Atmospheric input of anthropogenic organic particles into soils

Déposition atmosphérique de matière organique anthropogène dans les sols

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Introduction

This study addresses an important gap in our understanding of the quantitative importance of anthropogenically derived atmospheric organic particles in soils. Long-term disperse emissions of organic particles from industrial processes (coal, soot, coke) may accumulate in soils of industrialized areas. Such compounds can increase the quantity of organic matter in soils drastically and consequently may affect physical and chemical soil properties. The objective of this study was to determine the impact of atmospheric input of organic particles on soils from heavily industrialized areas. Two soils (Haplic Podzol, Haplic Phaeozem) presumably comprising anthropogenic atmospheric organic particles are compared to natural non-influenced soils as references. However, an input of organic particles was not visible macroscopically in all investigated soils.

Organic matter was investigated in non-fractionated soils and in particle size fractions. Content and structure of organic matter was investigated by a suite of complementary classical methods (elemental analysis, microscopy), spectroscopic methods (^{13}C CP MAS NMR spectroscopy) and ^{14}C dating.

Material and Methods

Two soils suspected to contain atmospheric organic particles from coal industries were sampled in the highly industrialized region of Halle (Haplic Phaeozem) and the Ruhr area (Haplic Podzol) in Germany and were classified according to FAO (1994). In these regions coal has been used for industrial processes since the beginning of the 19th century. The influenced soils are situated 2 to 10 km downwind of possible sources of pollution and are compared to corresponding reference soils from non-influenced sites. These natural reference soils were chosen to correspond as close as possible, regarding pedogenesis,

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texture, vegetation, soil type and climate, and were situated within 30 km distance from the influenced soil. Table 1 gives a short description of the investigated soils, detailed information is provided by SCHMIDT (1998).

Bulk material and particle size fractions of A and B horizons are studied. Particle size fractionation was performed by a combination of wet sieving and sedimentation following ultrasonic dispersion with 440 J/ml of ultrasonic energy (SCHMIDT *et al.*, 1998a, 1998b). A creation of artifacts due to ultrasonic dispersion was not detected (SCHMIDT *et al.*, 1997b). Carbon an nitrogen contents of the bulk soils and the various fractions were determined in duplicate with a Leco CNS 2000. Solid-state ^{13}C NMR spectra were obtained on a Bruker MSL 100 and a Chemagnetics M 100 (2.35 T) using the technique of cross polarization and magic angle spinning (CP MAS). To improve the resolution of the NMR spectra, samples were extracted with HF (10 %) according to SCHMIDT *et al.* (1997a). Experimental details of ^{14}C dating are provided by BECKER-HEIDMANN (1989).

Table 1: Chemical and physical characteristics of the soils. The soil influenced by atmospheric organic particles (*influenced*) is compared to a corresponding natural reference soil (*non-influenced*).

horizon[a]	depth	particle size class[b]			pH	OC	total N	C/N	bulk density
	cm	*sand*	*silt*	*clay*	*CaCl₂*	*g/kg*			*Mg/m³*
(a) Haplic Phaeozem									
influenced									
Ap1	0-25	8.1	79.4	12.7	6.2	138.6	3.6	39	0.84
Ap2	25-50	7.1	80.9	12.0	6.3	140.6	3.5	40	0.85
BvCv	50-90	4.2	78.5	16.9	7.4	12.4	1.1	11	1.42
non-influenced									
Ap	0-20	31.0	49.9	19.3	5.9	22.6	2.0	11	1.45
Ah	20-50	31.8	49.0	19.2	6.1	21.0	1.9	11	1.51
lCAh	>50	28.3	49.7	22.1	6.6	12.9	1.3	10	1.69
(b) Haplic Podzol									
influenced									
Aeh	0-8	73.7	20.9	5.9	3.1	102.0	3.8	27	0.80
Ae	8-17	91.0	8.8	1.3	3.2	30.1	1.0	30	1.32
Bhs	17-22	80.3	14.8	4.8	3.2	17.0	0.6	28	1.45
non-influenced									
Aeh	0-12	92.4	6.5	1.3	3.1	14.5	0.4	36	1.40
Ae	12-25	92.2	8.5	0.3	3.3	3.1	0.2	16	1.41
Bh	25-31	87.1	8.9	4.1	2.9	34.5	1.0	35	1.23
Bs	31-35	85.0	11.4	3.7	3.4	13.6	0.6	23	1.28

[a] horizon designations according to AG Boden (1994)
[b] sand: 63 to 2000 μm, silt: 6 to 63 μm, clay: < 2 μm

Results and Discussion

The chemical and physical characteristics (Table 1) of the natural reference soils are in the range typically expected for these soil types. Compared to the corresponding influenced soils, also the particle size distributions are rather similar with only minor differences, which may be explained by natural variation of the parent sediment. Also the pH is in the range expected for these soil types and does not exhibit evident differences between influenced and natural reference soil.

Comparing the elemental composition, striking differences between influenced and reference soil become apparent for the Ap and Aeh horizon, respectively. In the Ap1 horizon of the influenced Phaeozem the content of organic carbon is increased by a factor of 6 and a factor of 2 for N compared to the reference soil. Also for the Aeh horizon from the influenced Podzol organic matter content is higher compared to the non-influenced soil (C: factor 7 and N: factor 10). Bulk densities of both influenced horizons are lower compared to the reference horizons. These results indicate the input of a C-rich material with a low density in both investigated soils.

Figure 1 gives the C distribution of the particle size fractions after complete dispersion of the topsoils (Ap and Aeh horizon). Particle size fractions of both non-influenced soils show a distribution of organic C between the fractions, which is typical for natural soils. The clay and fine silt fractions, and to a lesser degree the medium silt fractions, comprise the majority of the whole soil C. A completely different pattern can be observed for the influenced soils. Here the sand fractions comprise high proportions of the whole soil C, whereas fine silt and clay fractions contribute only low proportions to the whole soil C. This implies that the airborne organic particles mainly accumulated in the sand to medium silt size fractions.
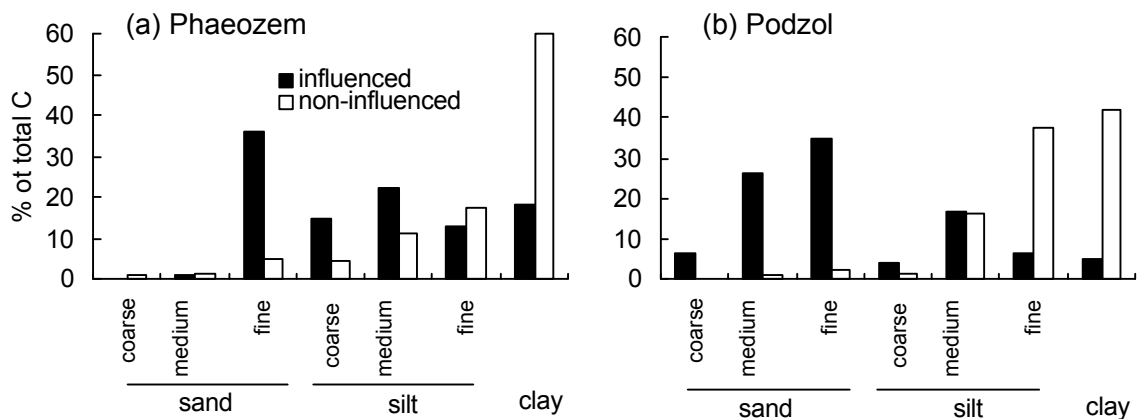

Figure 1: Distribution of organic C between particle size fractions obtained from (a) the Ap horizons of a Phaeozem and (b) the Aeh horizon of a Podzol. A soil influenced by atmospheric organic particles (*influenced*) and a corresponding natural reference soil (*non-influenced*) are compared. The fractions are coarse sand (2000-630 μm), medium sand (630-

200 μm), fine sand (63-200 μm), coarse silt (20-63 μm), medium silt (6-20 μm), fine silt (2-6 μm), and clay (<2 μm).

^{13}C CP MAS NMR spectroscopy

As an example, the spectra of the bulks soils from the Phaeozem are presented here. Figure 2 shows the solid-state ^{13}C CP MAS NMR spectra obtained from the plowed A horizons of the non-influenced (Ap) and the influenced Phaeozem (Ap1) compared to spectra of the anthropogenic organic particles tentatively deposited in the Ap1 horizon, i. e., brown coal and combustion residues like soot. The spectrum from the non-influenced Ap horizon reveals a typical pattern of organic matter which can be found in Phaeozems under agricultural practice, i.e., high intensities in the regions assigned to carbohydrates (110 to 45 ppm), alkyl C (45 to 0 ppm) and in the chemical shift region of carboxylic C (220 to 160 ppm). The presence of aromatic compounds is indicated by broad overlapping signals between 160 and 100 ppm. Similar spectra are reported for other natural Phaeozems.

The spectrum of the influenced Ap1 horizon shows a different pattern. The spectrum is dominated by signals in the alkyl C (45 to 0 ppm) and aromatic C (110 to 160 ppm) region. The brown coal sample shows a similar spectrum with more distinct peaks for alkyl C and aromatic C. The spectrum of the soot sample reveals a distinct peak around 130 ppm, exemplifying the highly aromatic structure of soot. The similarity of the spectra between the influenced Ap1 horizon and brown coal and soot, respectively, can be taken as an indication that these organic particles have been accumulating in the soil for decades without major alteration. Spectra of the particle size fractions reveal that mainly the fractions > 6 μm comprise these organic particles (SCHMIDT *et al*., 1996).
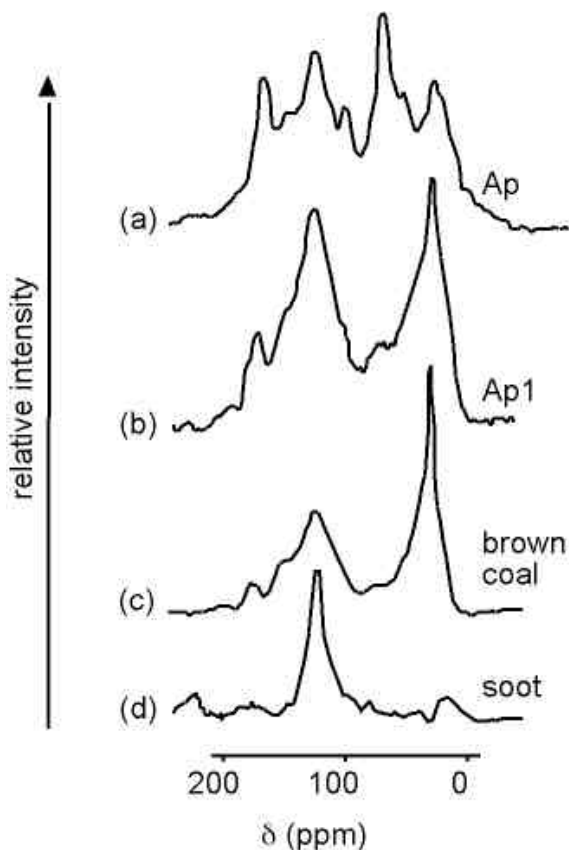
In the NMR spectra obtained from the Aeh horizon of the Podzol, signals in the aromatic region are dominant (data: SCHMIDT, 1998). This indicates the accumulation of more aromatic organic particles, e. g. bituminous coal and combustion products.

Figure 2: Solid-state ^{13}C NMR spectra of (a) non-influenced and (b) influenced horizon compared to (c) brown coal and (d) soot (spectrum (d): SERGIDES *et al*., 1987).

Reflected light microscopy

Reflected light microscopy of the Phaeozem clearly shows that the majority of the organic substances in the influenced Ap1 horizon is from brown coal dust and thermally altered coal and coke particles (SCHMIDT ET AL., 1996). Also the influenced Podzol contains atmospheric particles from coal processing industry, i. e., char from combustion, coke particles from coking plants as well as coal dust, which are not visible macroscopically but accumulated in the Aeh horizon of the influenced Podzol for decades (SCHMIDT, 1998).

Quantification of organic particles by ^{14}C dating

Considering the elevated age of coals, compared to soils, in case of contamination a much higher ^{14}C age in the influenced than in the natural soil should be expected, as a consequence of contamination by older material. For the Phaeozem, the anthropogenic organic particles (i.e., brown coal dust and combustion products) are beyond the time covered by ^{14}C determination. Organic matter in most modern soils with ^{14}C ages higher than 5000 years before present are very uncommon (Becker-Heidmann, 1989). ^{14}C analysis for the Ap horizon of the non-influenced Phaeozem revealed an age of about 1630 years before present, which is an expected value. In contrast, the Ap1 horizon of the influenced Phaeozem shows an unusually high ^{14}C age of 15,750 years before present. Taking into account the high amounts of organic carbon in the influenced soil and the very high apparent age of Tertiary brown coal, we conclude that brown coal itself or brown coal-derived products contribute greatly to the measured ^{14}C age. Assuming both Ap horizons originally had the same ^{14}C age, we can estimate the degree of contamination by the following equation (Becker-Heidmann, 1989):

$$t_r = -1\lambda \ln\left[(1-x)\, e^{-1\,t}\right]$$

where t_r = resulting ^{14}C age, λ= decay rate of ^{14}C, t= true ^{14}C age, x relative proportion of contaminating C. Taking the determined ^{14}C age of the Ap horizon as t, the mass of the contaminating C (x) can be calculated as 82 % of the total organic C. Together with the C content of brown coal (554,4 g C/kg) and the bulk density of the Ap1 horizon (Table 1) one can calculate an input of anthropogenic organic particles into the Ap1 horizon of about 35 kg/m^2.

Conclusion

For the first time, the combination of a suite of complementary methods allowed to differentiate between native soil organic matter and atmospheric organic particles from coal processing industries in soils, and to quantify the input of these organic particles. Disperse emissions of organic particles from coal processing have accumulated for decades in soils of industrialized areas, altering both content and structure of organic matter in these soils. As a consequence, the organic matter in the A horizons of these soils is a mixture of natural humic substances and organic particles from coal processing industries. Presumably anthropogenic organic particles accumulate also in other soils, neighboring industrialized areas, but remain undetected due to lower levels of deposition.

The high amount of atmospheric organic particles found in the influenced soils poses questions on possible effects on the soil properties. The organic particles may affect the physical soil properties (water holding capacity, structural stability), chemical properties (pH, C-content, cation exchange capacity, sorption) and biological properties (stability against biological degradation). As examples, i) coal can influence the sorptive capacity for organic pollutants drastically (GRATHWOHL, 1990), and ii) standard determination of organic

C in soils includes anthropogenically derived organic particles and consequently overestimates the content of native soil organic matter in soils comprising anthropogenic organic particles.

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