

1 **The effect of anthropogenic activity on BTEX, NO₂, SO₂, and CO concentrations in**
2 **urban air of the spa city of Sopot and medium-industrialized city of Tczew located in**
3
4 **North Poland**

5
6
7 Mariusz Marć^{*1}, Michalina Bielawska², Vasil Simeonov³, Jacek Namieśnik, Bożena
8 Zabiegała¹

9
10
11
12
13 ¹ *Department of Analytical Chemistry, Gdansk University of Technology, Gdansk, Poland*

14 ² *Agency of Regional Air Quality Monitoring in the Gdansk Metropolitan Area (ARMAAG),*
15 *Gdańsk, Poland*

16 ³ *Faculty of Chemistry and Pharmacy, University of Sofia, Sofia, Bulgaria*

17
18 * *Address for correspondence: Mariusz Marć, Department of Analytical Chemistry, Gdańsk*
19 *University of Technology, Narutowicza Str. 11/12, PL 80-233, Gdańsk, Poland.*
20
21 *e-mail: marmarc@pg.gda.pl*

22
23
24
25
26
27
28 **Abstract**

29
30
31
32 The major goal of the present study is to compare the air quality of two urban locations
33 situated in Northern Poland – the spa City of Sopot and the medium-industrialized city of
34 Tczew using chemometric methods. As a criterion for the assessment of atmospheric air
35 quality, measurements of benzene, toluene, ethylbenzene and total xylenes were used
36 (collected from atmospheric air using diffusion-type passive samplers) as well as
37 measurements of inorganic compounds - CO, NO₂ and SO₂, which were subject to routine
38 control and determined by means of automatic analysers. Studies related to determination of
39 defined chemical compounds in the urban air in the monitored area were performed from
40 January 2013 to December 2014. By interpreting the results obtained and using basic
41 multivariate statistical tools (cluster analysis and principal components analysis), major
42 sources of emissions of determined pollutants in the air in urbanized areas were defined. The
43 study also shows the potential influence of the sea breeze on concentrations of chemical
44 compounds in the atmospheric air in the spa city of Sopot.

45
46
47
48 **Keywords:** BTEX; inorganic compounds; urban air quality; Hierarchical Cluster Analysis;
49 Principal Components Analysis.

1. Introduction

Progressive urbanization of ever larger areas needs to be treated as a serious hazard to the environment. It is estimated that currently about 75% of the population of Europe lives in urban areas, and by 2020, this proportion will increase to 80% (EEA Report, 2006). As a result, urban expansion has a huge impact on the environment, and also acts directly on the quality of life of citizens.

The problems with urban air quality are related to at least two key trends: (i) the dramatic increase in traffic in urban areas and the corresponding increase in traffic / transport-related emissions and (ii) the mounting evidence that air pollution has significant effects on health.

Transport-related emissions have become the dominant component of air pollution in the recent years. Vehicles with petrol- and diesel-engines emit a wide variety of air pollutants, such as: CO, NO₂, SO₂, (Wu et al., 2011; Ghozikali et al., 2016) volatile organic compounds (VOCs) (Batterman et al., 2007), polycyclic aromatic hydrocarbons (PAHs) (Oros et al., 2007) and particulate matter (PM) (Bosco et al., 2005) which have an increasing impact on urban air quality. The rapid growth in vehicular traffic means that air pollution might continue to rise in the future.

Volatile organic compounds (VOCs) are an important class of air pollutants found in any urban and industrial region. It is estimated that volatile organic compound (VOC) emissions from transport-related sources account for ~35% of all VOC emissions to the atmosphere. In most EU countries emissions per vehicle have been falling, but the gains have been offset by the continuously increasing number of vehicles. Some VOCs are toxic (e.g. benzene, 1,3-butadiene) while many participate in complex photochemical reactions in the presence of sunlight. The products of VOCs photo-chemical reactions lead to an increase in the formation of airborne toxic chemicals, to production of tropospheric ozone (Shao et al., 2009; Derwent et al., 2003; Finlayson-Pitts and Pitts Jr, 1997) and secondary organic aerosol (SOA) (Hallquist et al., 2009; Carlton et al., 2009).

Nitrogen dioxide (NO₂) is a pollutant gas involved in many different chemical processes in the atmosphere. In the troposphere, it acts as a photocatalyst in a series of oxidation reactions of VOCs, generating ozone and low molecular weight aldehydes (Hallquist et al., 2009). In addition, NO₂ is a precursor in the formation of nitric acid, which participates in the formation of aerosols that can affect human health and modify cloud formation processes (Filho et al., 2015).

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000

In urban environments ozone production is often under a VOC-limited regime. Hence, management of VOC levels is very important for the development of an efficient air pollution abatement strategy and is the key for meeting the ozone concentration standards. Management of ambient concentrations of VOCs and NO_x is essential for maintaining low ozone levels in urban areas (Stranger et al., 2008; Zalel et al., 2008).

The aim of presented research was to assess the air quality in urban areas of the spa city of Sopot and a medium-industrialized city of Tczew in relation to the air components such as, BTEX compounds (benzene, toluene, ethylbenzene and sum of xylenes) as well as measurements of inorganic compounds - CO, NO₂ and SO₂; to determine the relationships between the concentrations of these pollutants and to estimate the influence of anthropogenic emission sources on the concentration of measured organic and inorganic compounds in the urban air using multivariate statistics. The monitoring of the concentration of CO, SO₂ and NO₂ in urban air has been performed by using automated analyzers, which are an integral part of monitoring stations located in the monitored area. The use of automated analyzers allows obtaining information on the monitored substances in real time at one-hour intervals. The BTEX compounds monitoring was performed based on passive sampling technique applying diffusion-type Radiello[®] passive samplers.

2. Materials and Methods

2.1 Description, location and meteorological conditions in monitoring areas.

Measurements of the BTEX compounds and selected inorganic compounds - CO, NO₂ and SO₂, were conducted using measuring techniques and devices installed at automatic monitoring stations. The monitoring stations are located in North Poland in two medium-sized cities - Sopot (54°26'31"N; 18°33'35"E) which belongs to the Tri-city agglomerations (metropolitan area in northern Poland consisting of three cities: Gdańsk, Gdynia and Sopot) and Tczew (54°05'31,89"N; 18°46'38,39"E) situated approx. 40 km away from this agglomeration. Sopot is a main spa resort, which is visited by many tourists in the summer seasons. Sopot is situated on the Gdańsk Bay with the population of 38 thousand and the surface area of 17.3 km². Tczew, on the other hand, is a medium-size medium-industrialized city situated on the Vistula River with the population of approx. 61 thousand and the surface area of 22.3 km². The locations of the automatic monitoring stations in these cities are



1 presented in Figure 1. Both stations are owned and administrated by the ARMAAG
2 Foundation (Agency of Regional Air Quality Monitoring in the Gdańsk Metropolitan Area).
3 To properly interpret data obtained (BTEX and CO, NO₂, SO₂, concentrations) it is very
4 important to have clear information about weather conditions including air temperature,
5 humidity, atmospheric pressure, wind speed and direction, insolation and precipitation but
6 also detailed descriptions of sampling locations with the indications of potential emission
7 sources. Detailed information about sampling locations and weather conditions in Sopot and
8 in Tczew in the monitored period (from January 2013 to December 2014), including the
9 influence of seasonal breeze circulation on the quality of atmospheric air in Sopot, wind roses
10 determined for areas under monitoring, area are presented in Supplementary Files
11 (Supplementary Information, Supplementary Table 1, Supplementary Figure 1).
12
13
14
15
16
17
18
19
20
21

22 **2.2 Analytical procedure used for determination of BTEX compounds in urban air**

23 **2.2.1 BTEX sampling technique**

24
25
26
27
28
29 Diffusion-type Radiello[®] passive samplers (Fondazione Salvatore Maugeri, Padova, Italy)
30 were used for analytes samples collection from the air. This sampling device consists of a
31 cylindrical adsorbing cartridge housed coaxially inside a cylindrical diffusive body of
32 polycarbonate and microporous polyethylene (diffusion zone length 150 mm; porosity 10 ± 2
33 µm). The analyte passes across a microporous diffusive body/membrane before reaching an
34 inner stainless steel net cylinder containing graphitized charcoal Carbograph 4 (300 ± 10 mg;
35 35-50 mesh) as the adsorbent. More detailed information on the design and application of
36 Radiello[®] passive samplers in the monitoring of atmospheric air quality were described in
37 (Plaisance et al., 2008; Woolfenden, 2010, Król et al., 2012; Maré et al., 2015).
38

39
40
41
42
43
44
45
46 During monitoring campaign, two diffusion-type Radiello[®] passive samplers were placed in
47 specially designed stainless steel shelters, 20 cm apart at each monitoring station. The
48 stainless steel shelters protect Radiello[®] passive samplers from the harmful influence of
49 atmospheric conditions (precipitation and wind). The shelters were located at a height of 3 m
50 above ground level. The exposure time of passive samplers was 14 days. After the defined
51 exposure time, the stainless steel net cylinder containing adsorbent was removed from
diffusion body and placed in a sealed glass container. Next, the new cylindrical containers
filled with a clean sorption bed were placed inside the diffusive membranes. Glass containers
with the sorption medium were then transported to the analytical laboratory.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52

During the entire period of the studies (the years 2013-2014), 96 samples were collected - 48 samples a year for each monitoring station.

2.2.2 Analytes liberation technique

The sorption media of the diffusion-type Radiello[®] passive samplers were removed from the sealed glass tubes and placed inside stainless-steel tubes (89 mm x 6.4 mm o.d.), which were then loaded into the thermal desorber (Omnisfera, Poland). In the first step, a tube was heated to 280°C and held at this temperature for 20 min with pure helium gas passing through it at a flow rate 40 ml/min to desorb the analytes and focus them in a cold trap kept at 1°C. The cold trap was packed with Tenax TA (37 mg) and Carbotrap (27 mg). The entire analyte mass desorbed from the Radiello sorption medium was transferred into the cold trap. In the second step, cold trap desorption, the cold trap's helium flow was inverted and the trap was heated rapidly to 300°C. The analytes were quickly desorbed from the trap and transferred into the chromatographic column (DB-1 (J&W), 30 m × 0.32 mm × 5 µm).

Detailed information about two-stage thermal desorption system, used for BTEX liberation, has been described elsewhere (Przyk et al., 2003; Zabiegała et al., 2007).

Gas chromatography analysis and final determination stage

The gas chromatography technique (Hewlett-Packard 5890 GC Series II) with a flame ionization detector (FID) was applied. The GC oven temperature program was initially set to 40°C for 1 min, then raised at a rate of 15°C/min up to 120°C, then increased at a rate of 10°C/min up to 220°C, and finally maintained for 5 min at 220°C. The temperature of the transfer line connecting the thermal desorber with a gas chromatograph was 150°C, while the temperature of the FID operation was 280°C. The GC carrier gas flow rate (high-purity helium) was 2.2 ml/min.

The external standard calibration method (ESTD) was performed using a volatile calibration mix containing 13 VOCs (containing BTEX compounds) in the methanol solution in which the concentration of each organic compound was 2000 µg/ml (VOC Mix 2, Supelco, Bellefonte, PA, USA). Two five-point calibration curves were created for two concentration ranges, 50 to 400 µg/ml and 400 to 2000 µg/ml.

Detailed characteristics of conducting the calibration of the TD-GC-FID system based on the external standard method together with the used devices were described in former papers

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000

(Zabiegała et al., 2011; Maré et al., 2014b). Based on the obtained equations of calibration curves the limit of quantification of the analytical procedure used (MQL) were calculated, which ranged from 0.020 $\mu\text{g}/\text{m}^3$ for p, m-xylene to 0.050 $\mu\text{g}/\text{m}^3$ for benzene (Maré et al., 2014a).

The time weighted average (TWA) concentrations of BTEX compounds were calculated based on the knowledge of the exposure time of the samplers, masses of the analytes trapped by the sorption medium (determined chromatographically), and analyte sampling rates (SR). The uptake rate values (Q), supplied by the manufacturer of diffusion-type Radiello[®] passive samplers, were determined at 25°C and 1013 hPa in a controlled atmosphere; consequently, they had to be adjusted for the actual mean sampling temperature (Fondelli et al., 2008; Dumanoglu et al., 2014). The uncertainty of the uptake rate values (Q) of BTEX compounds was also supplied by the manufacturer. These values fall within the range from 7.5% for benzene to 11.3% for p, m-xylene.

2.3 On-line analysers used for determination of selected inorganic compounds in urban air

Taking into account the requirements presented in Directive EU 2008/50/EC, monitoring stations situated in Tczew and Sopot which are administered by ARMAAG foundation are equipped with appropriate automatic analysers. At the monitoring station which is located in Tczew, the following automatic analysers were used to determine sulphur dioxide, nitrogen oxides and carbon monoxides: Thermo Environmental 43 C (SO₂), Teledyne T200 (NO-NO₂-NO_x) and Thermo Environmental 48 C (CO), respectively. At the monitoring station which is located in Sopot, the following automatic analysers were used: Thermo Environmental 43 C (SO₂), Thermo Environmental 42 C (NO-NO₂-NO_x) and Thermo Environmental 48 C (CO), respectively.

Information about the content of the determined inorganic compound in the atmospheric air is published on the ARMAAG foundation website on a continuous basis (www.armaag.gda.pl). Information about concentrations of inorganic compounds in the atmospheric air in the studied area is provided every hour. The operation of the aforementioned devices is monitored remotely and by periodic on-site service inspections by the personnel. The extended uncertainty of measurements obtained by means of automatic analysers at the monitoring stations was 15%.

2.4 Multivariate statistical methods

The chemometric methods used in the present study are already classical approach in many cases of classification, modelling and interpretation of environmental monitoring data. Cluster analysis (CA) and principal components analysis (PCA) were applied for intelligent data analysis. Both methods are well documented in scientific work presented by Vandeginste et al., 1998. In principle, hierarchical CA is used as a classification tool and PCA as a typical display method. It enables revealing the “hidden” structure of the data set. Interpretation of the results of PCA is usually carried out by visualization of the component scores and loadings. The software package used for calculations was STATISTICA 7.0 (StatSoft®, Poland)

3. Results and Discussion

3.1 Concentrations of the BTEX compounds in the atmospheric air in Tczew and Sopot

In accordance with information contained in Directive 2008/50/EC, the legislator recommends that studies related to the quality of atmospheric air in urbanized areas should include the monitoring of the content of 31 organic compounds classified as potential precursors for the formation of tropospheric ozone (O₃), which includes, amongst other things, compounds from the BTEX group and from the trimethylbenzene group. The aforementioned Directive, places special emphasis only on the monitoring of the benzene content whose average annual concentration in the atmospheric air must not exceed 5 µg/m³ in the urbanized area. According to literature reports and the report by the International Agency for Research on Cancer, benzene is classified in Group I as a chemical compound with carcinogenic properties (I.A.R.C., 1982). Excessive and long-term exposure of the human body to the harmful effects of benzene may be the cause of plastic anaemia and acute myeloid leukaemia (Pariselli et al., 2009; Schiavon et al., 2015). For this reason, in all monitoring tests related to the atmospheric air quality in urbanized areas, benzene contents are considered on an individual basis as opposed to other organic compounds from the BTEX group.

Interpretation of results of the research on the quality of atmospheric air in Tczew and Sopot conducted in the years 2013-2014 did not reveal exceeding of the limit value of annual average concentrations of benzene (<5 µg/m³) in the studied air in the monitored area. In



1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000

2013, the average time-weighted concentrations of benzene in atmospheric air in Tczew amounted to $0.75 \pm 0.55 \mu\text{g}/\text{m}^3$, while in Sopot it amounted to $0.53 \pm 0.43 \mu\text{g}/\text{m}^3$. For research performed in 2014, the average time-weighted concentrations of benzene in atmospheric air in Tczew amounted to $1.4 \pm 1.1 \mu\text{g}/\text{m}^3$, while in Sopot it amounted to $1.07 \pm 0.97 \mu\text{g}/\text{m}^3$. In 2013, the highest average monthly time-weighted benzene concentration in the atmospheric air in Tczew was recorded in March ($1.75 \mu\text{g}/\text{m}^3$), while the lowest in August ($0.10 \mu\text{g}/\text{m}^3$). For research conducted in the same year in Sopot, the highest average monthly time-weighted benzene concentration in the atmospheric air was recorded in December ($1.21 \mu\text{g}/\text{m}^3$), while the lowest in August where the determined average monthly time-weighted concentration was similar to the numerical value of MQL ($0.050 \mu\text{g}/\text{m}^3$). As regards the research conducted in the area in which atmospheric air was monitored in 2014, the highest average monthly time-weighted benzene concentration in the atmospheric air in Tczew was recorded in February ($3.48 \mu\text{g}/\text{m}^3$), while the lowest in June ($0.25 \mu\text{g}/\text{m}^3$). As regards to the quality of atmospheric air in Sopot, the highest average monthly time-weighted concentration of benzene was recorded in February ($2.92 \mu\text{g}/\text{m}^3$), while the lowest was recorded in June ($0.16 \mu\text{g}/\text{m}^3$).

Temperature is a significant meteorological factor which needs to be considered in the interpretation of research results related to the benzene content in the atmospheric air. Figure 2 presents graphically the relationship between the temperature and the average monthly time-weighted benzene concentration determined in the atmospheric air in the monitored area (the Tczew and Sopot city) in the years 2013-2014. As regards the data presented in Figure 2, it can be noticed that both in Tczew and in Sopot, there is a moderate relationship between the temperature and the benzene content. This can lead to the conclusion that a decrease in the atmospheric air temperature in the urbanized area may influence the benzene content. To confirm this thesis, the period of research including a given calendar year should be divided into two basic seasons: the heating season which lasts from the beginning of October to the end of April in Poland (7 months); the summer season which includes the period from the beginning of May to the end of September (5 months). As regards the research conducted in Tczew in the years 2013 and 2014, the values of time-weighted average benzene concentration determined in the atmospheric air in the heating season were: $1.13 \pm 0.36 \mu\text{g}/\text{m}^3$ and $2.0 \pm 1.1 \mu\text{g}/\text{m}^3$, respectively, while in the summer season it were: $0.201 \pm 0.090 \mu\text{g}/\text{m}^3$ and $0.49 \pm 0.24 \mu\text{g}/\text{m}^3$, respectively. The temperature of the atmospheric air in Tczew in the years 2013 and 2014 in the heating season was 3.2°C and 4.8°C , respectively and in the summer season: 16.8°C and 17.1°C , respectively. A comparison of the heating and summers seasons in

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000

the years 2013 and 2014 in Tczew revealed that the average time-weighted benzene concentrations determined in the atmospheric air in the heating season were over 4 (year 2013) and over 5 (year 2014) times higher than in the summer season. Similarly, while analysing information obtained from monitoring research conducted in Sopot area in the year 2013 and 2014, the values of time-weighted average benzene concentration determined in the atmospheric air in the heating season were: $0.84 \pm 0.27 \mu\text{g}/\text{m}^3$ and $1.58 \pm 0.98 \mu\text{g}/\text{m}^3$, respectively, while in the summer season it were: $0.096 \pm 0.064 \mu\text{g}/\text{m}^3$ and $0.36 \pm 0.21 \mu\text{g}/\text{m}^3$, respectively. The temperature of the atmospheric air in Sopot in the heating season in the years 2013 and 2014 was: 4.2°C and 5.5°C , respectively and in the summer season: 15.8°C and 16.1°C , respectively. A comparison of information about the quality of atmospheric air in the heating season and the summer season in Sopot revealed that the concentrations of benzene determined in the atmospheric air in the heating season was nearly 9 times higher in 2013 and over 4 times higher in 2014 as compared to the summer season.

All previously mentioned pieces of information confirm the thesis that the temperature of the atmospheric air in the urbanized area can have a significant influence on the benzene content in the atmospheric air. The traffic of vehicles with internal combustion engines is the main anthropogenic factor causing an increase in benzene concentrations in the atmospheric air in the urbanized area in the autumn-winter period (low temperatures of the atmospheric air). The time necessary for the achievement of the optimal liquid fuel combustion temperature in internal combustion engines is considerably extended, due to, amongst other things, an increase in the fuel density. For this reason, at the initial stage of using a mechanical vehicle, the process of incomplete liquid fuel combustion may occur, which may result in benzene emissions into the atmospheric air. Moreover, internal combustion engines installed in cars use much more liquid fuel in the autumn-winter period, than in the summer season. This is related, amongst other things, to the intensive use of the heating system inside the car and longer use of the external lighting of the vehicle in the autumn-winter period than in the summer season.

Another anthropogenic factor which influences the increase in the benzene content in the atmospheric air in the autumn and winter period in the urbanized area is the heating of flats and houses using low-performance heating systems (e.g. a tiled stoves or furnaces). In such systems, wood or low-quality coal can be used, which, together with the low performance of the system, may cause benzene emissions into the atmospheric air. Together with a decrease in the external temperature, the intensity of the use of heating systems in flats and houses grows to keep the optimal temperature of residential rooms. Low-performance tiled stoves or



1
2
3
4
furnaces can be usually found in very old houses or flats where the heat-transfer line from the
main city power plant was not installed or in small-sized buildings situated in recreational and
allotment areas.

5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
Higher benzene concentrations in the atmospheric air in the autumn and winter season than in
the summer season in the urbanized areas may also result from lower intensity of
physicochemical transformations occurring in the atmosphere. According to information
contained in the literature, the phenomenon of reduction in the thickness of the boundary layer
and the intensity of air mass mixing/circulation is reduced (Tao et al., 2007; Choi et al., 2011;
Zhang et al., 2015). Moreover, as a result of low temperatures of the atmospheric air and
considerably limited availability of solar radiation in the layer of the air over the urbanized
area, photochemical reactions between benzene and strong oxidiser (tropospheric ozone or
hydroxyl radical) are slowed down. As a result, the so-called lifetime of benzene in the
atmospheric air is extended (on a standard basis of approx. 9.4 days), which has a significant
influence on the content of this compound in the atmospheric air in the urbanized area
(Monod et al., 2001).

27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
Through the interpretation of results obtained, it was found that the annual average benzene
concentration determined in the atmospheric air in Tczew, both in 2013 and 2014, was higher
(by 40% and 28%, respectively) than the concentration of benzene determined in the
atmospheric air in Sopot during the same time. A similar phenomenon was observed while
comparing the benzene contents determined in atmospheric air in the autumn and winter
period. The following factors may have an influence on higher benzene concentrations in the
atmospheric air in Tczew, as compared to Sopot, obtained in the research: the location of the
station - the monitoring station in Tczew is situated in close vicinity of the main traffic node
(Wojska Polskiego Street), the railway node and seasonally used recreational allotments; the
smoothness of vehicle traffic – the traffic is very often considerably slowed down or stopped
at this traffic node, the age and type of buildings – low-performance tiled stoves or furnaces
are still used in some of the buildings and low-quality coal as a solid fuel is used.

49
50
51
52
Figure 3 presents the results of monitoring tests which were aimed at obtaining analytical
information on the levels of toluene, ethylbenzene and total xylenes determined in the
atmospheric air in Tczew and Sopot in 2013 and 2014. The average time weighted
concentrations of toluene, ethylbenzene and total xylenes determined in the atmospheric air in
Tczew in 2013 were: $2.2 \pm 1.0 \mu\text{g}/\text{m}^3$, $0.99 \pm 0.76 \mu\text{g}/\text{m}^3$, $4.4 \pm 3.4 \mu\text{g}/\text{m}^3$, respectively while in
2014: $3.1 \pm 2.5 \mu\text{g}/\text{m}^3$, $1.12 \pm 0.56 \mu\text{g}/\text{m}^3$, $4.5 \pm 2.4 \mu\text{g}/\text{m}^3$, respectively. As regards the average
time weighted concentrations of toluene, ethylbenzene and total xylenes which were

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000

determined in the atmospheric air in Sopot in 2013, they amounted to: $1.34 \pm 0.72 \mu\text{g}/\text{m}^3$, $0.23 \pm 0.13 \mu\text{g}/\text{m}^3$, $0.95 \pm 0.59 \mu\text{g}/\text{m}^3$, respectively while in 2014: $1.90 \pm 0.52 \mu\text{g}/\text{m}^3$, $0.44 \pm 0.17 \mu\text{g}/\text{m}^3$, $1.80 \pm 0.66 \mu\text{g}/\text{m}^3$, respectively. It should be noticed that both in Tczew and Sopot, the content of toluene, ethylbenzene and total xylenes determined in the atmospheric air in 2014 was higher than in 2013. Moreover, the average annual time weighted concentrations of organic compounds determined in the atmospheric air were higher in Tczew than in Sopot both in 2013 and 2014.

While interpreting data which is graphically summarized in Figure 3, it can be noticed that there is no clear relationship between the season (the heating season or the summer season) and the average monthly time weighted concentration of the selected organic compound determined in the atmospheric air in the monitored area. This is mostly caused by the fact that, according to the literature data, toluene, ethylbenzene and compounds from the xylenes group are characterized by a very short lifetime in the atmospheric air (from a few to a few dozen hours) in the urbanized area. These compounds which are present in the atmospheric air undergo photochemical reactions more easily with the participation of strong oxidisers, such as hydroxyl radical ($\cdot\text{OH}$) than benzene (Monod et al., 2001). Moreover, in the case of toluene, ethylbenzene and total xylenes, their presence in the atmospheric air may result not only from vehicle traffic or symptoms of the activity of tiled stoves or furnaces for residential buildings (burning low-quality coal) and also the activity of various types of industrial or commercial centres situated in the monitored area, e.g. a company dealing with the collection and management of various types of solid, liquid and electronic waste. The main means of transport used for transporting various types of waste are trucks with diesel engines.

3.2 Variations in the inter-species ratios of $\text{B} \div \text{T} \div \text{E} \div \text{X}$ in the monitored area in the period 2013-2014

To perform preliminary comparison of two or more areas which are monitored in terms of the influence of main sources of emissions of the BTEX compounds on the quality of atmospheric air, two analytical approaches are commonly used in the literature. The first is related to the definition of the influence of vehicle traffic on the levels of the BTEX compounds in the atmospheric air and is defined as the ratio of benzene, toluene and total xylenes concentrations to the ethylbenzene concentration determined in the atmospheric air in the monitored area, $\text{B} \div \text{E}$, $\text{T} \div \text{E}$ and $\text{X} \div \text{E}$, respectively. Under ideal conditions, where the only

1 source of emissions of BTEX compounds is vehicle traffic, the numerical values of the
2 $B \div T \div E \div X$ parameter is $3 \div 4 \div 1 \div 5$ and $B \div E < 5$, and $T \div E < 6$ (Chiang et al., 1996; Wang et al.,
3 2002; Khoder, 2007). It is possible to obtain similar numerical values of the $B \div T \div E \div X$
4 parameter only if weather conditions observed in comparable monitored areas are similar, the
5 vehicle traffic has similar intensity, vehicles use the same type of fuel which is characterized
6 by similar quality and the age of mechanical vehicles falls within the same range. Moreover,
7 concentrations of the BTEX compounds may not be influenced by other sources of emissions
8 in any of the monitored areas, such as the activity of local industrial and commercial centres
9 or the location of green areas (Vardoulakis et al., 2011; Lan and Minh, 2013).

16 The other analytical approach allows preliminary estimation of the so-called photochemical
17 age of air mass (“freshness” of the source of emissions) and determination of the distance
18 from the place with vehicle traffic. It makes it possible to define whether pollutants are
19 transported to the monitored area from sources of emissions situated near the monitoring
20 station or whether they are transported by the movement of air masses from other sources of
21 emissions situated at a considerable distance from the monitoring station. In this case, the
22 numerical values of the following parameters are being set, which depend on concentrations
23 of the BTEX compounds which are determined in atmospheric air in the monitored area:
24 toluene÷benzene (Tol/Benz); (m,p)-xylene÷benzene ((m,p)-Xyl/Benz); o-xylene÷benzene (o-
25 Xyl/Benz); (m,p)-xylene÷ethylbenzene ((m,p)-Xyl/Et.benz). In the analytical practice, two
26 parameters are used for the interpretation of the results obtained and comparison of the quality
27 of atmospheric air in monitored areas, these are toluene÷benzene (Tol/Benz) and (m,p)-
28 xylene÷ethylbenzene ((m,p)-Xyl/Et.benz) (Zhang et al., 2008; Baltrenas et al., 2011;
29 Yurdakul, et al., 2013). If the level of the BTEX compounds in the atmospheric air in
30 urbanized areas is mostly influenced by vehicle traffic, the Tol/Benz content falls within the
31 range from 1.3 up to even 4.3 (Miller et al., 2010; Rad et al., 2014). The higher the value of
32 this parameter, the more distinct the influence of vehicle traffic is on the concentration of the
33 BTEX compounds in the atmospheric air in the monitored area. However, when the source of
34 emissions of organic compounds from the BTEX group is located at a close distance from the
35 measuring/monitoring station (a “fresh” source of emissions), the value of the (m,p)-
36 Xyl/Et.benz parameter is higher than 3.3 (Hsieh et al., 2011; Miller et al., 2011; Cerón-Bretón
37 et al., 2015).

47 Table 1 presents average numerical values of the $B \div T \div E \div X$ ratio parameters and the
48 toluene÷benzene and (m,p)-xylene÷ethylbenzene parameters determined on the basis of the
49 results obtained in the atmospheric air quality studies in Tczew and Sopot in the years 2013-

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51

2014. While interpreting data summarized in Table 1 as regards the value of the $B \div T \div E \div X$ ratio parameter, it can be noticed that the first additional condition was met both in Tczew and in Sopot, i.e. the $B \div E$ and $T \div E$ parameters were below previously defined values. Such a result may lead to the preliminary conclusion that vehicle traffic is one of the sources of emissions of the BTEX compounds in Tczew and Sopot. In each case, both in 2013 and 2014, the values of the $B \div E$ and $T \div E$ parameter determined for Sopot were much higher than for Tczew. Furthermore, the values of the total $B \div T \div E \div X$ ratio parameter as determined for atmospheric air in Sopot in the years 2013 and 2014 are closer to the reference values ($3 \div 4 \div 1 \div 5$) than those determined for atmospheric air in Tczew. Such information may lead to the conclusion that in Sopot vehicle traffic was the main source of emissions of the BTEX compounds into atmospheric air throughout the research period. This is confirmed by the fact that Sopot is considered to be one of the most popular Polish resorts and health spas and is visited by a lot of tourists from Poland and abroad. Moreover, there is a lack of large industrial centres or service and commercial concerns in Sopot, which considerably facilitates the interpretation of the research results obtained. The fact that Sopot is situated on the Gdańsk Bay (proximity of the Baltic Sea) also seems significant. For this reason, the final result of determinations may be influenced by the sea breeze and emissions from ships with diesel engines which are stationed near Sopot. Differences between the year 2013 and 2014 in the determined $B \div T \div E \div X$ ratio parameters in Sopot may result from varying intensity of vehicle traffic - not only from cars which are used by the local community but also by tourists which visit this city seasonally. In the case of the total $B \div T \div E \div X$ ratio parameter determined for atmospheric air in Tczew in the year 2013 and 2014, it can be observed that these values significantly diverge from the reference values ($3 \div 4 \div 1 \div 5$). The occurrence of this phenomenon shows that vehicle traffic is not the only source of emissions of the BTEX compounds into the atmospheric air in the monitored area. The level of the BTEX compounds in the air in Tczew can be influenced by the activity of other factors situated in the monitored area, such as low-performance tiled stoves or furnaces in houses, seasonal use of recreational allotment areas and activity of industrial centres or service and commercial concerns.

Referring to the data contained in Table 1 which is related to the average content of the determined Tol/Benz parameter for atmospheric air in Tczew and Sopot in the years 2013-2014, it was observed that these values fall within the range from 1.3 to 4.3. This shows that vehicle traffic is not the only source of emissions of the BTEX compounds into the atmospheric air in the monitored area. It was noticed that both in 2013 and 2014, higher values of the Tol/Benz coefficient were observed for the atmospheric air in Tczew (2.96 and

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000

2.29, respectively). This results from the fact that the monitoring station in Tczew is located near the main communication node where the vehicle traffic is often slowed down or stopped. Moreover, there is no increased circulation and exchange of air resulting from the vicinity of the Gdańsk Bay (the sea-breeze has no influence on the quality of atmospheric air). For this reason, the activity of the vehicle traffic as a source of emissions, i.e. the vehicle traffic, has a consequential influence on the content of the BTEX compounds in the atmospheric air in Tczew, even it is not the only emission source of BTEX compounds.

Interpretation of parameters presented in Table 1 which are related to the (m,p)-Xyl/Et.benz parameter, whose determination allows preliminary specification of the proximity of the sources of emissions of the BTEX compounds, it was noticed that both in 2013 and in 2014 the greatest values were observed in Tczew (3.04 and 2.74, respectively). This can constitute the basis for drawing a conclusion that an intensive source of emissions of the BTEX compounds, i.e. vehicle traffic, is situated near the monitoring station. Moreover, the BTEX compound levels are influenced by the “fresh” source of emissions, which probably is increased vehicle traffic in the monitored area. In Sopot, the values of the (m,p)-Xyl/Et.benz parameter determined in the year 2013 and 2014 were similar and they amounted to 2.70 and 2.63, respectively. This shows that the source of emissions of the BTEX compounds into the atmospheric air (vehicle traffic) in the monitored area is situated at the same distance from the monitoring station. Moreover, the values of the (m,p)-Xyl/Et.benz parameter which were designated for Sopot may lead to the conclusion that the intensity of the source of emissions of the BTEX compounds (vehicle traffic) is more balanced than in the case of data obtained for Tczew.

3.3 Concentrations of selected inorganic compounds CO, NO₂, SO₂ in the monitored urban areas in the period 2013-2014.

Table 2 presents information about the average annual levels of the content of selected inorganic compounds determined in the atmospheric air in the monitored areas – Tczew and Sopot in 2013-2014. The summary takes into account the division of the research results obtained into two basic time periods: the heating season (autumn-winter) and the summer season. Automatic analysers installed at the monitoring stations which were used in the studies for determining inorganic compounds in the atmospheric air make it possible to obtain information connected with the concentration of a given inorganic compound at one-hour intervals. To better interpret and present the results obtained, Figure 4 presents the levels of

1 the NO₂, SO₂ and CO content determined in the atmospheric air in the monitored areas in the
2 form of average monthly concentrations.

3 As regards information summarized in Table 2, it can be noticed that the values of the annual
4 average concentrations of inorganic compounds determined in the atmospheric air in Tczew
5 were higher than in Sopot, virtually throughout the research period. This can be caused by the
6 fact that the monitoring station is situated in close vicinity of the main urban traffic node and
7 a company dealing with a system of waste collection and management, where trucks with
8 diesel engines are used.
9

10 The annual average concentration of nitrogen oxides determined in the air is an exception in
11 the areas monitored in 2014, which was higher in Sopot than in Tczew. The occurrence of
12 such a phenomenon can be caused by a higher intensity of use of vehicles powered by
13 combustion engines in close vicinity of the monitoring station in Sopot. Another reason,
14 which results from the fact that Sopot is one of the most popular seaside resorts and spa cities
15 situated in Poland can be a seasonal increase (especially in the summer) in the number of
16 vehicles with internal combustion engines in the monitored area.
17

18 While interpreting data presented graphically in Figure 4 and in Table 2, it can be noticed that
19 both in Tczew and in Sopot in the heating season (the autumn and winter period), the average
20 annual concentrations of inorganic compounds determined in the atmospheric air were much
21 higher than in the summer. The process of liquid fuel combustion in internal combustion
22 engines of vehicles is main source of emissions of nitrogen oxides and carbon monoxide into
23 the atmospheric air in urbanized areas. Just as in the previously described phenomenon of
24 benzene emissions into the atmospheric air, also in this case the quantity of determined
25 inorganic compounds (especially carbon monoxide resulting from incomplete combustion of
26 organic compounds) released into the air, is influenced by the optimal temperature of liquid
27 fuel combustion in the engine of a vehicle, an increase in the fuel density resulting from lower
28 air temperatures and the method of using the vehicle in the autumn and winter period.
29 Moreover, the quantity of carbon monoxides in the atmospheric air in the urbanized area is
30 influenced by the use of low-performance tiled stoves or furnaces where the solid fuel (coal)
31 burning process may not be complete. A comparison of the values of carbon monoxide
32 concentrations determined in the atmospheric air in monitored areas reveals a clear difference
33 between the heating season and the summer season. In the case of atmospheric air in Tczew in
34 the period of research, the carbon monoxide concentrations in the summer were on average by
35 40% lower than in the heating season. The interpretation of data on carbon monoxide
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51

1 concentrations in the atmospheric air in Sopot shows that carbon monoxide concentrations are
2 on average by 30% lower in the summer than in the heating season.

3 In very rare cases in urbanized areas, vehicles can also be a source of SO₂ emissions.
4 However, the condition must be met that the fuel used in vehicles is contaminated with
5 sulphur compounds. Interpretation of data summarized in Table 2 shows that sulphur dioxide
6 concentration in the atmospheric air in Tczew and Sopot is very low. This can result from the
7 fact that high-quality liquid fuels are used in vehicles, which are virtually free from sulphur
8 compounds. The presence of sulphur compounds in the atmospheric air in urbanized areas can
9 also result from burning low-quality coal contaminated with sulphur compounds. Such fuels
10 can be used for heating houses or flats using low-performance tiled stoves or furnaces. Due to
11 the fact that such buildings are situated in close vicinity of the monitoring station in Tczew,
12 the average annual concentrations of SO₂ in atmospheric air are higher than in Sopot. This
13 thesis is also confirmed by higher concentration of SO₂ in the atmospheric air in Tczew than
14 in Sopot also in the heating season (the autumn and winter period).
15
16
17
18
19
20
21
22
23
24
25
26

27 **3.4 Multivariate statistical data mining to detect relationships between measured** 28 **chemical compounds and identification of potential emission sources in the monitored** 29 **urban area** 30 31

32
33
34 As already mentioned to determine potential anthropogenic sources of emissions of chemical
35 compounds determined in the atmospheric air in the monitored areas, Hierarchical Cluster
36 Analysis (HCA) was applied. This multivariate statistical analysis involving the grouping of
37 variables or objects described by the variables (obtained from research results) made it
38 possible to obtain information on the occurrence of relationships between the results obtained
39 from the two monitored areas situated at a considerable distance from each other and differing
40 in topography of the area around the monitoring station.
41
42
43
44
45
46

47 In the first case, Hierarchical Cluster Analysis was separately performed on the input data sets
48 from Tczew and Sopot. The goal was to find links between variables (values of chemical
49 compound concentrations determined). The output of the clustering aimed to interpret
50 potential sources of emissions of chemical compounds determined in the atmospheric air in
51 both monitored areas. Figure 6 presents graphically the clustering results for variables in
Sopot and in Tczew in the years 2013-2014. The information presented in Figure 5 shows that
2 main clusters have been formed. Cluster 1 includes the chemical features toluene,
ethylbenzene, o-xylene, p, m-xylene and sum of xylenes and, additionally, the temperature

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000

being rather an outlier that member of cluster K1; Cluster 2 (K2) consists of the chemical variables benzene, NO₂, SO₂, CO. It could be concluded that there is a clear separation between organic pollutant sources (combustion sources – wood and coal or activity of local industrial centres) and inorganic pollutant sources (transport vehicles, soil and road dust). The inclusion of benzene into the group of inorganic pollutant sources results from the fact that vehicle traffic and the use of low-performance tiled stoves or furnaces in old buildings belong to main sources of emissions of this compounds. Moreover, this can lead to the conclusion that a potential increase in the activity of sources of emission of inorganic compounds into the atmospheric air may also influence an increase in the benzene content.

In order to confirm the results discussed above PCA was additionally carried out. Table 3 presents the results of the analysis for all data obtained from the monitoring tests in Sopot and Tczew from 2013 to 2014 (factor loadings table). The results listed in the Table 3 clearly indicate the role of 3 latent factors (PCs) which explain almost 90% of the total variance: PC1 – organic factor containing ethylbenzene, o-xylene, p, m-xylene and sum of xylenes, PC2 – inorganic factor reversely correlated to the temperature containing NO₂, SO₂, CO and as it was presented earlier benzene, PC3 – toluene factor with a separate impact.

For the PC2, the occurrence of the inverse relation between the content in the atmospheric air of chemical compounds (benzene, NO₂, SO₂, CO) and the air temperature, confirms, in principle, the output of the cluster analysis that a decrease in the temperature causes an increase in the intensity of sources of emissions of benzene, NO₂, SO₂ and CO into the atmospheric air. As it was mentioned before, these anthropogenic sources of emissions whose intensity depends on the season of the year (heating season) include, amongst other things, vehicle traffic (with internal combustion engines) and the low operational efficiency of the heating system in closed rooms where poor quality coal can be used as the fuel. Identification of a separate factor related only to the toluene content (PC3) in the atmospheric air in the monitored area may result from the fact that this compound comes probably from many sources of emission characterized by a varying degree of intensity, such as: activity of industrial centres situated near the monitoring stations, commercial plants, vehicle traffic involving cars with internal combustion engines, the use of low-performance tiled stoves or furnaces, petrol stations, rail traffic - diesel engines. Moreover, toluene is also commonly used in various branches of industry as a basic solvent at many production stages.

Next step in multivariate statistical data mining was clustering of the objects of observation (measuring points in different sampling seasons). Figure 6 presents graphically the results of hierarchical clustering of the individual periods of sample collection in the years 2013-2014.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52

It is clearly seen that two major clusters are formed for significance level $2/3 D_{\max}$ and three clusters – for significance level $1/3 D_{\max}$. In both situations there is distinct separation between winter samples (C1, C2, C3, C12, C13, C14, C15, C24 – all events from January, February, March and December for both years of observation) which form one of the clusters and summer samples (which include also autumn and spring observations). Special exception is November – November 2014 (C_23) belongs to the typical winter cluster while November 2013 – to the summer grouping (C_11). This separation is traditional for studies where seasonal properties are sought. In the case of the Tczew area a very well defined winter cluster is formed. As for the cluster created for the Sopot area, again two major sub-clusters are formed. In this location, however, the well expressed group of winter samples (C1, C2, C3, C4, C12, C13, C14, C15, C16, C24) also includes autumn events (C10, C11, C22, C23). For this location the seasonal pattern “winter” involved also months from late autumn. The second cluster consists of the remaining sampling events from summer and spring.

In general, the seasonal separation at both locations is very similar but, probably, due to meteorological and geographical conditions there is a slight difference in the grouping patterns. The major conclusion is that winter – summer seasonal separation is observed and proven. The winter – summer patterns are, in general, kept. There is also a relatively well expressed spatial separation between both locations – the Tczew and Sopot areas.

4. Conclusions

Result of determination of BTEX and CO, NO₂, SO₂ in the period from January 2013 to December 2014, to assess the quality of atmospheric air in two cities situated in northern Poland - Tczew and Sopot, were compared. The interpretation of the results of the monitoring research obtained and the use of basic statistical and parametric tools allowed preliminary identification of potential sources of emissions of pollutants into the atmospheric air in the monitored areas. The use of basic statistical tools made it possible to conclude that the pollutants determined in the atmospheric air (both in Tczew and in Sopot) can be classified in two main groups: the so-called inorganic group including concentrations of NO₂, CO, SO₂ and benzene and the so-called organic group including the concentrations of toluene, ethylbenzene and xylenes.

For Tczew, a medium-industrialized city, vehicle traffic involving cars with internal combustion engines has the main influence on the concentrations of benzene, ethylbenzene, xylenes, CO and NO₂. This results from the fact that the monitoring stations is located in very

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000

close vicinity of the main urban traffic node where the traffic is very often slowed down or stopped. Furthermore, as a result of the research, it was found that the level of the benzene and SO₂ content in the atmospheric air in Tczew can be significantly influenced by low-performance tiled stoves or furnaces in old residential buildings which use low-quality coal. Additionally, the very close location of recreational allotments and a plant dealing with the collection and management of different types of solid waste may also influence an increase in concentrations of the BTEX compounds, CO, SO₂ and NO₂ in the atmospheric air in the Tczew. Based on the interpretation of the results of statistical analysis, it was also concluded that the level of toluene in the atmospheric air can be influenced by other, additional sources of emissions such as rail traffic (diesel engines), the activity of industrial plants or commercial plants.

As regards, the atmospheric air quality in the resort city of Sopot, the traffic of vehicles with internal combustion engines is the main source of emissions of the BTEX compounds and NO₂, CO and SO₂. However, according to the research conducted and interpretations of the results obtained, it can be concluded that the intensity of the influence of mechanical vehicles on the quality of atmospheric air in Sopot is lower than in Tczew. This can result from the fact that the measuring station in Sopot is not located in close vicinity of the city's main traffic node. Moreover, during the interpretation of the results of the research, it can be concluded that the influence of the activity of low performance individual heating systems in old buildings or apartments (tiled stoves or furnaces), or large industrial centres on the atmospheric air quality in Sopot is negligible. Additionally, lower levels of the content of chemical compounds determined in Sopot than those determined in the atmospheric air in Tczew are result from the close vicinity of the Baltic Sea. This is probably related to the influence of the sea breeze on the type and quantity of pollutants in the atmospheric air. Despite the fact that Sopot is one of the most popular resorts and spa cities in Poland and it is visited by lots of tourists from Poland and abroad (who very often use cars), it does not have a significant influence on the quality of atmospheric air in terms of the level of the content of the BTEX compounds and NO₂, SO₂ and CO.

5. Acknowledgements

The authors are grateful to the Agency of the Regional Air Quality Monitoring Foundation in the Gdansk Metropolitan Area (ARMAAG Foundation) for the access to the monitoring stations and for providing meteorological data.

Conflict of interest

The authors have declared no conflict of interest.

6. References

Baltrenas, P., Baltrenaite, E., Šereviciene, V., Pereira, P., 2011. Atmospheric BTEX concentrations in the vicinity of the crude oil refinery of the Baltic region. *Environ. Monit. Assess.* 182, 115-127

Batterman, S., Jia, C., Hatzivasilis, G., 2007. Migration of volatile organic compounds from attached garages to residences: A major exposure source. *Environ. Res.* 104, 224-240

Bosco, M.L., Varrica, D., Dongarra, G., 2005. Case study: Inorganic pollutants associated with particulate matter from an area near a petrochemical plant. *Environ. Res.* 99, 18-30

Carlton, A.G., Wiedinmyer, C., Kroll, J.H., 2009. A review of Secondary Organic Aerosol (SOA) formation from isoprene. *Atmos. Chem. Phys.* 9, 4987-5005

Cerón-Bretón, J.G., Cerón-Bretón, R.M., Kahl, J.D.W., Ramírez-Lara, E., Guarnaccia, C., Aguilar-Ucán, C.A., Montalvo-Romero, C., Anguebes-Franceschi, F., López-Chuken, U., 2015. Diurnal and seasonal variation of BTEX in the air of Monterrey, Mexico: preliminary study of sources and photochemical ozone pollution. *Air Qual. Atmos. Health.* 8, 469-482

Chiang, P.C., Chiang, Y.C., Chang, E.E., Chang, S.C., 1996. Characteristics of hazardous air pollutants emitted from motor vehicles. *Toxicol. Environ. Chem.* 56, 85-104

Choi, W., Faloona, I.C., McKay, M., Goldstein, A.H., Baker, B., 2011. Estimating the Atmospheric Boundary Layer Height over Sloped, Forested Terrain from Surface Spectral Analysis during BEARPEX. *Atmos. Chem. Phys.* 11, 6837-6853

Comin, A.N., Miglietta, M.M., Rizza, U., Acevedo, O.C., Degrazia, G.A., 2015. Investigation of sea-breeze convergence in Salento Peninsula (southeastern Italy). *Atmos. Res.* 160, 68-79

Derwent, R.G., Jenkin, M.E., Sanders, S.M., Pilling, M.J., Simmonds, P.G., Passant, N.R., Dollard, G.J., Dumitrean, P., Kent, A., 2003. Photochemical ozone formation in northwest Europe and its control. *Atmos. Environ.* 37, 1983-1991

Directive 2008/50/EC of the European Parliament and of the Council

Dumanoglu, Y., Kara, M., Altioek, H., Odabasi, M., Elbir, T., Bayram, A., 2014. Spatial and seasonal variation and source apportionment of volatile organic compounds (VOCs) in a heavily industrialized region. *Atmos. Environ.* 98, 168-178

European Environment Agency and Joint Research Centre (Eds.), 2006. *Urban sprawl in Europe – The ignored challenge*, Copenhagen, pp. 1-56

Filho, J.P., Petrucci, J.F.S., Alves, A., 2015. Development of a simple method for determination of NO₂ in air using digital scanner images. *Talanta*. 14, 73-80

Finlayson-Pitts, B.J., Pitts Jr, J.N., 1997. Tropospheric Air Pollution: Ozone, Airborne Toxics, Polycyclic Aromatic Hydrocarbons, and Particles. *Science*. 276, 1045-1051

Fondelli, M.C., Bavazzano, P., Grechi, D., Gorini, G., Miligi, L., Marchese, G., Cenni, I., Scala, D., Chellini, E., Costantini, A.C., 2008. Benzene exposure in a sample of population residing in a district of Florence, Italy. *Sci. Total Environ.* 392, 41-49

Ghozikali, M.G., Heibati, B., Naddafi, K., Kloog, I., Oliveri Conti, G., Polosa, R., Ferrante, M., 2016. Evaluation of Chronic Obstructive Pulmonary Disease (COPD) attributed to atmospheric O₃, NO₂, and SO₂ using Air Q Model (2011–2012 year). *Environ. Res.* 144, 99-105

Hallquist, M., Wenger, J.C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N.M., George, C., Goldstein, A.H., Hamilton, J.F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M.E., Jimenez, J.L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T.F., Monod, A., Prévôt, A.S.H., Seinfeld, J.H., Surratt, J.D., Szmigielski, R., Wildt, J., 2009. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.* 9, 5155-5236

Hsieh, L.T., Wang, Y.F., Yang, H.H., Mi, H.H., 2011. Measurements and Correlations of MTBE and BETX in Traffic Tunnels. *Aerosol Air Qual. Res.* 11, 763-775

I.A.R.C (International Agency for Research on Cancer), 1982. *IARC Monographs on the evaluations of carcinogenicity risk of chemicals to humans. Some industrial chemicals and dyestuffs.* 29, pp. 93-148

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000

Król, S., Zabiegała, B., Namieśnik, J., 2012. Measurement of benzene concentration in urban air using passive sampling. *Anal. Bioanal. Chem.* 403, 1067-1082

Lan, T.T.N., Minh, P.A., 2013. BTEX pollution caused by motorcycles in the megacity of HoChiMinh. *J. Environ. Sci.* 25, 348-356

Marć, M., Bielawska, M., Wardencki, W., Namieśnik, J., Zabiegała, B., 2015. The influence of meteorological conditions and anthropogenic activities on the seasonal fluctuations of BTEX in the urban air of the Hanseatic city of Gdansk, Poland. *Environ. Sci. Pollut. Res.* 22, 11940-11954

Marć, M., Namieśnik, J., Zabiegała, B., 2014a. BTEX concentration levels in urban air in the area of the Tri-City agglomeration (Gdansk, Gdynia, Sopot), Poland. *Air Dual. Atmos. Health.* 7, 489-504

Marć, M., Zabiegała, B., Namieśnik, J., 2014b. Application of passive sampling technique in monitoring research on quality of atmospheric air in the area of Tczew, Poland. *Inter. J. Environ. Anal. Chem.* 94, 151-167

Mavrakou, T., Philippopoulos, K., Deligiorgi, D., 2012. The impact of sea breeze under different synoptic patterns on air pollution within Athens basin. *Sci. Total Environ.* 433, 31-43

Miao, Y., Hu, X.M., Liu, S., Qian, T., Xue, M., Zheng, Y., Wang, S., 2015. Seasonal variation of local atmospheric circulations and boundary layer structure in the Beijing-Tianjin-Hebei region and implications for air quality. *J. Adv. Model. Earth Syst.* 10.1002/2015MS000522.

Miller, L., Lemke, L.D., Xu, X., Molaroni, S.M., You, H., Wheeler, A.J., Booza, J., Grgicak-Mannion, A., Krajenta, R., Graniero, P., Krouse, H., Lamerato, L., Raymond, D., Reiners, J., Weglicki, L., 2010. Intra-urban correlation and spatial variability of air toxics across an international airshed in Detroit, Michigan (USA) and Windsor, Ontario (Canada). *Atmos. Environ.* 44, 1162-1174

1 Miller, L., Xu, X., Wheeler, A., Atari, D.O., Grgicak-Mannion, A., Luginaah, I. 2011. Spatial
2 variability and application of ratios between BTEX in two Canadian cities. *Sci. World J.* 11,
3 2536-2549
4

5
6 Monod, A., Sive, B.C., Avino, P., Chen, T., Blake, D.R., Sherwood Rowland, F., 2001.
7 Monoaromatic compounds in ambient air of various cities: a focus on correlations between
8 the xylenes and ethylbenzene. *Atmos. Environ.* 35, 135-149
9

10
11
12 Oros, D.R., Ross, J.R.M., Spies, R.B., Mumley, T., 2007. Polycyclic aromatic hydrocarbon
13 (PAH) contamination in San Francisco Bay: A 10-year retrospective of monitoring in an
14 urbanized estuary. *Environ. Res.* 105, 101-118
15
16

17
18
19 Papanastasiouand, D.K., Melas, D., 2009. Climatology and impact on air quality of sea breeze
20 in an urban coastal environment. *Int. J. Climatol.* 29, 305-315
21
22

23
24 Pariselli, F., Sacco, M.G., Ponti, J., Rembges, D., 2009. Effects of toluene and benzene air
25 mixtures on human lung cells (A549). *Exp. Toxicol. Pathol.* 61, 381-386
26
27

28
29 Plaisance, H., Leonardis, T., Gerboles, M., 2008. Assessment of uncertainty of benzene
30 measurements by Radiello diffusive sampler, *Atmos. Environ.* 42, 2555-2568
31
32

33
34 Przyk, E., Switaj-Zawadka, A., Konieczka, P., Szczygelska-Tao, J., Biernat, J.F., Namieśnik,
35 J., 2003. Thermal decomposition of surface compounds for the generation of small quantities
36 of acetaldehyde Calibration of a thermal desorption–gas chromatography–flame ionization
37 detection, *Anal. Chim. Acta.* 488, 89-96
38
39

40
41
42 Rad, H.D., Babaei, A.A., Goudarzi, G., Angali, K.A., Ramezani, Z., Mohammadi, M.M.,
43 2014. Levels and sources of BTEX in ambient air of Ahvaz metropolitan city. *Air Qual.*
44 *Atmos. Health.* 7, 515-524
45
46

47
48
49 Schiavon, M., Redivo, M., Antonacci, G., Rada, E.C., Ragazzi, M., Zardi, D., Giovannini, L.,
50 2015. Assessing the air quality impact of nitrogen oxides and benzene from road traffic and
51 domestic heating and the associated cancer risk in an urban area of Verona (Italy). *Atmos.*
Environ. 120, 234-243

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000

Shao, M., Zhang, Y., Zeng, L., Tang, X., Zhang, J., Zhong, L., Wang, B., 2009. Ground-level ozone in the Pearl River Delta and the roles of VOC and NO_x in its production. *J. Environ. Manage.* 90, 512-518

Stranger, M., Krata, A., Kontozova-Deutsch, A., Bencs, L., Deutsch, F., Worobiec, A., Naveau, I., Roekens, E., Van Grieken, R., 2008. Monitoring of NO₂ in the ambient air with passive samplers before and after a road reconstruction event. *Microchem. J.* 90, 93-98

Tao, S., Wang, Y., Wu, S., Liu, S., Dou, H., Liu, Y., Lang, C., Hu, F., Xing, B., 2007. Vertical Distribution of Polycyclic Aromatic Hydrocarbons in Atmospheric Boundary Layer of Beijing in Winter. *Atmos. Environ.* 41, 9594-9602

Vandeginste, B., Massart, D.L., Buydens, L., DeJong, S., Lewi, P., Smeyers-Verbeke, J., 1998. *Handbook of Chemometrics and Qualimetrics. Part A and B.* Elsevier, Amsterdam.

Vardoulakis, S., Solazzo, E., Lumberras, J., 2011. Intra-urban and street scale variability of BTEX, NO₂ and O₃ in Birmingham, UK: implications for exposure assessment. *Atmos. Environ.* 45, 5069-5078

Wang, X., Sheng, G., Fu, J., Chan, C., Lee, S.C., Chan, L.Y., Wang, Z., 2002. Urban roadside aromatic hydrocarbons in three cities of the Pearl River Delta, People's Republic of China. *Atmos. Environ.* 36, 5141-5148

Woolfenden, E., 2010. Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air Part 1: Sorbent-based air monitoring options. *J. Chromatogr. B.* 1217, 2674-2684

Wu, J., Wilhelm, M., Chung, J., Ritz, B., 2011. Comparing exposure assessment methods for traffic-related air pollution in an adverse pregnancy outcome study. *Environ. Res.* 111, 685-692

Yurdakul, S., Civan, M., Tuncel, G., 2013. Volatile organic compounds in suburban Ankara atmosphere, Turkey: sources and variability. *Atmos. Res.* 120-121, 298-311

Zabiegała, B., Partyka, M., Gawrońska, A., Wasilewska, A., Namieśnik J., 2007. Screening of volatile organic compounds as a source for indoor pollution. *Int. J. Environment and Health.* 1, 13-28

1 Zabiegała, B., Sarbu, C., Urbanowicz, M., Namieśnik, J., 2011. A Comparative Study of the
2 Performance of Passive Samplers. *J. Air Waste Manage. Assoc.* 61, 260-268.

3
4 Zalel, A., Yuval., Broday, D.M., 2008. Revealing source signatures in ambient BTEX
5 concentrations. *Environ. Pollut.* 156, 553-562
6

7
8
9 Zhang, H., Wang, Y., Hu, J., Ying, Q., Hu, X.M., 2015. Relationships between
10 meteorological parameters and criteria air pollutants in three megacities in China. *Environ.*
11 *Res.* 140, 242-254
12
13

14
15
16 Zhang, J., Wang, T., Chameides, W., Cardelino, C., Blake, D., Streets, D., 2008. Source
17 characteristics of volatile organic compounds during high ozone episodes in Hong Kong,
18 Southern China. *Atmos. Chem. Phys.* 8, 4983-4996
19
20
21

22 **7. Figure captions**

23
24 **Figure 1.** Location of the air quality monitoring stations AM6 in Sopot and (AM7) in Tczew,
25 Poland.
26

27
28 **Figure 2.** The average monthly time-weighted benzene concentration determined in the
29 atmospheric air in the period 2013-2014 in the Tczew and Sopot area.
30

31
32 **Figure 3.** The average monthly time-weighted toluene, ethylbenzene and sum of xylenes
33 concentration determined in the atmospheric air in the period 2013-2014 in the Tczew and
34 Sopot area.
35

36
37 **Figure 4.** The monthly average concentrations of inorganic compounds – NO₂, SO₂ and CO
38 determined in the atmospheric air in the period 2013-2014 in the Tczew and Sopot area.
39

40
41 **Figure 5.** Clustering of variables for Sopot and Tczew data obtained in the period 2013-2014.
42

43
44 **Figure 6.** Clustering of sampling events from Sopot and Tczew data obtained in the period
45 2013-2014 where: C_1 is January 2013, C_2 – February 2013 and so on till C-24 – December
46 2014.
47

48
49 **Supplementary Figure 1.** Annual wind rose in Sopot and Tczew area in the period 2013-
50 2014.
51



Table 1. The average BTEX inter-species concentration ratios in the monitoring urban area (Tczew and Sopot) in the period 2013-2014

The average BTEX inter-species ratios in the monitoring area in 2013				
Sampling area	Benzene	Toluene	Ethylbenzene	Sum of Xylenes
Tczew	0.76	2.24	1	4.48
Sopot	2.30	5.88	1	4.20
Sampling area	<i>Tol/Benz</i>	<i>(m,p)-Xyl/Benz</i>	<i>o-Xyl/Benz</i>	<i>(m,p)-Xyl/Ethylbenz</i>
Tczew	2.96	4.02	1.90	3.04
Sopot	2.56	1.17	0.65	2.70
The average BTEX inter-species ratios in the monitoring area in 2014				
Sampling area	Benzene	Toluene	Ethylbenzene	Sum of Xylenes
Tczew	1.23	2.82	1	3.98
Sopot	2.42	4.29	1	4.07
Sampling area	<i>Tol/Benz</i>	<i>(m,p)-Xyl/Benz</i>	<i>o-Xyl/Benz</i>	<i>(m,p)-Xyl/Ethylbenz</i>
Tczew	2.29	2.22	1.01	2.74
Sopot	1.77	1.08	0.59	2.63

Table 2. Annual average concentration of measured inorganic compounds in atmospheric air over the monitoring urban area in the period 2013-2014.

Concentration of measured inorganic compounds in atmospheric air in 2013						
Parameter	NO₂ [µg/m³]		SO₂ [µg/m³]		CO [µg/m³]	
	Tczew	Sopot	Tczew	Sopot	Tczew	Sopot
Average ± SD	14.1 ± 2.6	12.2 ± 2.9	6.0 ± 2.1	5.2 ± 1.8	385 ± 108	299 ± 57
Median	13.8	12.5	5.4	4.6	365	285
Max	18.8	17.0	10.0	9.3	582	376
Min	9.4	8.0	3.8	3.4	256	212
Average heating season ± SD	15.6 ± 2.1	14.2 ± 1.8	7.3 ± 1.9	6.3 ± 1.6	458 ± 80	336 ± 42
Average summer season ± SD	12.0 ± 1.6	9.4 ± 1.2	4.3 ± 0.5	3.7 ± 0.3	282 ± 15	248 ± 25
Concentration of measured inorganic compounds in atmospheric air in 2014						
Parameter	NO₂ [µg/m³]		SO₂ [µg/m³]		CO [µg/m³]	
	Tczew	Sopot	Tczew	Sopot	Tczew	Sopot
Average ± SD	13.0 ± 3.1	13.8 ± 4.9	4.9 ± 1.2	4.8 ± 2.0	330 ± 114	317 ± 93
Median	13.8	13.5	4.9	4.6	330	301
Max	17.1	25.4	7.6	8.9	541	528
Min	8.1	8.3	3.3	2.3	168	215
Average heating season ± SD	15.4 ± 1.4	16.5 ± 4.5	5.7 ± 1.0	5.7 ± 2.0	405 ± 80	367 ± 91
Average summer season ± SD	10.3 ± 2.0	10.0 ± 1.9	3.9 ± 0.6	3.6 ± 1.1	225 ± 47	247 ± 31

SD – standard deviation

Table 3. Factor loadings for all data combined from Tczew and Sopot area (marked loadings are statistically significant)

	Factor - 1	Factor - 2	Factor - 3
Benzene	0.057	0.725	0.556
Toluene	0.225	0.071	0.923
Etylbeznene	0.973	-0.005	0.158
o-Xylene	0.970	-0.072	0.099
P,m-Xylene	0.993	-0.034	0.074
Sum of Xylenes	0.995	-0.046	0.083
NO₂	0.015	0.882	0.159
SO₂	-0.120	0.891	-0.217
CO	0.032	0.912	0.179
Temperature	0.127	-0.897	-0.007
Expl.Var	3.949	3.747	1.312
Prp.Totl	39.5%	37.5%	13.1%

* only statistically significant loadings are marked by bold

Figure 1
[Click here to download high resolution image](#)

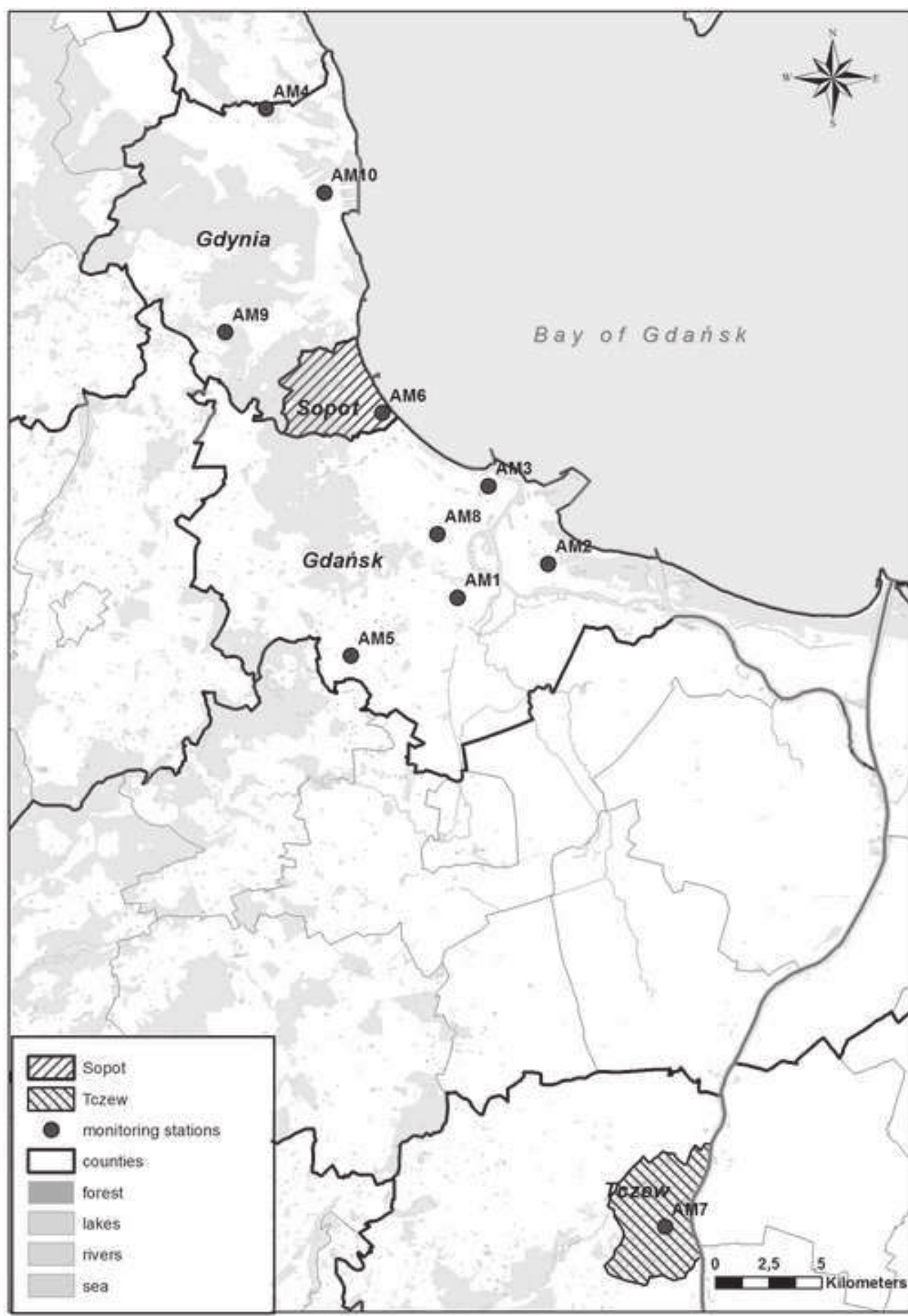


Figure 2

[Click here to download high resolution image](#)

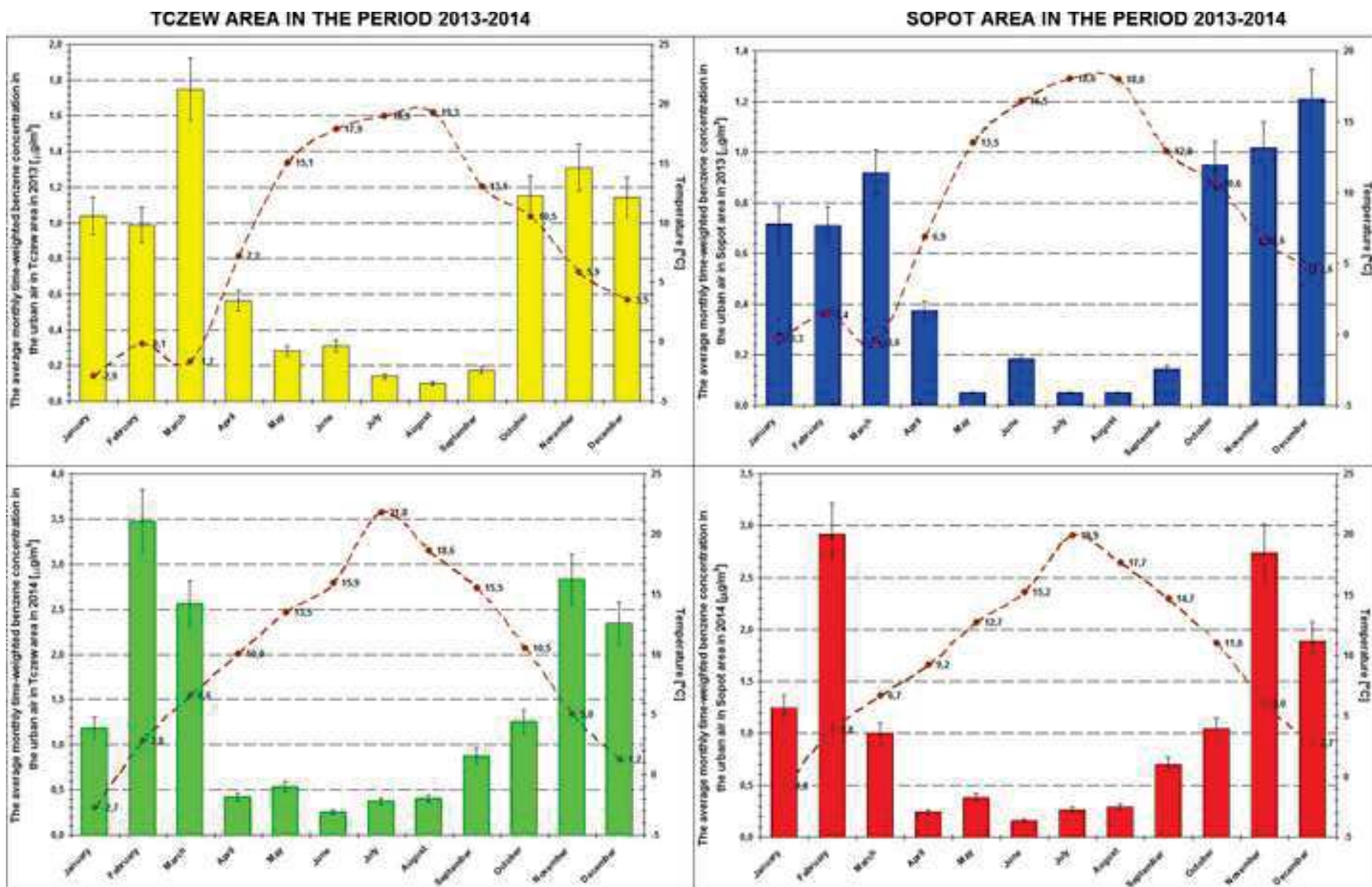


Figure 3
[Click here to download high resolution image](#)

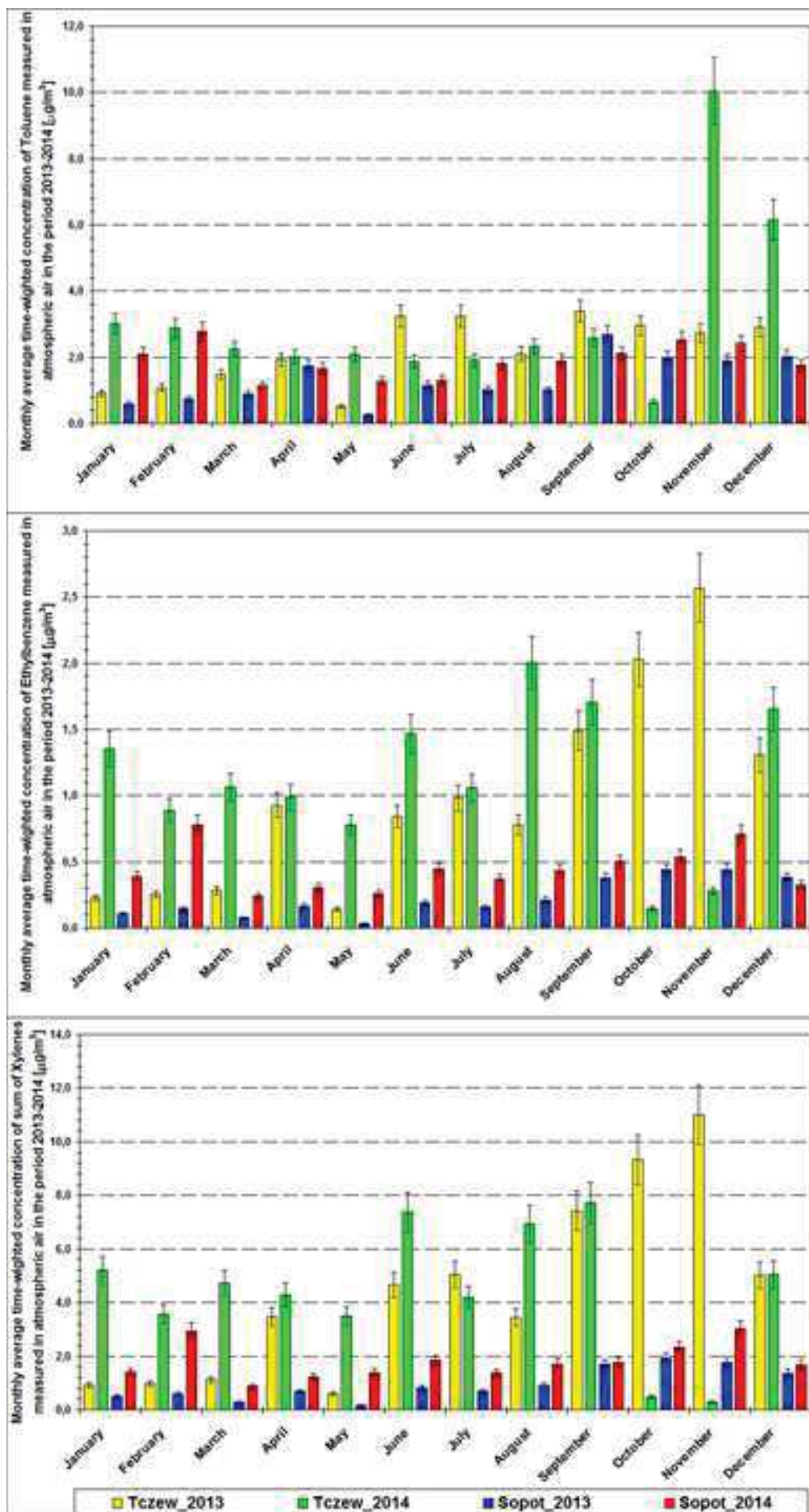


Figure 4
[Click here to download high resolution image](#)

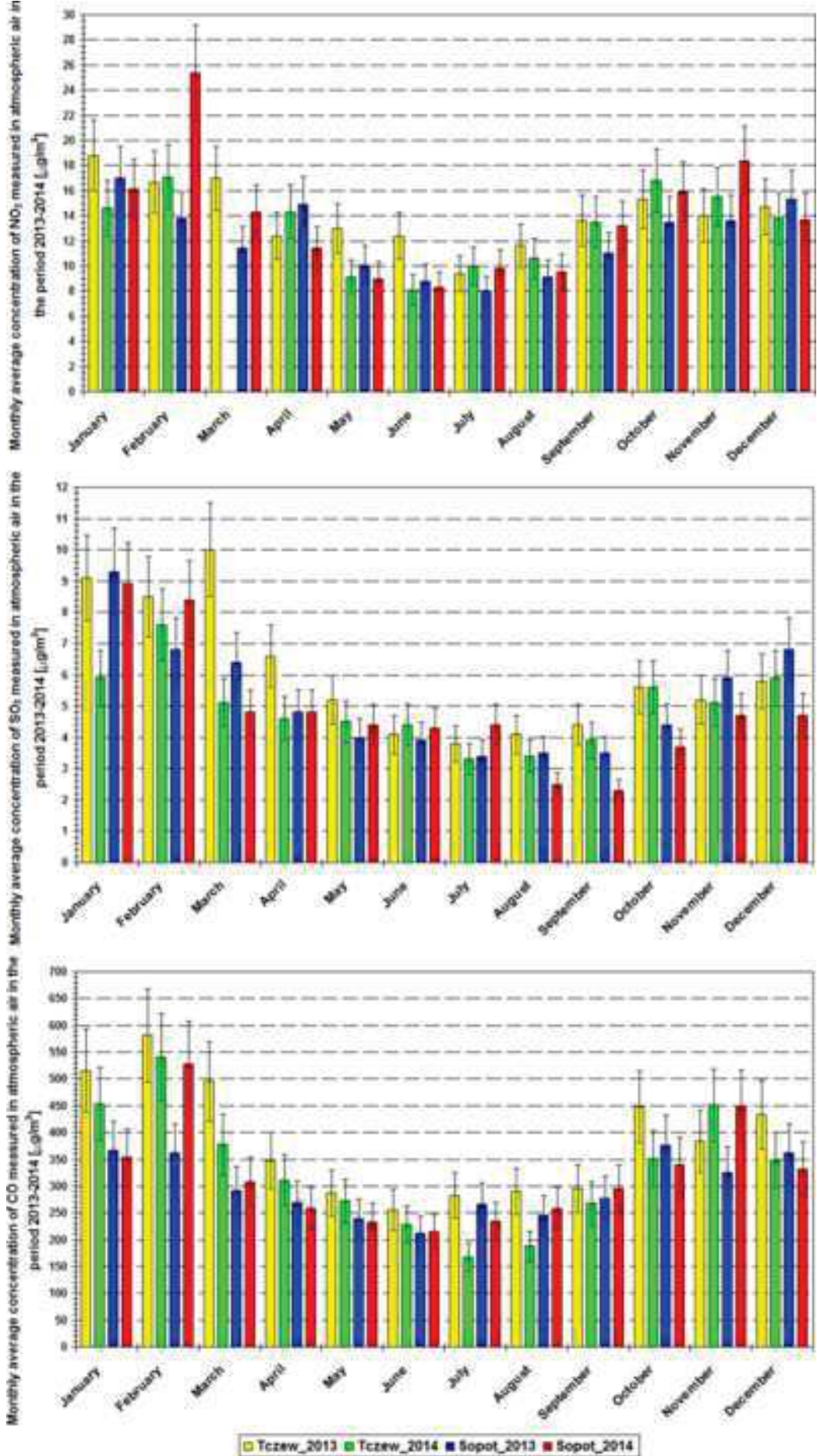


Figure 5
[Click here to download high resolution image](#)

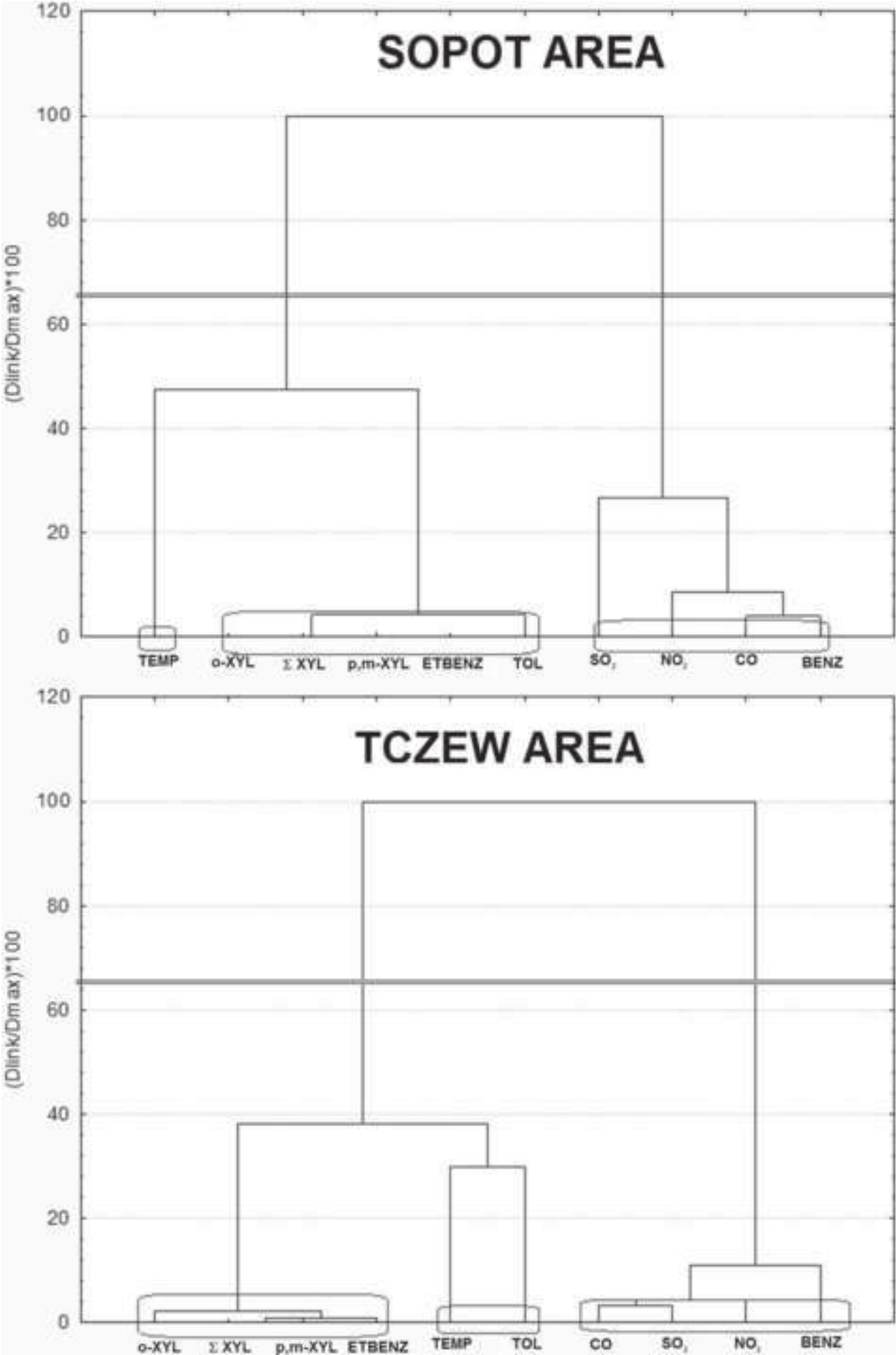


Figure 6
[Click here to download high resolution image](#)

