Mineralization of Forest Soil Carbon: Interactions with Metals

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Summary – Zusammenfassung

Biodegradability of natural dissolved organic compounds was tested in laboratory experiments. Organic matter was extracted from organic and mineral forest soil horizons and was isolated from soil solutions collected by suction cups. Carbon moieties were fractionated into hydrophobic acids, hydrophilic acids, and hydrophilic neutral compounds. Degradability of the organic compounds ranged from less than 5% (acid compounds) to 15% (neutral compounds). Metals (Ca, Al) and solid Al_2O_3 were added to assess the effect of complexation reactions as well as the adsorption of organic ligands to mineral surfaces on the rate of mineralization. The rate of CO_2 respiration was used to measure the degradability. Glucose was used as reference compound and we found that the addition of metals retarded its mineralization. On the contrary the degradation of natural soil organic carbon was not affected, or was even enhanced, with Ca or Al added. Adsorption of organic matter to Al_2O_3 decreased the respiration rate by one order of magnitude.
Key words: biodegradation / natural dissolved organic matter / XAD-resins / forest soils

Mineralisierung von Kohlenstoff aus Waldböden – Interaktion mit Metallen

In Laborexperimenten wurde die biologische Abbaubarkeit von organischen Verbindungen aus Waldböden untersucht. Es wurden Wasserextrakte des Auflagehumus und des Mineralbodens und Bodenlösungen aus Saugsonden verwendet. Die organischen Verbindungen wurden in hydrophobe Säuren, hydrophile Säuren und hydrophile neutrale Verbindungen aufgetrennt. Die Abbaubarkeit reichte von weniger als 5% (saure Verbindungen) zu 15% (neutrale Verbindungen). Metalle ($CaCl_2$, $AlCl_3$) und festes Al_2O_3 wurden zugesetzt, um den Effekt der Komplexbildung und der Adsorption von organischen Liganden an der mineralischen Festphase des Bodens auf die Mineralisierungsrate zu studieren. Als Maß für die Abbaubarkeit diente die Rate der CO_2-Bildung. Als Referenzmaterial wurde Glukose verwendet. Die Abbaubarkeit von Glukose wurde durch die Metallzugabe verringert. Hingegen wurde die Abbaubarkeit der organischen Verbindungen aus Böden durch die Zugabe von Ca und Al nicht beeinträchtigt oder sogar beschleunigt. Die Adsorption der organischen Verbindungen an Al_2O_3 verringerte die Respirationsrate um eine Zehnerpotenz.

Introduction

Forest soils are a major reservoir of terrestrial carbon. Soil carbon consists of both labile and refractory fractions. Dissolved organic carbon (DOC) represents a small pool of soil organic matter but may be particularly important as it is partially labile and it complexes metals in solution. Recent studies on the degradability of dissolved and water/salt extractable soil carbon have shown that at least part of it is utilized by microorganisms (*Amon* and *Benner*, 1994; *Boissier* and *Fontvielle*, 1993; *Qualls* and *Haines*, 1992; *Lovley* et al., 1996; *Zsolnay* and *Steindl*, 1991).

Dissolved organic carbon is a mixture of degradation products from above- and below-ground biomass, root exudates, and microbial biomass. Its dynamics depend on the leaching rate, adsorption of organic ligands at mineral soil surfaces, and degradation by microorganisms. The rate of leaching of organic carbon from forest soils is usually small (*Guggenberger*, 1992). A substantial part is adsorbed to the solid phase and is thereby resistant to biodegradation (*Boudot* et al., 1988; *Jardine* et al., 1989; *Keil* et al., 1994; *Mayer*, 1994). Biodegradability of dissolved soil organic carbon depends on its molecular structure, complex formation, and the presence of organic and inorganic surfaces.

Here we present the results of laboratory incubation experiments that investigate biodegradation of DOC. The underlying concept is that soil carbon must be released to the soil solution prior to microbial utilization. The soil solution consequently is the bottleneck, that is passed by soil carbon prior to its conversion into CO_2 or to its incorporation into microbial biomass (*Ellert* and *Gregorich*, 1994). To accomplish these studies organic carbon isolated from soils and soil solutions was used as substrate in a series of incubation experiments. In another experiment aluminum oxide was added instead of a soluble aluminum salt to test influence of adsorption on biodegradability.

Methods

Sample collection and preparation

Water extractable carbon was obtained from samples of the forest floor and the mineral soil, collected at the HJ Andrews Experimental Watershed, Cascades, Oregon. The site is located at an altitude of 630 m and the soils are classified as Inceptisols. A soil description is given in *Jandl* and *Sollins* (1997). The stand consists of approximately 40-year old second growth Douglas fir. Organic carbon was extracted

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with distilled water (100 g field moist forest floor material or 50 g mineral soil in 150 ml water). Soil samples were shaken overnight, centrifuged (6500 g for 30 min), and sterilized by filtration through 0.2 µm membrane filters.

DOC samples were from soil solutions from the Findley Lake Experimental Watershed, Cascades, Washington. The site is located at 1130 m, the soils are classified as Spodosols, and the stand consists of old growth Pacific Silver fir and hemlock. A detailed soil description is given in *Sletten* (1995). Solutions were collected from the upper DOC-rich soil horizons and filtered through 0.2 µm membrane filters. Samples were concentrated at 35°C using a rotary evaporator to obtain solutions of approximately 20 mg C l^{-1}.

Inoculum

A mixture of mineral soil and forest floor material was added to distilled water and shaken. The slurry was sequentially filtered through 5 and 0.2 µm membrane filters. The filtrate retained on the second filter was resuspended in distilled water and was used as inoculum. It had a concentration of 10 mg C l^{-1} and was stored frozen in liquid N_2 until used. Incubation of the thawed inoculum on nutrient agar plates gave high bacterial counts. It was therefore considered viable.

Fractionation

Samples were fractionated into hydrophobic acids, hydrophilic acids, and hydrophilic neutrals using a modified version of *Leenheer*'s (1981) method. Briefly, the samples were pumped through a series of columns filled with resin (Fig. 1). The XAD-8 column retained hydrophobic acids, the XAD-4 column retained hydrophilic acids, and hydrophilic neutrals passed through all the columns including an anion exchange column (Duolite A-7). Organic moieties adsorbed by the resins were eluted with 50 ml of 1 *M* NaOH and cations were removed by passing through a cation-exchange resin (BioRad AG-MP 50). For details on resin clean-up and organic fractionation procedures see *Sletten* (1995), properties of the individual fractions are given in *Guggenberger* and *Zech* (1994). The

XAD-fractionation-method was used since it allows the recovery of high amounts of reasonably well defined organic fractions. The inclusion of the cation- and anion-exchange columns allows to obtain samples of organic compounds that are free of inorganic ions.

Incubation experiments

Organic fractions experiment

Twenty ml of each test solution with a DOC concentration of approximately 20 mg C l^{-1} was put into autoclaved 50 ml serum bottles. All samples were amended with NH_4NO_3 to obtain an C:N ratio of 10 since an earlier pilot incubation study had indicated N deficiency. Then 20 µl of the inoculum was added and the bottles were sealed with rubber septa. The ambient air in the headspace was initially replaced with CO_2-free air. The incubation was carried out at 22°C in the dark. Respiration was assessed initially after 3 days and thereafter every 2 weeks by collecting and measuring p_{CO_2} in the headspace using a gas chromatograph (Hewlett Packard 5730A). At the beginning and the end of the experiment the DOC was measured using a Dohrman DC-80 analyzer; samples were acidified to pH 2 with phosphoric acid and sparged with N_2 to purge inorganic carbon. Treatments are listed in Tab. 1. Sufficient $CaCl_2$ and $AlCl_3$ respectively was added to obtain a molar ratio of 1 between metals and carbon. Since hydrolysis reactions of Al lowered the pH to 4.5, all samples were adjusted to this pH. At the end of the experiment, samples from the experiments without metal addition were combined and re-fractionated in order to determine if biodegradation led to structural changes.

A companion experiment was set up using a respirometer (Micro-Oxymax V4, Columbus Intruments, Ohio) to measure both O_2 uptake and CO_2 production every ten hours for 41 days. It checked the respiration rates in the early phase of the biodegradation process and the reproducibility of the 'organic fractions' experiment.

The effect of Al addition on the molecular size of the organic compounds was tested by means of ultrafiltration. Three replicates of water extracted organic carbon (3 ml) with and without addition of 20 µl $AlCl_3$ (molar ratio C:Al = 1) were centrifuged and separated into the
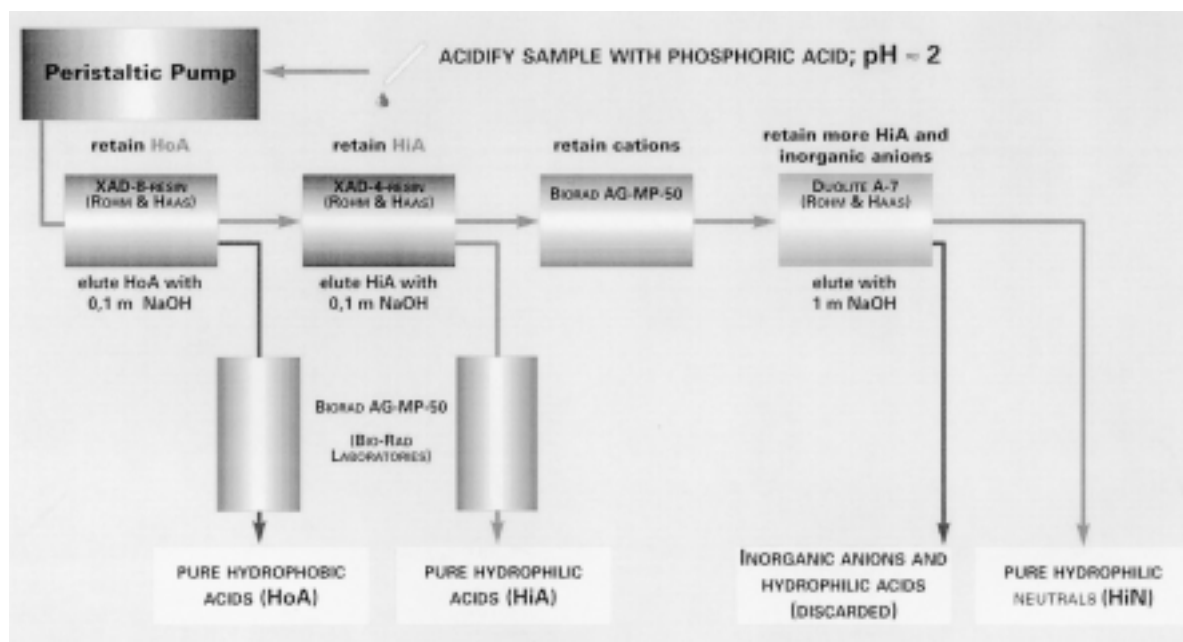

Figure 1: Experimental setup to fractionate organic matter into the fractions hydrophobic acids, hydrophilic acids, and hydrophilic neutrals.
Abbildung 1: Versuchsanordnung, um die gelöste organische Substanz in hydrophobe Säuren, hydrophile Säuren und hydrophile neutrale Gruppen aufzutrennen.

Table 1: Summary of the experimental setup of the incubation experiments: sources of carbon, replications.
Tabelle 1: Zusammenfassung der Versuchsanordnung: Ursprung des Kohlenstoffs und Anzahl der Wiederholungen.

Carbon Source	Soil Type	Incubated Fraction of organic matter	Added Reagent		
(A) Glucose Experiment (duration: 27 weeks)			none	Ca	Al
Glucose 20 mg C/l			3	3	3
Glucose 20 mg C/l C:N = 10			4	4	4
(B) Organic Fractions Experiment (15 weeks)			none	Ca	Al
Litter layer extract	Inceptisol	hydrophobic acid	2	1	1
	Inceptisol	hydrophilic acid	1	1	1
	Inceptisol	hydrophilic neutral	2	1	1
Mineral soil extract	Inceptisol	hydrophobic acid	1		
	Inceptisol	hydrophilic acid	1		
	Inceptisol	hydrophilic neutral	1		
Soil solution litter layer	Spodosol	hydrophobic acid	1	1	
Soil solution mineral soil	Spodosol	hydrophobic acid	1	1	1
	Spodosol	hydrophilic acid	1		1
	Spodosol	hydrophilic neutral	1		1
(C) Surface Experiment (duration 5 weeks)			Phosphate additon		
			none	C:P = 150:1	C:P = 150:100
Litter layer extract	Inceptisol	hydrophobic acid	1	1	1
Soil solution litter layer	Spodosol	hydrophobic acid	2	2	2

molecular weight fractions of 0–1, 1–10 and 10–100 kdaltons. The C concentration in the supernatant solution was measured with a Dohrman DC-80 carbon analyzer.

Glucose experiment

Glucose incubation experiments served as a reference system for the mineralization of natural dissolved organic matter. Twenty ml of 2 mM glucose solution were placed in bottles, inoculated and amended with NH_4NO_3 as described above.

Adsorption experiment

Twenty ml of substrate solution were filled in 50 ml serum bottles and inoculated. Sufficient aluminum oxide (δ-Al_2O_3, Degussa Company) was added so that all functional groups of the dissolved carbon could potentially adsorb to the oxide surface. Aluminum released from the oxide was expected to form complexes with organic ligands. A pilot study had shown that 25 ml of soil extract and 50 ml of the soil solution with concentrations as given in Tab. 1 were required to saturate the surface. The pH was set to 4.5 and the C:N-ratio to 10. Phosphate was added in this experiment at different levels (Tab. 1). Prior to incubation the experiment was modeled with MINEQL Version 2. Complex formation constants were assumed to have log K-values of 7 (complexes between Al and DOC), -8, -3, and 23 (complexes between Al and phosphate species), according to *Sposito* (1989) and *Stumm* and *Morgan* (1981). The estimated speciation suggested that for any concentration of phosphate relevant for forest soils, Al-P complexes will form. Hydrophobic acids extracted from mineral soil extracts (20 mg C l^{-1}) and soil solutions (50 mg C l^{-1}) were chosen as substrate, since this fraction is usually the most abundant form of dissolved organic matter and readily adsorbs to mineral soil horizons (*Jardine* et al., 1989).

Results

With the water extract we obtained only a small part of total carbon. Between 1.1 and 1.4% of total C was extracted from the litter layer and only 0.03 to 0.09% from the mineral soil. Water extractable C from the litter layer is 2 orders of magnitude greater than from the mineral soil. In the soil solution of the Spodosol the maximum C concentration is found in the upper mineral soil, which is the eluvial horizon of a Spodosol (Tab. 2).

Glucose experiment

Under N-limited conditions the utilization of glucose remained far from complete. Even with N added, glucose was not totally respired (Fig. 2). During the first 50 days of the experiment the respiration rate was high, but decreased later on. Limitations of other nutrients (e.g. P) may have occurred. Both glucose experiments show a consistent response to metal additions. Calcium addition slowed down respiration to a lesser degree than Al. Fig. 2 shows that N limitation affects mostly the no-metal

Table 2: Composition of soil water extracts and soil solutions, used as substrate in the incubation experiments.
Tabelle 2: Zusammensetzung der wässrigen Bodenextrakte und der Bodenlösungen, die in den Inkubationsversuchen als Substrat verwendet wurden.

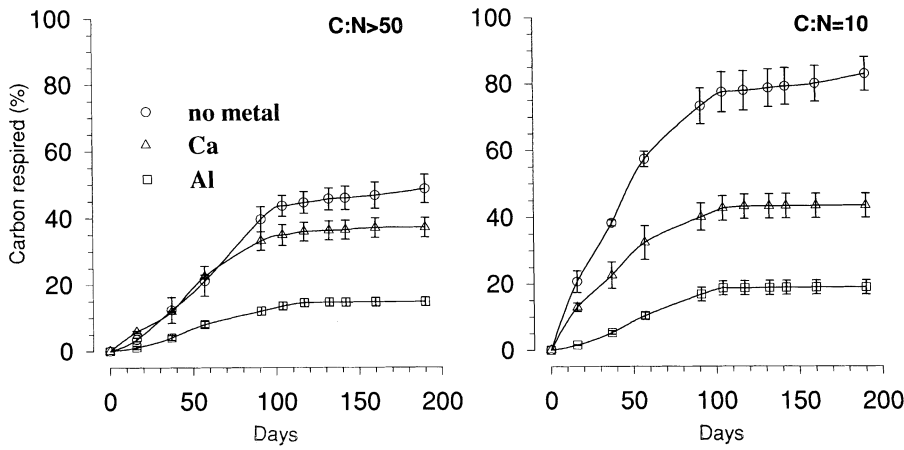|	Soil Type	Amount of carbon	hydrophobic acids [%]	hydrophilic acids [%]	hydrophilic neutrals [%]
Litter layer extract	Inceptisol	240–500 [µg Cextr/g soil]	62.9	20.6	16.4
Mineral soil extract	Inceptisol	11– 45 [µg Cextr/g soil]	42.3	25.5	32.2
Soil solution litter layer	Spodosol	15– 35 [mg/l]	73.3	12.7	10.6
Soil solution mineral soil	Spodosol	4– 85 [mg/l]	60.1	14	25.9

Figure 2: Respiration of glucose – effect of Ca and Al addition.
Abbildung 2: Respiration von Glukose – Effekt der Zugabe von Ca und Al; C:N >50 (links), C:N = 10 (rechts). Die Fehlerbalken zeigen den Standardfehler des Mittelwertes.
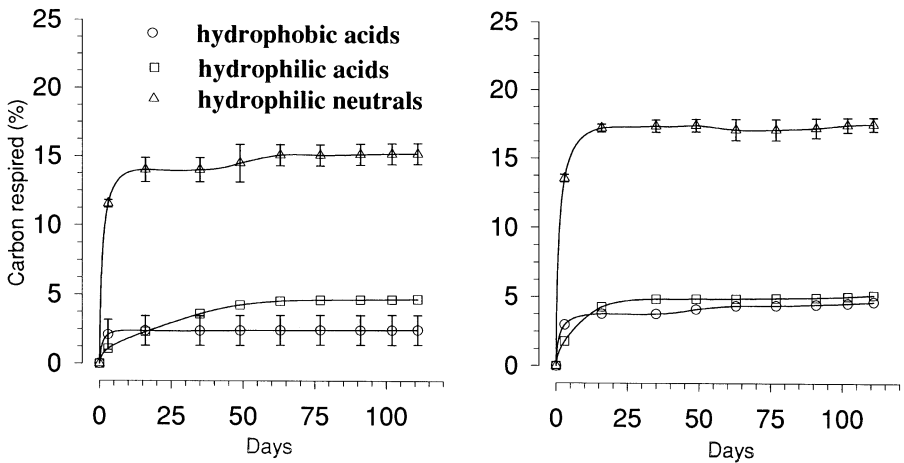

Figure 3: Respiration of water extractable carbon; litter extract (left graph) and mineral soil extract (right graph).
Abbildung 3: Respiration von Kohlenstoff aus wässrigen Bodenextrakten; Extrakt des Auflagehumus (links) und Extrakt des Mineralbodens (rechts).

Table 3: Mineralization of natural dissolved soil organic carbon obtained by water extraction of soil material and from soil solutions respectively.
Tabelle 3: Mineralisierung der Kohlenstoffverbindungen aus wässrigen Bodenextrakten und aus Bodenlösungen.

		Respiration of carbon [%]		
Source of organic matter	**Fraction of organic matter**	Metal addition		
		none	**Ca**	**Al**
Litter layer extract	hydrophobic acid	2.42	14.84	2.19
	hydrophilic acid	4.66	1.52	0.08
	hydrophilic neutral	14.78	14.89	0.05
Mineral soil extract	hydrophobic acid	4.24		
	hydrophilic acid	5.32		
	hydrophilic neutral	17.35		
Soil solution litter layer	hydrophobic acid	2.9	4.48	
Soil solution mineral soil	hydrophobic acid	2.21	7.36	9.3
	hydrophilic acid	2.15		
	hydrophilic neutral	2.55	6.8	

treatment, whereas N addition has only a small effect on the respiration rates of Ca and Al treatments.

Organic fractions experiment

In all fractions of organic carbon respiration progresses at high rates early on and levels off within 20 days. The potential degradability varies between 2 and 15% of the carbon in the substrate. Hydrophilic neutrals from water extractable material are by far more degradable than hydrophobic and hydrophilic acids (Fig. 3 and Tab. 3). Hydrophilic neutrals isolated from the soil solution samples are only slightly more degradable than the acidic fractions.

The effects of metal amendments were inconsistent. Calcium addition to the samples of water extractable carbon considerably increased the potential degradability

of hydrophobic acids, but had no effect on the degradation of hydrophilic acids and hydrophilic neutrals. The degradability of DOC from soil solutions was clearly enhanced by Ca (Tab. 3). Hydrophobic acids and hydrophilic neutrals are initially quickly respired, similar to the control treatment. In contrast to the control the respiration rate does not level off. Even after 100 days of incubation considerable amounts of C are respired. Similar statements hold for the Al addition: Al had no adverse or even a positive effect on the utilization of hydrophobic acids.

The ultrafiltration of a solution of water extractable carbon demonstrates that Al addition increases the molecular size of the organic moieties in solution (Tab. 4).

Upon completion of the incubation study we combined samples of each type and re-fractionated them. Hydrophobic and hydrophilic acids were mostly recovered in the original fraction, whereas approximately 50% of the hydrophilic neutrals were converted to organic acids (Tab. 5).

Adsorption experiment

Addition of δ-Al_2O_3 reduced the degradation rate (Fig. 4). The shape of the cumulative respiration function is quite different from the other experiments: the initial respiration rate is low, but respiration shows no tendency to level off. The cumulative respiration rate revealed no maximum value. The addition of P had no consistent effect, neither as nutrient nor as anion competing with organic ligands for adsorption sites.

Table 4: Distribution of ultrafiltered water extractable carbon solutions from an Inceptisol with and without Al-DOC-complex formation over classes of molecular weight.
Tabelle 4: Einfluß der Komplexbildung zwischen Al und organischer Substanz auf das Molekulargewicht von Kohlenstoff aus wässrigen Bodenextrakten.

Sample	Molecular size range [kdalton]		
	0–1	1–10	10–100
C extracted of Inceptisol	40%	22%	38%
C extracted of Inceptisol + Al	30%	18%	52%

Discussion

The negative effect of aluminum on many microbial processes is well known. Decreased respiration rates due to Ca addition were unexpected, however. We had assumed that calcium addition would increase the mineralization rate. Calcium and aluminum form complexes of different stability with organic ligands (*Tam* and *McColl*, 1990), but no complexes with glucose have been described. Presumably calcium and aluminum form complexes with metabolites of glucose, which are more stable than glucose and can, to some extent, protect organic molecules from biodegradation.

The early stage of the mineralization process is similar for all fractions of DOC, as initially CO_2 is respired at high rates. Obviously all fractions contain some labile moieties. This implies that the fractions are not as discrete with respect to biodegradability, as they are with respect to structure and physico-chemical properties (*Candler* et al., 1997; *Qualls* and *Haines*, 1992). Small amounts of labile components (e.g. carbohydrate side chains, proteins, and amino acids) are presumably cleaved from the complex molecules and differences between fractions are initially remarkably small (Fig. 3). When the pool of labile organic moieties is exhausted the larger recalcitrant and structurally different part of the molecules (aromatic structures of hydrophobic and hydrophilic acids, chains of fatty acids, polysaccharides of hydrophilic neutrals) remains as substrate and differences in degradability between fractions become evident. This explanation is consistent with *Zsolnay* and *Steindl* (1991), who found that salt-extractable carbon in agricultural soils can basically be divided into an non-degradable and a highly degradable fraction. The measured differences between organic fractions in potential degradability are in accordance with *Qualls* and *Haines* (1992). They showed that hydrophilic neutrals consist of up to 50% of carbohydrates, which, at least partially, are easily degradable (*Amon* and *Benner*, 1994).

The response of the potential degradability of natural dissolved soil organic matter to metal addition differed from the pattern observed in the glucose experiment (Fig. 2 and Tab. 3). Our data suggest that Al delays the respiration process at an early stage. Even though

Table 5: Transformation of fractions of natural dissolved organic matter upon microbial degradation.
Tabelle 5: Transformation der Gruppen von Kohlenstoffverbindungen im Zuge des mikrobiellen Abbaus.

Original fraction/sample type			Fraction after incubation		
Source of sample		Initial Fraction	hydrophobic acids [%]	hydrophilic acids [%]	hydrophilic neutrals [%]
Soil solution	mineral soil	hydrophobic acids	86	12	2
Soil solution	litter layer	hydrophobic acids	73	9	18
Soil solution	mineral soil	hydrophilic neutrals	40	9	51
Water extract	litter layer	hydrophobic acids	80	15	5

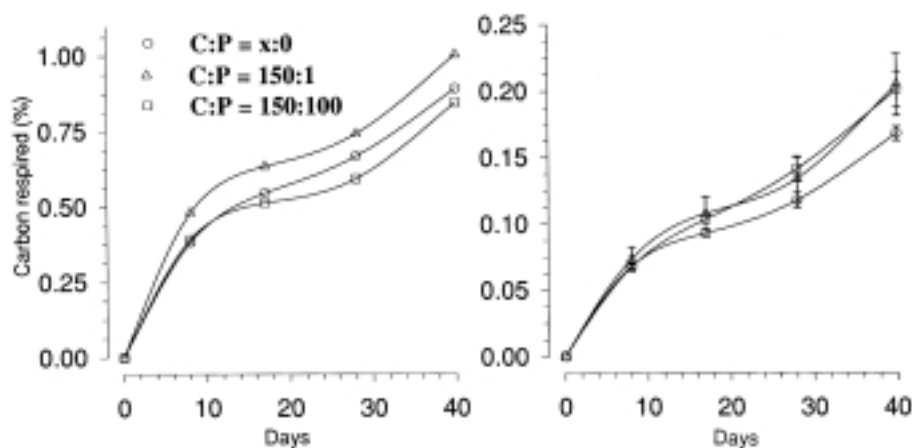**Figure 4:** Respiration of hydrophobic acids with forced surface complex formation at aluminum oxide (δ-Al_2O_3) under different P regimes. HoA from soil water extracts (left graph) and soil solutions (right graph).
Abbildung 4: Respiration von hydrophoben Säuren bei der erzwungenen Formierung von Oberflächenkomplexen und der Konkurrenz mit Phosphat. Hydrophobe Säuren aus wässrigen Bodenextrakten (links) und der Bodenlösung (rechts).

complexes between Al and Ca and organic ligands are thermodynamically stable, part of the individual fractions is degradable. It was proposed by *Oades* (1996) that such interactions of organic and inorganic components increase the turnover rate of organic material. We believe that the high rates of respiration in the Al treatment can even be a consequence of complex formation and flocculation (Tab. 4), as large structures can provide attachment for colonies of microorganisms.

Small differences in degradability between carbon from the litter layer and carbon from the mineral soil suggest that labile C moieties do not only exist at the soil surface. There freshly fallen leaves undoubtedly contain easily degradable carbohydrates. However, root exudates may provide equally degradable carbon moieties deeper in the mineral soil.

For natural conditions the adsorption experiment suggests that organic ligands get closely attached to fresh surfaces that become exposed upon rock weathering. Indeed the mineral surface of soils and sediments is intimately covered with an at least monomolecular layer of organic material (*Mayer*, 1994). During this stage, degradation of adsorbed carbon is low. Later, presumably upon formation of colonies of microbes at the surface, biodegradation accelerates. However, the respiration rate in the Surface Experiment always remained lower than in the Organic Fraction Experiment.

The results of Tab. 5 corroborate that acid fractions are the final stage of the degradation process, whereas hydrophilic neutrals undergo structural transformation upon biodegradation.

Conclusions

Our experiments show that simple experiments with the classical XAD-fractionation of natural dissolved soil organic matter provide valuable information which adds to investigations employing the ^{13}C-NMR technique.

For C turnover the less abundant, but highly degradable hydrophilic neutrals are equally important as the quite abundant, but more recalcitrant hydrophobic and hydrophilic acids. Only small amounts of DOC (usually far less than 0.1% of total C) are present in forest soils. Nevertheless, this constant influx of DOC from the forest canopy and the litter layer provides a valuable energy source for microbes.

Acknowledgements

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