

Contents

1	Introduction	3
1.1	Problem definition	3
1.2	Aims and scope	4
1.3	State of the art	5
1.4	Study area	6
1.4.1	Topography	6
1.4.2	Climate	6
1.4.3	Soil	7
1.4.4	Land use and emission scenarios	7
2	Pollutant accumulation on <i>Pinus nigra</i> needles	9
2.1	Accumulation histories of magnetic particles	9
2.1.1	Sampling methods	10
2.1.2	Analytical Methods	11
2.1.3	Results	13
2.1.4	Discussion	20
2.1.5	Conclusions	25
2.2	Accumulation histories of major and trace elements	26
2.2.1	Sampling methods	27
2.2.2	Analytical Methods	27
2.2.3	Results	28
2.2.4	Discussion	32
2.2.5	Conclusions	38
2.3	Accumulation history of airborne phenanthrene derivatives	39
2.3.1	Sampling	42
2.3.2	Analytical Methods	42
2.3.3	Results	43
2.3.4	Discussion	47
2.3.5	Conclusions	53
3	Cologne City - local-scale biomonitoring	54
3.1	Cologne City air quality - optical and magnetic properties	54
3.1.1	Sampling	55
3.1.2	Analytical methods	57
3.1.3	Results	58
3.1.4	Discussion	63
3.1.5	Conclusions	66
3.2	Cologne City air quality - major and trace elements	67
3.2.1	Sampling	69
3.2.2	Analytical methods	69
3.2.3	Results and discussion	70
3.2.4	Summary and Conclusions	78
3.3	Cologne City air quality - polycyclic aromatic hydrocarbons (PAH)	78
3.3.1	Sampling	79

3.3.2	Methods	80
3.3.3	Results and discussion	81
3.3.4	Summary and Conclusions	91
4	Cologne Conurbation - regional-scale biomonitoring	94
4.1	Cologne Conurbation air quality - enviromagnetic proxies	94
4.1.1	Sampling	94
4.1.2	Analytical methods	95
4.1.3	Results	95
4.1.4	Discussion	97
4.1.5	Conclusion	100
4.2	Cologne Conurbation air quality - major and trace elements	101
4.2.1	Sampling methods	101
4.2.2	Analytical methods	101
4.2.3	Results	102
4.2.4	Discussion	105
4.2.5	Conclusions	116
4.3	Cologne Conurbation air quality - parent PAH	117
4.3.1	Sampling	117
4.3.2	Analytical methods	118
4.3.3	Results	119
4.3.4	Discussion	125
4.3.5	Conclusions	137
4.4	Cologne Conurbation air quality - parent and alkylated three-ring PAH	138
4.4.1	Sampling	139
4.4.2	Analytical methods	139
4.4.3	Results and Discussion	140
4.4.4	Conclusions	146
4.5	Cologne Conurbation air quality - a synthesis	146
4.5.1	Sampling and Analysis	147
4.5.2	Results	147
4.5.3	Discussion	152
4.5.4	Conclusion	159
5	Synthesis and outlook	160
Appendix		212

List of Figures

1	Topography and soils of the Cologne Conurbation.	6
2	Land use and emission characteristics of the Cologne Conurbation.	7
3	Land use and locations of temporally-resolved sample set in the Cologne Conurbation	10
4	Biplots of physiological versus enviromagnetic properties.	14
5	Electron microprobe scan of needle surface.	15
6	Mineral and grain size diagnostic enviromagnetic parameters	16
7	Magnetic concentration parameters on pine needles in the Cologne Conurbation	18
8	Temporal accumulation trends of magnetic parameters.	19
9	Variations of enviromagnetic grain size and oxidation parameters versus time.	21
10	Schematic diagram displaying hypothetical end-member grain size distribution curves	24
11	Element concentrations of <i>Pinus nigra</i> needles versus exposure time.	29
12	Element enrichment factors for summer and winter samples.	32
13	Element enrichment factors of pine needles versus exposure time.	33
14	Identification of dimethylphenanthrenes	43
15	PAH-3 concentrations versus needle exposure time.	48
16	Phenanthrenes ratios versus needle exposure time.	51
17	Land use and sampling sites in Cologne City.	56
18	SEM and microprobe analysis of pine needle surfaces.	57
19	Sample treatment: cleaning with water and organic solvents.	60
20	Correlation of iron and magnetite concentration of pine needles.	60
21	High temperature susceptibility curve.	61
22	Magnetic properties of pine needles in Cologne City.	62
23	Grain-size effects on susceptibility and ARM analysis.	63
24	Seasonal changes in enviromagnetic properties of needles.	64
25	Enviromagnetic isopleths maps of Cologne City, I	65
26	Enviromagnetic isopleths maps of Cologne City, II	66
27	Trace element concentration ranges of pine needles in Cologne City.	70
28	Trace element and sulfur concentrations of pine needles in Cologne City.	72
29	Seasonal variations of elements on a pine in Cologne City.	74
30	Annual variations of elements in pine needles in the Dübener Heath, NE-Germany.	75
31	Biplots of traffic pollution proxy iron against lead, cadmium and zinc.	76
32	Isopleths maps of Cd and Pb in Cologne City	77
33	Generalized model of PAH transportation and deposition.	80
34	SEM scans of <i>Pinus nigra</i> needle surfaces.	82
35	Seasonal variation in wax and PAH content of pine needles.	83
36	Relation between wax content and total PAH load of pine needles.	86
37	PAH distribution profiles of pine and spruce needles.	88
38	Bivariate plots of selected PAH ratios.	89
39	Correlation of a magnetic concentration parameter to pyrene.	90

40	Isopleths maps of PAH concentrations and isomer ratios in Cologne City.	92
41	Enviromagnetic properties on pine needles in the Cologne Conurbation.	97
42	Isopleths maps of enviromagnetic proxies in the Cologne Conurbation.	99
43	Element enrichment (EF) on pine needles in the Cologne Conurbation.	105
44	Elements of geogenic origin in the Cologne Conurbation.	108
45	Elements attributed to local geogenic sources and mineralic input.	109
46	Elements attributed to traffic emissions.	112
47	Elements attributed to industrial emissions.	113
48	Elements attributed to municipal waste incineration.	115
49	Accumulation trends of PAH on pine needles in the Cologne Conurbation.	126
50	Isopleths maps of PAH on pine needles in the Cologne Conurbation.	128
51	Spatial distribution of Ip, BeP, BbjFla, Py, BaA, and CpcdPy in the Cologne Conurbation.	130
52	Trends of PAH ratios versus time of needle exposure.	134
53	Bivariate plots of source indicative PAH.	136
54	Isopleths maps of PAH ratios.	137
55	Locations, emission characteristics and spatial analyses of PAH-3 in the Cologne Conurbation.	142
56	Biplots of selected phenanthrenes concentrations.	143
57	Bivariate plots of PAH, elements and enviromagnetic proxies.	151
58	Pollutant distribution characteristic for urban emissions.	154
59	Pollutant distribution characteristic for lignite combustion and geogenic dust.	156
60	Pollutant distribution characteristic for waste incineration and industrial emissions.	158
61	Molecular structure of parent and alkylated PAH	191
62	Land use and emission characteristics of the Cologne Conurbation (transparency).	218

List of Tables

1	Emission scenarios in the Cologne Conurbation	11
2	Statistical analyses of enviromagnetic parameters	12
3	Spearman's rank correlation of enviromagnetic and plant physiological parameters.	13
4	Weighted means of element concentrations on pine needles.	30
5	Kruskal-Wallis- <i>H</i> test for major and trace elements.	30
6	Element enrichment factors.	31
7	Factor analyses of major and trace element EFs.	35
8	Physico-chemical properties of PAH-3.	41
9	Statistics of PAH accumulation on pines.	45
10	Linear regression parameters for PAH-3 versus time.	45
11	Compilation of trace element data for pine needles.	71
12	Compilation of PAH biomonitoring data for pine needles.	85

13	Source diagnostic potential of enviromagnetic biomonitoring in the Cologne Conurbation	100
14	Element loads on pine needles in the Cologne Conurbation.	102
15	Factor analyses of element loads on pine needles in the Cologne Conurbation.	104
16	Sources for major and trace elements in the Cologne Conurbation.	116
17	Abbreviations and classification of PAH.	118
18	Statistics of PAH accumulation on pine needles.	120
19	PAH median concentrations on pine needles in the Cologne Conurbation.	121
20	Factor analysis of PAH concentrations on pine needles in the Cologne Conurbation.	131
21	Source diagnostic potential of PAH biomonitoring in the Cologne Conurbation.	138
22	Factor analysis of PAH-3 concentrations on pine needles.	140
23	Source diagnostic compounds and proxies established on pine needles in the Cologne Conurbation.	148
24	Spearman´s rank correlation of organic, inorganic and enviromagnetic air quality proxies.	150
25	Abbreviations	190
26	Enviromagnetic and physiological parameters, temporal study, I	192
27	Enviromagnetic and physiological parameters, temporal study, II	193
28	Enviromagnetic and physiological parameters, temporal study, III	194
29	Averaged magnetic properties for sampling sites	195
30	Mean, medians and standard deviation of magnetic properties	196
31	Enviromagnetic and physiological parameters for each needle cohort	197
32	Major and trace element concentrations temporal study	198
33	Enrichment factors (EF), temporal study	199
34	Concentration of 3-ring PAH on pine needles, temporal study	200
35	Enviromagnetic parameters on pine needles in the Cologne Conurbation.	201
36	Major and trace element concentrations and enrichment factors (EF) on pine needles in the Cologne Conurbation (data sheet 1-10).	202
37	Major and trace elements in the Cologne Conurbation, II	203
38	Major and trace elements in the Cologne Conurbation, III	204
39	Major and trace elements in the Cologne Conurbation, IV	205
40	Major and trace elements in the Cologne Conurbation, V	206
41	Major and trace elements in the Cologne Conurbation, VI	207
42	Major and trace elements in the Cologne Conurbation, VII	208
43	Major and trace elements in the Cologne Conurbation, VIII	209
44	Major and trace elements in the Cologne Conurbation, IX	210
45	Major and trace elements in the Cologne Conurbation, X	211
46	Parent PAH on pine needles of different age needle age, sheet I.	212
47	Parent PAH on pine needles of different age needle age, sheet II.	213
48	Parent PAH in <i>Pinus nigra</i> needles of the Cologne Conurbation, I.	214
49	Parent PAH in <i>Pinus nigra</i> needles of the Cologne Conurbation, II.	215
50	Three-ring PAH in <i>Pinus nigra</i> needles of the Cologne Conurbation, I.	216
51	Three-ring PAH in <i>Pinus nigra</i> needles of the Cologne Conurbation, II.	217