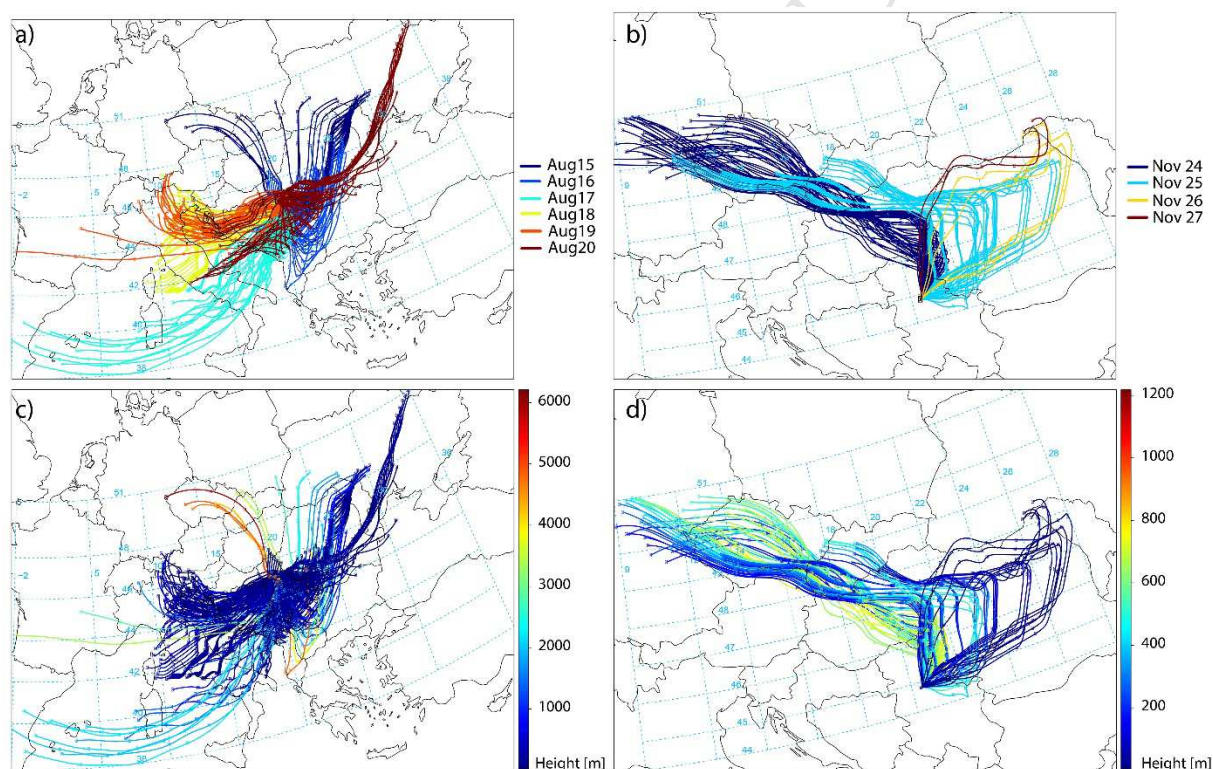
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220 3. Results and discussion

221 Light showers, with occasional thunderstorms, constituted a considerable part of summer rain
 222 events. Scattered and broken clouds in the form of cumulonimbus or towering cumulus were
 223 observed at the height of 400 to 1000 m. In the autumn campaign, the vast majority of rain events
 224 were light and sporadically followed by mist. Scattered clouds were registered at levels below 300 m,
 225 whereas broken clouds were observed from 100 to 900 m.

226 As expected, both aqueous and gaseous BTEX concentrations were higher during the cold part of the
 227 year. Lower BTEX concentrations in summer can be attributed to intense photochemical removal and
 228 washout effects associated with more sunny and rainy days (Lee et al., 2002), whereas higher
 229 concentrations of BTEX in autumn can be associated with individual combustion fireboxes widely
 230 spread in the vicinity of the sampling site. Furthermore, aqueous B concentrations in summer were
 231 below DL.

232 As can be seen in Figure 1, each rain event was associated with air masses coming from different
 233 source regions and heights. During summer rain events, air flows from all directions were followed by
 234 significant variations in physico-chemical properties of rainwater, whereas N and NE air masses in
 235 autumn were associated with a more uniform rainwater composition. Gaseous concentrations of
 236 volatile species, particularly B, were relatively stable during rain events, which can be explained by
 237 the fact that the sampling site was dominated by local BTEX sources.



238
 239 Figure 1. Back trajectories a day before (August 15 and November 24) and during summer (a) and
 240 autumn (b) rain events and corresponding trajectory heights (c, d).

241 3.1 Physico-chemical characteristics of rainwater

242 Basic statistics for all rainwater parameters and BTEX concentrations is given in Table S2,
 243 Supplementary material. The average rainwater pH was 6.01, while the turbidity was below 10 NTU,
 244 indicating that the samples contained moderate amounts of suspended particles from the
 245 atmosphere. As illustrated in Figure S1, conductivity, as well as high concentrations of most ions
 246 (SO_4^{2-} , NO_3^- , Ca^{2+} , Mg^{2+} , K^+ and Na^+) were influenced by the high-speed SW wind (20 to 30 m s^{-1}),
 247 while only NH_4^+ concentrations were increased with the wind of moderate speed (10 m s^{-1}) from NE
 248 direction.

249 The rainwater pH varied from 3.70 to 8.20 with the volume weighted mean of 6.01, which is mainly
 250 due to scavenging of alkaline species (Ca^{2+} and SO_4^{2-}). The average pH value is also close to the 5-
 251 year-mean (6.1) obtained as a part of the regular air quality monitoring in Belgrade. The contribution
 252 of SO_4^{2-} to the rainwater acidity was confirmed by ($\text{Cl}^- + \text{NO}_3^-$) and (SO_4^{2-}) ratio below 1 (Tiwari et al.,
 253 2016). As shown, Ca^{2+} was the dominant neutralization component, followed by NH_4^+ , Mg^{2+} and K^+ ,
 254 with mean of 77%, 14%, 7% and 2.3%, respectively.

255 As shown in Figure S2, significant correlations were observed as follows: > 0.80 ($\text{NO}_3^- - \text{SO}_4^{2-}$, $\text{NH}_4^+ -$
 256 aq. B, $\text{NH}_4^+ - \text{gas. B}$, $\text{NH}_4^+ - \text{EF}_B$); $0.70 - 0.80$ ($\text{F}^- - \text{SO}_4^{2-}$, $\text{F}^- - \text{NO}_3^-$, $\text{F}^- - \text{aq. B}$, $\text{F}^- - \text{gas. B}$, $\text{F}^- - \text{EF}_B$, $\text{K}^+ -$
 257 Na^+); and $0.60 - 0.70$ ($\text{NO}_3^- - \text{Mg}^{2+}$, $\text{SO}_4^{2-} - \text{Mg}^{2+}$, $\text{SO}_4^{2-} - \text{EF}_{\text{EX}}$, $\text{Na}^+ - \text{Mg}^{2+}$). Furthermore, high
 258 correlations were noted between aq. and gas. BTEX concentrations (≥ 0.80), as well as between aq.
 259 EX and aq. B (0.67) and aq. T (0.67), suggesting that these species might share the common source.

260 As can be seen in Tables S3, S4 and S5, four factors were derived using Unmix. With high
 261 contributions of volatile BTEX species (99%, 44.5% and 52.2%) and a relatively high share of UV
 262 extinction (33.3%), the first factor was recognized as organic compounds in the gaseous form. The
 263 second factor, characterized by the highest contribution of TOC (71.6%) and turbidity (79.7%),
 264 represented the solid fraction dissolved in the atmospheric water. Significant shares of K^+ (58.0%),
 265 SO_4^{2-} (42.2%) and NO_3^- (31.3%) were also apportioned to this factor, as a result of fossil fuel burning
 266 and traffic exhaust (Rao et al., 2016; Tiwari et al., 2016). The high shares of crustal-related elements,
 267 Na^+ (61.8%) and Mg^{2+} (61.4%), were apportioned to the third factor (Cao et al., 2008; Sapek, 2014).
 268 Moderate to significant shares ($> 30\%$) of all species except Na^+ , K^+ and B were apportioned to the
 269 fourth factor, being recognized as the aerosol fraction. Apart from gaseous oxides (SO_2 and NO_2),
 270 which react with ozone and OH· radicals in the presence of Ca^{2+} and Mg^{2+} (Seinfeld and Pandis, 2006),
 271 BTEX are susceptible to photo-oxidation that can also lead to SOA formation. BTEX reactions include
 272 oxidation with ozone and OH·, but also with NO_x and SO_2 , which results in multi-functional oxy
 273 products that are further deposited onto the existing aerosol or initiate the formation of SOA by self-
 274 nucleation. BTEX behave differently in the atmosphere due to differences in the methyl chain
 275 substituent and the alkyl chain length. Benzene is considered being extremely stable compared to T
 276 and EX (Słomińska et al., 2014), and it is less susceptible to the heterogeneous reactions and
 277 formation of SOA in the atmosphere.

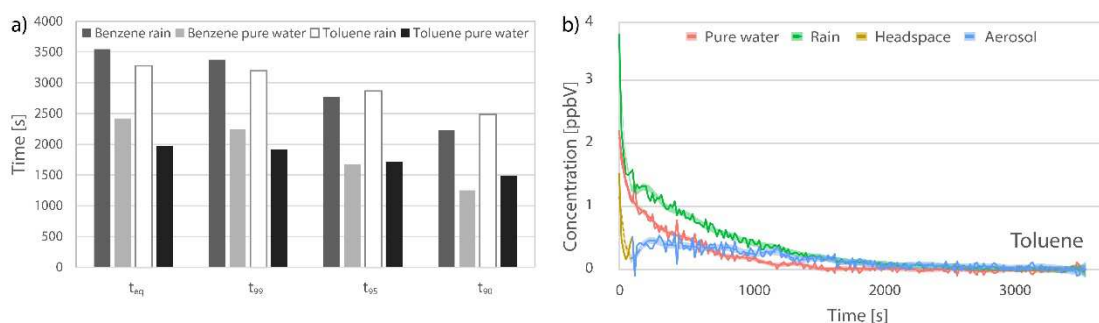
278 The contributions of the gaseous organic- and aerosol-related factors were mostly associated with N
 279 wind of moderate speed ($< 10 \text{ m s}^{-1}$), which clearly reflects their local origin, while the solid- and
 280 crustal-related factors were associated with the air masses from SW direction and high wind speed
 281 (20 to 30 m s^{-1}) (Figure S3). The contribution of the factor assigned to aerosols declined during rain
 282 events due to wet deposition, while similar behavior was not observed for other factors.

283 TEX air mixing ratios and rain concentrations decreased during the first two hours of the rainfall, but
 284 tend to rise afterwards probably as a result of rainfall intensity decrease (Figure S4, Supplementary
 285 material). The highest TEX enrichment, caused by air mixing ratio decrease, was detected during the
 286 second hour. Typical washout effect was observed for source contributions related to the rainwater
 287 aerosol and solid components, and was less pronounced for crustal factor. Unlike TEX, only a slight
 288 decrease in benzene air mixing ratios was noticeable, which is reflected in a constant EF_B increase.

289 3.2 BTEX distribution between gaseous and aqueous phases

290 The exsufflation time required for the equilibrium to be achieved was different for rainwater samples
 291 and ultrapure water, which suggests that physico-chemical properties and BTEX content distributed
 292 between different phases have certain impact on the adsorption to the aqueous phase (Figure 2,
 293 left). However, the correlations were registered only between the concentrations of B, and F^- (-0.72)
 294 and NH_4^+ (0.83) (Figure S2, Supplementary material). The impact of rainwater physico-chemical
 295 properties on the BTEX retention was further examined by insufflating 2 ppbV of BTEX in 10 pre-
 296 exsufflated rainwater samples, as described in our previous paper (Šoštarić et al., 2015). The results
 297 showed slightly longer exsufflation periods for rainwater samples compared to the pure water,

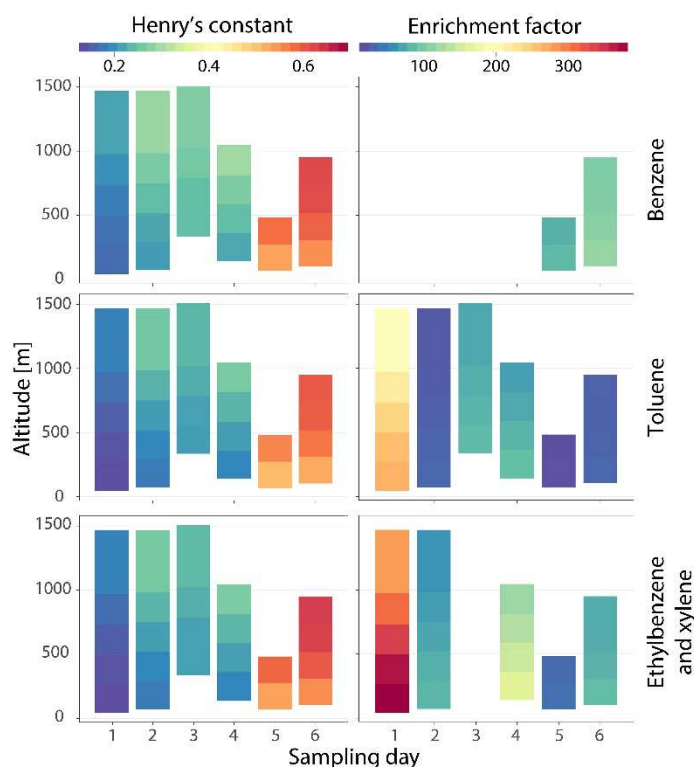
298 indicating that physico-chemical properties are not the main contributor to the extended retention in
 299 the rainwater. The comparative qualitative analysis of rainwater and ultrapure water exsufflation
 300 time series obtained by real-time PTR-MS measurements showed that different capacities for BTEX
 301 retention can be mainly associated with BTEX aerosol fraction (Figure 2, right).



302
 303 Figure 2. The time required to reach equilibrium (t_{eq}) and 99, 95 and 90% quantity of benzene and
 304 toluene to be exsufflated (left), and toluene exsufflation from ultra-pure water and rainwater (right).

305 Generally, due to very small K_H values of aromatic compounds, BTEX concentrations in rainwater are
 306 expected to be low (Słomińska et al., 2014). However, according to the results, EF values were in the
 307 range from 61 to 128, from 8 to 209, and from 25 to 295 for B, T and EX, respectively, indicating that
 308 the BTEX amounts in the aqueous phase significantly exceeded the theoretically predicted levels.
 309 Both lower and higher EF values have been reported in the literature. According to the studies
 310 dealing with the distribution of chlorinated hydrocarbons and monocyclic aromatic hydrocarbons
 311 between air and rainwater, EF ranged from 2.4 to 34 for BTEX (Okochi et al., 2004; Sato et al., 2006),
 312 whereas the study of Valsaraj et al. (1993) reported several hundred to a thousand-fold enrichment
 313 of hydrophobic organic compounds in fog samples. The enhanced BTEX transfer to urban dew water
 314 was also shown by Okochi et al. (2005), with the reported EF values ranging from 7.87 to 20.2.
 315 Furthermore, Fries et al. (2007) showed that the concentrations of aromatic hydrocarbons including
 316 ethylbenzene, xylenes and 1,2,4-trimethylbenzene, have been significantly lower in rain ($15\text{--}53\text{ ng L}^{-1}$)
 317 than in snow ($71\text{--}2200\text{ ng L}^{-1}$). In the later study, Fries et al. (2008) found that in-cloud scavenging
 318 could be a possible explanation for the occurrence of VOC in fallen snow.

319 Figure 3 illustrates the K_H and EF altitude distribution for BTEX. It should be mentioned that K_H and EF
 320 for B and EX exhibit the similar pattern. As can be seen, K_H and consequently EF, change as the
 321 raindrop falls to the ground. K_H values calculated using the average temperature on the path of the
 322 raindrop differ $\pm 20\%$ from those obtained using the rainwater temperature. Such agreement
 323 indicates that the rainwater temperature measured at the ground level is a good indicator of
 324 atmospheric conditions under which reactions with BTEX takes place. Moreover, in the study of Lin et
 325 al. (2011), it was concluded that, at higher altitudes in locations with dominant local sources, VOC
 326 concentrations were generally lower, and hence, higher K_H values would not be expected to affect C_{R} ,
 327 nor calculated values of D_{OBS} and EF.



328

329 Figure 3. Henry's constant and EF BTEX altitude distributions.

330 As suggested by the field studies (Valsaraj et al., 1993; Goss, 1994; Okochi et al., 2004; Starokozhev
 331 et al., 2009), as well as the laboratory experiments (Bruant and Conklin, 2000; Bruant and Conklin,
 332 2002; Raja et al., 2002; Raja and Valsaraj, 2004; Šoštarić et al., 2016), the interfacial adsorption might
 333 be the major mechanism associated with the enhanced VOC transfer to the aqueous phase.

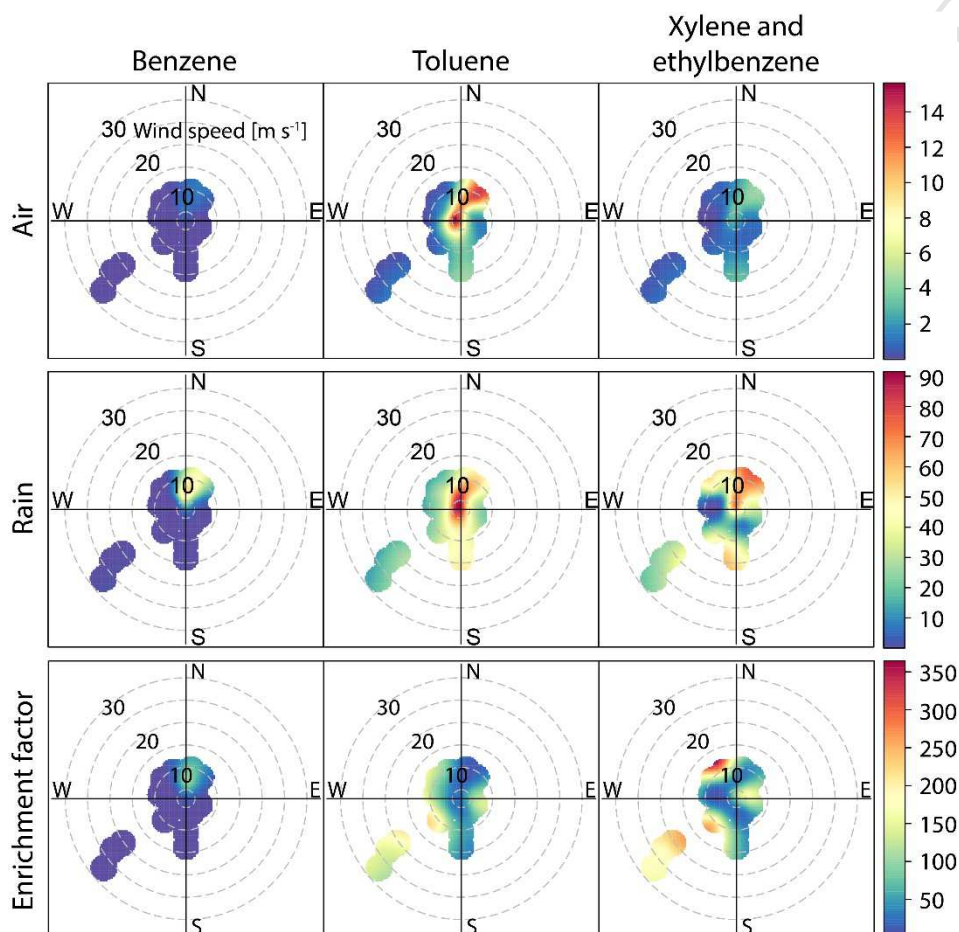
334 Some previous studies have examined the composition of atmospheric water and the impact of
 335 different species, including nitric acid, anionic and nonionic surfactants, as well as the impact of
 336 salinity and pH on air-water VOC distribution (O'Sullivan et al., 1996; Vane and Giroux, 2000; Sato et
 337 al., 2006; Allou et al., 2011). The supersaturation of VOC in rain samples was explained by decreased
 338 rainwater polarity associated with the presence of different organic compounds (Sato et al., 2006).
 339 The presence of colloidal organic matter with its large binding capacity for many hydrophobic species
 340 was found in fog droplets (Valsaraj et al., 1993). Similarly, in the study of Okochi et al. (2005), the
 341 enhanced dissolution of VOC species in urban dew compared to rainwater was explained by the fact
 342 that dew forms near the ground and contain more humic-like substances that could lead to a
 343 decrease in water surface tension and consequently result in higher VOC enrichment.

344 The present study considers several factors that could contribute to BTEX enrichment in rainwater,
 345 including BTEX concentrations, rainwater physico-chemical properties, rainfall intensity, air masses
 346 origin, meteorological conditions and adsorption at the air/water interface.

347 As regards the physico-chemical characteristics of rainwater, only F^- and SO_4^{2-} can be considered
 348 important for the prediction of EF_B (-0.73) and EF_{EX} (0.62), respectively. The latter indicates that
 349 SO_2 -rich coal burning emissions are also a significant source of EX, while the results for B should be
 350 taken with caution due to the small data size.

351 Higher rainwater T enrichment was mostly observed for low gaseous T concentrations, high TOC
 352 ($8-12 \text{ mg L}^{-1}$) and turbidity (Supplementary file 1), although the strict link between rainwater
 353 enrichment and gaseous concentrations cannot be established. The exsufflation dynamics (Figure 2)
 354 and the EF values suggest that prolonged BTEX retention could also be attributed to the adsorption
 355 to aerosol fraction. We have considered T partitioning, not only because T concentrations were in a
 356 relatively broad range, but also because of the significant number of samples collected in both

357 seasons with comparable concentrations, despite the fact that similar findings were observed for the
 358 rainwater enrichment with EX (Supplementary file 2). As can be observed in Figure 4 and Table S6 of
 359 the Supplementary material, higher T enrichment was mostly associated with a higher wind speed at
 360 the sampling site (up to 30 m s^{-1}) and air masses coming from SW area, whereas the lowest rainwater
 361 enrichment was registered under relatively stable atmospheric conditions ($w_s < 5 \text{ m s}^{-1}$). Similar
 362 associations were also observed for EX. Higher rainwater enrichment could be the result of the
 363 prolonged contact time between the aqueous and the gaseous phases, when strong wind-driven
 364 raindrops were falling obliquely.



365
 366 Figure 4. The relationship between BTEX air mixing ratios (ppb), rain concentrations (nM) and
 367 enrichment factor and wind characteristics.

368 According to GRRF results (Table S7, Supplementary material), physico-chemical rainwater properties
 369 and gaseous T concentrations appear to be of greater importance than meteorological factors for
 370 predicting T and EX rainwater enrichment. Furthermore, these findings also indicate that ground
 371 level gaseous concentrations have higher impact on the transfer of species to the aqueous phase
 372 than the polluted air masses coming from greater atmospheric heights.

373 Out of 24 examined MVA regression methods, some of which were previously successfully applied
 374 for prediction of PM_{10} and VOC emissions (Stojić et al., 2015d; Perišić, 2016), it has been shown that
 375 RF, IBk and IBkLG can provide predictions of EF_T and EF_{EX} based on the variables of the highest
 376 importance derived by GRRF with relative errors of approx. 20%, *i.e.* 27%, and correlation coefficients
 377 around 0.95 and 0.87, respectively (Table 1). Conversely, the prediction of EF_T and EF_{EX} based on
 378 Unmix derived source contributions was less accurate (K^* : 36.3% relative error and correlation
 379 coefficient 0.79). As can be concluded, functional description of EF_T and EF_{EX} can be based on certain
 380 rainwater properties and gaseous T concentrations. In addition to ambient and rainwater B

381 concentrations, EF_B is affected by meteorological conditions (sample and ambient temperature and
 382 Rh), but these results should be taken with caution due to the small B data size.

383

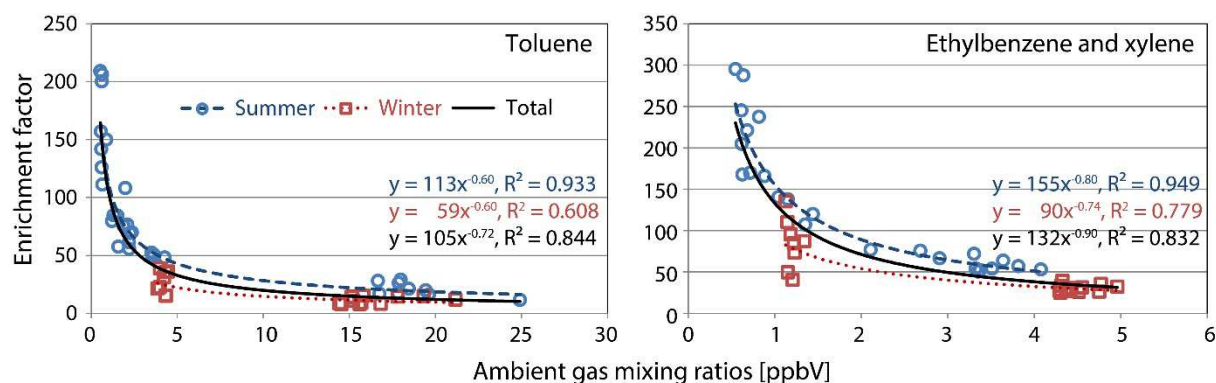
384 Table 1. MVA method performance comparison for enrichment factor prediction based on the
 385 measured parameters and Unmix-derived source contributions: absolute error, relative error and
 386 correlation coefficient (r).

Method	EF_T						EF_{EX}					
	Measured			Unmix derived			Measured			Unmix derived		
	Abs.	Rel.	r	Abs.	Rel.	r	Abs.	Rel.	r	Abs.	Rel.	r
Alternating Model Tree	18.5	34.8	0.88	40.8	76.4	0.67	33.8	42.0	0.78	59.2	111.0	0.53
Conjunctive Rule	26.1	48.9	0.64	32.0	59.9	0.40	39.2	48.7	0.55	43.4	81.2	0.41
Decision Stump	25.5	47.8	0.57	29.3	54.9	0.46	36.4	45.2	0.57	39.4	73.8	0.45
Decision Table	17.8	33.3	0.85	25.3	47.4	0.68	33.9	42.1	0.71	44.8	83.9	0.46
Elastic Net	15.2	28.5	0.88	22.3	41.9	0.77	29.4	36.5	0.74	38.6	72.4	0.62
Gaussian	16.1	30.2	0.88	21.9	41.0	0.79	30.6	38.0	0.72	41.0	76.8	0.60
IBk	11.6	21.7	0.95	20.6	38.5	0.79	22.4	27.8	0.89	31.9	59.8	0.68
IBkLG	11.6	21.7	0.95	20.6	38.5	0.79	22.4	27.8	0.89	31.9	59.8	0.68
Isotonic	13.7	25.7	0.93	31.4	58.9	0.54	34.9	43.3	0.62	39.5	74.0	0.58
K*	11.9	22.3	0.92	19.4	36.3	0.79	22.0	27.4	0.87	31.0	58.1	0.68
Least MedSq	17.4	32.7	0.87	35.6	66.8	0.67	52.7	65.4	0.29	47.4	88.8	0.50
Linear Regression	15.5	29.1	0.89	22.7	42.5	0.78	30.8	38.2	0.74	39.0	73.2	0.61
LWL	15.9	29.7	0.91	26.7	50.0	0.72	35.5	44.1	0.70	39.4	73.9	0.53
M5P	13.9	26.1	0.91	21.6	40.5	0.78	29.7	36.9	0.74	40.4	75.7	0.60
M5Rules	15.0	28.1	0.90	22.9	42.9	0.74	30.8	38.3	0.74	42.2	79.1	0.59
Multilayer	17.7	33.1	0.92	24.2	45.4	0.80	37.5	46.5	0.74	49.5	92.7	0.55
Pace Regression	15.9	29.8	0.88	22.7	42.6	0.77	30.1	37.4	0.74	38.6	72.4	0.62
Random Forest	11.6	21.7	0.95	22.5	42.2	0.76	27.8	34.5	0.76	34.9	65.4	0.62
Random Tree	13.8	25.9	0.89	28.6	53.7	0.59	32.8	40.8	0.67	41.7	78.1	0.54
RBF Network	29.9	56.0	0.45	30.4	57.0	0.65	44.8	55.7	0.49	52.8	98.9	0.40
RBF Regressor	14.7	27.6	0.91	23.6	44.2	0.78	28.1	34.9	0.83	40.9	76.6	0.56
REP Tree	13.9	26.1	0.91	22.5	42.1	0.72	36.9	45.8	0.58	42.0	78.8	0.43
Simple Linear Regression	29.9	56.1	0.49	30.3	56.7	0.55	34.3	42.7	0.71	40.5	75.8	0.61
SMOreg	14.7	27.5	0.88	21.5	40.3	0.79	28.8	35.8	0.75	39.0	73.2	0.61

387

388 Figure 5 represents EF for T and EX as a function of their ambient gas phase mixing ratios. As can be
 389 seen, EF values increased in summer, due to ambient air temperature, which is one of the most
 390 important factors for the decrease of the surface tension leading to enhanced interfacial adsorption
 391 (Bruant and Conklin 2000, 2002). Another important feature of Figure 5 is the power functional
 392 dependence of EF on ambient gas phase mixing ratios, as adsorption processes are generally more
 393 efficient for lower adsorbate concentrations and are characterized by the power functions. These
 394 findings are in compliance with the findings of Sato et al. (2006) who showed that rainwater
 395 enrichment is especially significant for the species with lower atmospheric concentrations.

396



397
398 Figure 5. The relationship between T and EX enrichment factors and their gaseous concentrations.
399

400 4. Conclusions

401 The transfer of BTEX and other VOC from the atmosphere to various forms of atmospheric water is
402 an important process that affects the global transport of air pollutants, environmental fate and
403 enables the transfer of these species to terrestrial and aquatic systems. The purpose of this study
404 was to investigate the scavenging potential of rainwater and consider the potential mechanisms and
405 factors associated with this phenomenon.

406 As shown, BTEX concentrations observed in the aqueous phase exceeded the theoretically predicted
407 values. Given that the interfacial adsorption is assumed to be the major mechanism underlying the
408 enhanced rain scavenging of BTEX, the removal process was observed to be more efficient for lower
409 gas mixing ratios, mainly due to equal surface available for smaller number of molecules and the
410 prolonged contact time between the two phases when wind-driven rain drops were falling obliquely.
411 Accordingly, theoretical predictions are probably more accurate in the area of larger gaseous
412 concentrations, whereas in the case of lower concentrations, transfer to the aqueous phase is often
413 underestimated. Furthermore, the results of the presented regression multivariate analysis suggest
414 that multiple factors determine the spatio-temporal BTEX distribution in the environmental
415 multiphase system, including ambient mixing ratios, physico-chemical properties of rainwater and
416 meteorological data. More specifically, the functional description of EF_T and EF_{EX} can be based on
417 certain rainwater properties. On the other hand, it has been shown that EF_B is affected by
418 meteorological conditions (sample and ambient temperature, and R_h), as well as B ambient and
419 rainwater concentrations (however, these results should be interpreted with caution due to the small
420 B data size).

421

422 Acknowledgments

423 This paper was realized as part of projects No III43007 and No III41011, which were financed by the
424 Ministry of Education, Science and Technological Development of the Republic of Serbia for the
425 period 2011-17, and was supported by the Institute of Public Health of Belgrade, Serbia.

426

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Highlights

- Potential of rainwater for BTEX scavenging from ambient air was examined
- BTEX concentrations in rain samples exceeded the theoretically predicted values
- BTEX retention could be associated with BTEX aerosol fraction
- Random forest and instance based algorithms provide reliable enrichment predictions
- Gas mixing ratios, rainwater characteristics and meteorology affect BTEX distribution