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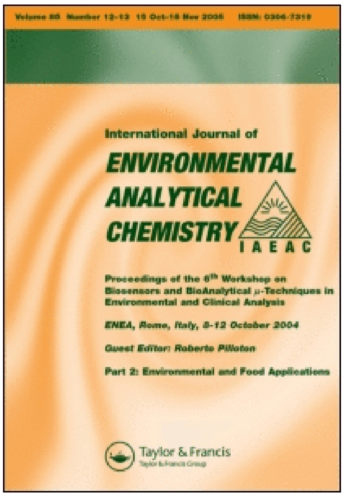

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Soil Organic Matter Extraction Using Water at High Temperature and Elevated Pressure (ASE) as Compared to Conventional Methods

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SOIL ORGANIC MATTER EXTRACTION USING WATER AT HIGH TEMPERATURE AND ELEVATED PRESSURE (ASE) AS COMPARED TO CONVENTIONAL METHODS

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Large amounts of soil organic matter can be extracted when using salt solutions or organic solvents, but these extracts do not represent the organic matter soluble under natural conditions. The objective of our study was to evaluate the usefulness of water at high-temperature and elevated pressure for soil organic matter extraction. Soil samples were extracted with water at different temperatures under high pressure (10 MPa), using an Accelerated Solvent Extractor (ASE). These extracts were compared to extracts obtained by conventional methods using distilled water, NaOH and $Na_4P_2O_7$ solutions. Yields of ASE extracts were up to twenty-fold higher than those of conventional water extracts. UV spectra as well as ^1H and ^{13}C NMR spectra revealed high similarity between conventional water extracts and ASE extracts up to 150°C. At higher temperatures, ASE extracts were enriched in aromatic and depleted in O-alkyl-C structures, strongly resembling the NaOH and $Na_4P_2O_7$ extracts.

Keywords: Soil organic matter; extraction; ASE; NMR

INTRODUCTION

When extracting soil organic matter the objective is to (i) gather a high yield of (ii) chemically unaltered soil organics. These two aims, however, are somewhat contradictory. High yields are obtained using NaOH, $Na_4P_2O_7$ or organic solvents like EDA (ethylenediamine), DMSO (dimethylsulfoxide) or DMF (dimethylformamide), because these solvents solubilize organic matter that would be

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almost insoluble under natural conditions [1]. Most of the extractants mentioned above also tend to alter the chemical characteristics of the extracted material. NaOH enhances autoxidation of humic substances, even if extractions are carried out in an inert gas atmosphere [2]. Furthermore $Na_4P_2O_7$ stimulates oxidation processes, but to a much lower extent than NaOH [3]. Among the organic extractants EDA has the disadvantage that it enriches the extracted material with nitrogen [1].

To obtain an extract that represents the actually available fraction of soil organic matter, water, which is the natural solvent in the field, should be used. Water, however, has the disadvantage of extracting only small amounts of organics. This requires concentration procedures like adsorption to resins or freeze drying to reach concentration ranges that allow a chemical characterization. But also adsorption-desorption procedures may alter the chemical quality of the organics extracted [4]. The yield of soil organics in water extracts may be improved by use of elevated temperatures [5] or ultrasonication [6], methods that did not find a broad range of application so far.

The intention of our work was to evaluate the usefulness of a high temperature water extraction for soil organic matter using a commercially available solvent extractor. We wanted to test whether such an equipment allows an easy to handle and reproducible extraction of soil organic matter and find out the conditions under which the highest yield of chemically unaltered material can be obtained.

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EXPERIMENTAL

Samples were taken from the Waldstein experimental plot, a 140 year old Norway spruce stand (*Picea abies*) in the Fichtelgebirge (NE Bavaria). The soil was a Cambic Podzol (FAO Classification) derived from granitic bedrock (for details see [7]), dried and sieved to 2mm.

Extractions were done using an ASE200 solvent extractor (Dionex Corporation, Sunnyvale CA, USA). Soil samples were filled into extraction cells having a capacity of 22 ml, the amount of soil used for extraction depending on its density (see Table I). During the automatic extraction there were seven main steps:

- loading the cell to the extraction position
- filling the cell with solvent (in our case water)
- heating the cell to the desired temperature
- time for static extraction
- flushing the cell with fresh solvent
- purging the solvent from the system by inert gas
- unloading the cell

TABLE I Parameter settings used for water extraction with the ASE200 system

Sample amount	Oh: 10g; E: 25g; Bhs: 20g; Bw: 28g
Solvent	distilled water
Extraction temperature	50, 100, 150 and 200°C
Extraction time	10 min
Extraction pressure	10 MPa
flush volume	13.2 mL (60% of cell volume)

During the heating and extraction steps pressure was applied to the sample to maintain the solvent in a liquid state. The extraction parameters used in our study are given in Table I. As inert gas we used N_2 (quality 5.0). The extraction time of 10 min was optimal, longer extraction times did not improve the yield.

Reproducibility of the ASE extraction was estimated by extraction of 11 samples each of E and Bhs material at a temperature of 100 °C. The content of total organic carbon in the extracts was determined by persulfate-digestion to calculate the amount of extracted carbon.

To compare the extracts gathered by the ASE200 system with conventional methods, we also made soil extracts with distilled water, 0.5 M NaOH and 0.1 M $Na_4P_2O_7$ solutions [17,18]. The water extracts were performed with a soil-to-water ratio of 1:2 for the mineral horizons and 1:4 for material of the Oh layer. Extraction time was 24 hours, manually stirring the system five times.

Extractions with NaOH and $Na_4P_2O_7$ solutions were done with soil-to-extractant ratios of 1:2.5 for mineral soil material and 1:5 for material of the humic layer. Extractions were carried out overnight by shaking with an end-over-end shaker. For details of soil and solution amounts see Table II.

TABLE II Preparation and recovery of conventional extracts

Horizon	*NaOH*	*$Na_4P_2O_7$*	*Water Extract*
	g soil + mL extractant (recovery of extractant %)		
Oh	20 + 100 (52%)	20 + 100 (51%)	250 + 1000 (44%)
E	40 + 100 (71%)	40 + 100 (73%)	500 + 1000 (65%)
Bhs	40 + 100 (54%)	40 + 100 (71%)	500 + 1000 (55%)
Bw	40 + 100 (79%)	40 + 100 (81%)	1000 + 2000 (83%)

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To obtain comparable solutions, the conventional extracts were centrifuged and filtered through glass-fibre filters, retaining particles > 1 µm. The same filters were placed on the bottom of the extraction cells of the solvent extractor to avoid a discharge of soil material.

With the ASE extractor we produced two sets of samples. One was taken for all analyses that require liquid samples (UV spectra, cations, anions), and the second was freeze-dried for elemental analysis and NMR spectroscopy. The conventional water extract was also divided into two subsamples, liquid and freeze-dried. Because of their high salt content the NaOH and $Na_4P_2O_7$ extracts were divided into three subsamples, one liquid, one freeze-dried and one freeze-dried after dialysis. The latter was taken for NMR spectroscopy. Dialysis was done against water until electric conductivity of the dialysate was below 80 µS (dialysis tubing SERVAPOR, Serva Germany).

Total metal contents were measured by ICP-AES (Inductively coupled plasma – atomic emission spectroscopy, Integra XMP, GBC Australia), elemental analysis was done by a CHN-analyzer (CHN-O-Rapid, Elementar Germany) and the C content of liquid samples was measured by persulfate digestion (liquiTOC, Astro USA). As an indicator for the composition of the extracted organic matter in the liquid samples, UV absorption was measured in the range from 200 to 400 nm (Uvicon 930, Kontron Germany) with all samples diluted 1:6. Major anions were measured by capillary electrophoresis (Phoresis 1000, TSP USA) using a pyromellitic acid buffer system [8].

NMR spectra of freeze-dried samples (150 mg) dissolved in 0.5 M NaOD solution were obtained on a Bruker Avance DRX 500 NMR spectrometer (11.7 T) at a temperature of 290 K under the following conditions:

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^{13}C NMR

10-mm sample tubes; spectrometer frequency, 125 MHz; inverse-gated decoupling; acquisition time, 0.16 s; delay time, 1.84 s; line-broadening factor, 100 Hz.

^{1}H NMR

5-mm sample tubes; spectrometer frequency, 500 MHz; homonuclear presaturation for solvent suppression; acquisition time, 1.16 s; delay time, 1 s; line broadening factor, 2 Hz.

^{31}P NMR

Spectrometer frequency, 202.5 MHz; no proton decoupling; acquisition time, 0.1 s; 90° pulse; relaxation delay, 0.2 s; line broadening factor, 20 Hz. Chemical shifts were measured relative to 85% H_3PO_4 in a 5-mm tube inserted into the 10-mm sample tube before the measurement of each sample.

TABLE III Yields and elemental analyses of freeze-dried samples

Sample	*Extraction*	*Yield mg/g soil*	*Yield % of C_{tot}*	*C*	*H*	*N*	*C/H*	*C/N*
					%			
Oh	H_2O	3.7	0.5	39.0	5.9	1.9	6.7	20.1
	50°C	9.5	1.3	39.8	5.9	1.9	6.7	20.9
	100°C	16.5	2.3	41.0	5.7	2.1	7.2	19.5
	150°C	94.7	14.0	43.4	6.0	2.3	7.2	18.9
	200°C	124.1	20.6	48.7	5.9	4.9	8.3	9.9
	NaOH	133.8	18.4	40.4	5.4	2.1	7.5	19.2
	$Na_4P_2O_7$	79.0	5.9	21.9	2.6	1.0	8.4	21.9
E	H_2O	0.9	0.7	36.5	4.9	1.7	7.4	21.5
	50°C	2.3	1.9	39.3	5.2	1.6	7.6	24.6
	100°C	6.1	5.3	40.5	4.8	1.4	8.4	28.9
	150°C	18.5	16.7	42.5	5.2	2.1	8.2	20.2
	200°C	15.7	15.9	47.6	5.4	3.7	8.8	12.9
	NaOH	47.0	25.1	25.1	4.3	1.2	5.8	20.9
	$Na_4P_2O_7$	66.6	24.0	17.0	2.3	0.7	7.4	24.3
Bhs	H_2O	0.6	0.3	32.5	5.1	1.7	6.4	19.6
	50°C	1.3	0.7	35.6	5.4	2.0	6.6	17.8
	100°C	3.8	2.0	37.0	5.2	1.6	7.1	23.1
	150°C	17.5	9.7	39.6	5.0	2.3	7.9	17.2
	200°C	18.6	11.4	43.7	5.3	4.4	8.2	9.9
	NaOH	65.8	19.9	21.5	3.0	0.9	7.2	23.9
	$Na_4P_2O_7$	92.8	21.0	16.1	2.5	0.6	6.4	26.8
Bw	H_2O	0.1	0.02	21.3	3.9	1.6	5.5	13.3
	50°C	0.1	0.04	24.3	4.1	1.8	5.9	13.5
	100°C	0.2	0.1	28.1	4.3	1.5	6.5	18.7
	150°C	1.9	1.3	38.9	5.1	2.6	7.6	15.0
	200°C	4.1	3.2	45.0	5.1	4.1	8.8	11.0
	NaOH	31.8	5.1	9.1	4.6	0.5	2.0	18.2
	$Na_4P_2O_7$	76.9	8.3	6.2	1.7	0.4	3.6	15.5

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RESULTS

Freeze-dried samples

The yield of freeze-dried soil extract from the ASE increased with temperature for all horizons and was higher than the yield of the conventional water extract (see Table III). Except for the Oh horizon, NaOH and $Na_4P_2O_7$ extracts yielded highest C amounts if calculated as percentage of total C present in each soil horizon. Considering the C/H and C/N ratios as a measure for the chemical quality of the extracted organic matter, we found that there were no big differences among the extracts. The only exception was the ASE extract at 200°C, where the C/N ratio, especially in the horizons influenced by humic substances, was clearly lower. There was also a trend of increasing C/H ratio with increasing temperature.

The low yields of the conventional extraction procedures are also due to the fact that we used air dried samples. Especially the Oh material took up a lot of extractant that could not be regained by the centrifugation/filtration procedure (see Table II).

The ^1H and ^{13}C NMR spectra (Figures 1 and 2) showed that the ASE extracts up to 150°C were very similar to the conventional water extract. The spectra of the 200°C ASE extracts, however, were similar to those of NaOH and $Na_4P_2O_7$ extracts, and had higher proportions of aromatic and alkyl structures, whereas O-alkyl structures were clearly diminished (see Tables IV and V).

Orthophosphate was the main phosphorous species in the extracts (Figure 3, resonance at 6.3 ppm). However, phosphate esters (6–0 ppm) and condensed phosphates (around –5 and –20 ppm) were also present in the conventional water extracts. With increasing temperatures, these species were progressively hydrolyzed to orthophosphate, hydrolysis being almost complete at 150°C.

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Liquid samples

With respect to their UV spectra, as a characteristic for the amount and quality of dissolved organic matter, NaOH and $Na_4P_2O_7$ extracts of E and Bhs horizons were very similar (Figure 4). The NaOH extracts of the Oh showed a higher, that of the Bw a lower absorption than the $Na_4P_2O_7$ extracts. The spectra of the ASE extracts at a temperature of 50°C were nearly identical with those of conventional water extracts. The spectra of the 100°C and 150°C extracts were also similar to the water extracts, but on a higher absorption level. In the 200°C extracts, however, the UV absorption showed a local maximum at the wavelength of 280 nm, which is the specific wavelength for phenolic compounds [9]. This absorption maximum was strongest in the extracts of Oh and E and less apparent in the Bhs and Bw horizon.

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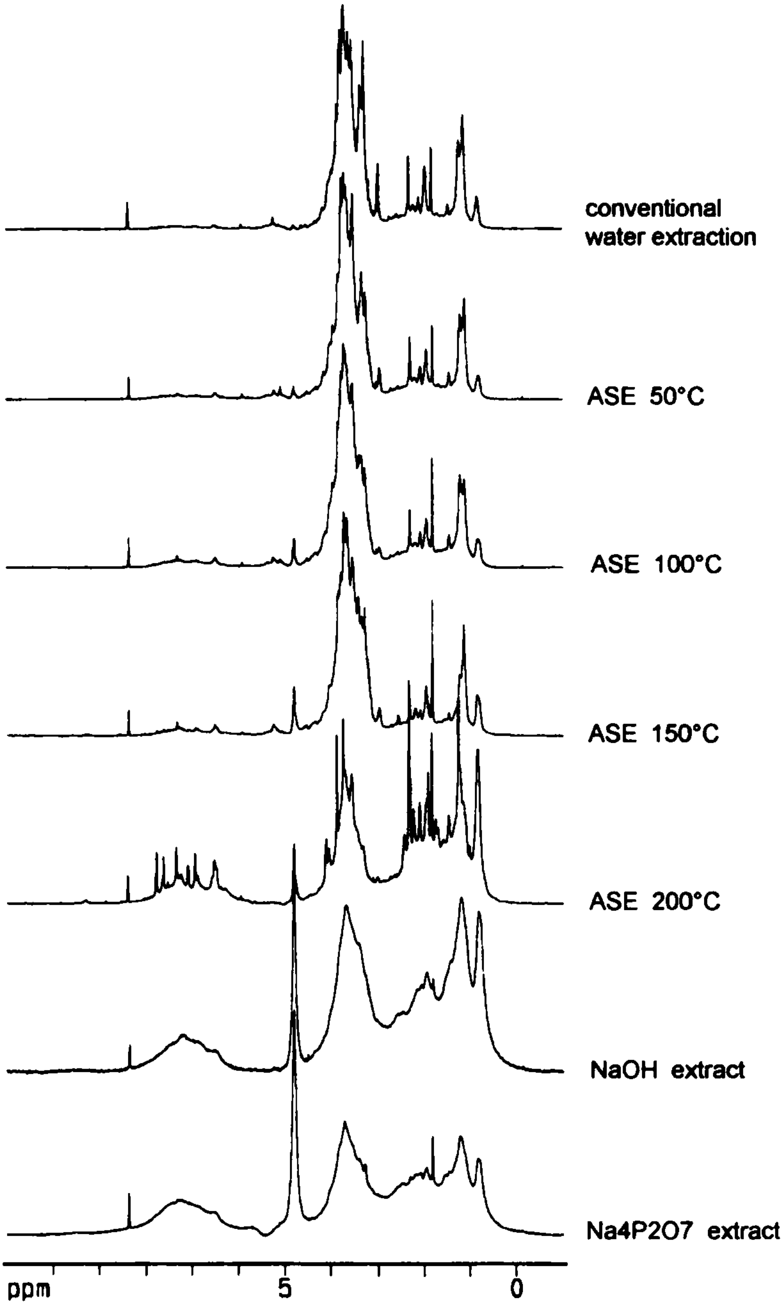

FIGURE 1 ^{1}H NMR spectra of the extracts obtained from the Oh horizon

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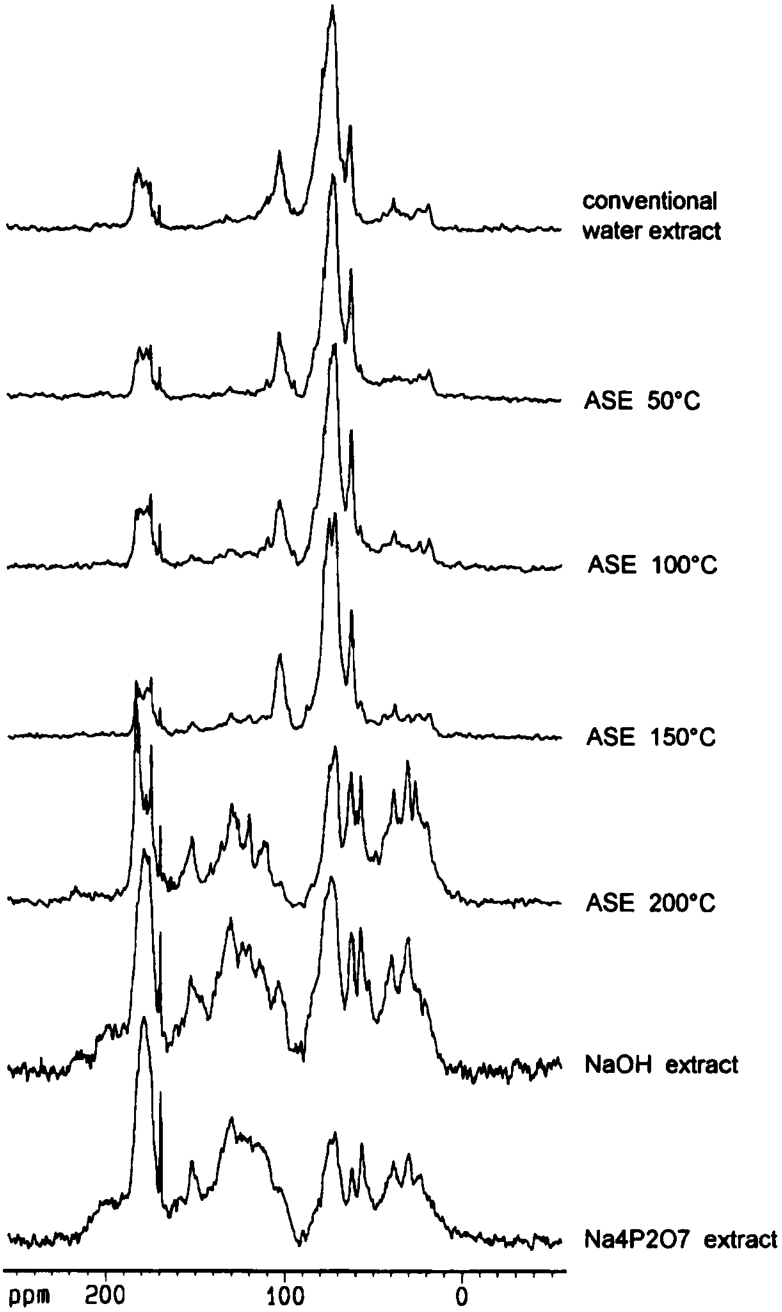

FIGURE 2 ^{13}C NMR spectra of the extracts obtained from the Oh horizon

TABLE IV Relative proportions of functional groups as derived from ^{1}H-NMR integration

Extraction	*relative proportions of functional groups (%)*			
	0–1.8 ppm alkyl	*1.8–3.0 ppm ketones α-carboxyl*	*3.0–4.6 ppm O-alkyl*	*7.5–10 ppm aromatic aldehyde*
Oh				
H_2O	17	13	68	2
50°C	16	12	68	4
100°C	17	13	64	6
150°C	16	13	65	6
200°C	33	23	29	15
NaOH	35	20	33	12
$Na_4P_2O_7$	27	22	31	20
E				
H_2O	22	19	58	3
100°C	20	20	52	8
150°C	20	17	57	8
200°C	40	25	22	12
NaOH	50	24	16	10
$Na_4P_2O_7$	33	24	23	20

TABLE V Relative proportions of functional groups as derived from ^{13}C-NMR integration

Extraction	*relative proportions of functional groups (%)*			
	0–50 ppm alkyl	*50–110 ppm O-alkyl*	*110–160 ppm aromatic*	*160–220 ppm carbonyl*
Oh				
H_2O	12	69	8	12
50°C	15	67	6	12
100°C	15	61	11	13
150°C	13	65	11	11
200°C	30	26	25	19
NaOH	20	30	30	20
$Na_4P_2O_7$	19	20	34	27
E				
H_2O	21	53	8	18
50°C				
100°C	18	48	13	21
150°C	16	50	15	19
200°C	31	25	24	20
NaOH	21	23	32	24
$Na_4P_2O_7$	18	22	35	25

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TABLE VI Yield of several elements in liquid samples in mg kg^{-1} soil

Sample	*Extraction*	*Al*	*Ba*	*Ca*	*Fe*	*K*	*Mg*	*Mn*	*S*	*Si*	*Zn*
		mg/kg									
Oh	H_2O	22.0	0.4	12.4	6.9	18.3	3.5	0.4	45.6	7.3	0.6
	50°C	38.6	2.8	25.5	9.7	46.0	5.4	0.7	86.5	0.0	1.9
	100°C	65.1	12.0	61.4	65.1	79.8	9.0	1.2	131.6	21.5	10.7
	150°C	176.9	37.2	173.0	421.4	172.2	28.4	4.1	438.6	296.5	42.1
	200°C	153.9	20.2	177.3	310.5	223.6	31.1	3.3	554.3	699.2	82.1
	NaOH	1189.6	13.0	185.2	815.4	190.2	52.8	4.2	577.3	2009.0	6.1
	$Na_4P_2O_7$	1674.9	8.1	168.4	1120.1	79.6	34.0	5.2	209.8	462.2	6.1
E	H_2O	20.9	0.2	3.9	13.0	4.8	1.6	0.1	12.8	12.8	0.2
	50°C	18.2	1.2	5.2	16.5	6.8	1.3	0.1	18.2	1.1	0.8
	100°C	45.1	4.7	8.4	112.5	19.6	1.7	0.2	34.0	14.9	4.7
	150°C	65.8	15.7	20.1	359.2	28.3	3.2	1.0	87.7	57.6	16.3
	200°C	27.4	9.6	24.7	255.0	46.3	3.2	0.8	109.1	140.2	30.7
	NaOH	1243.4	6.9	29.3	1266.7	176.5	41.0	2.7	148.8	1603.8	2.4
	$Na_4P_2O_7$	2683.1	5.2	39.2	2362.5	320.3	129.7	3.5	88.2	2564.3	2.5
Bhs	H_2O	18.1	0.1	1.1	8.5	1.6	1.3	0.5	10.4	9.6	0.1
	50°C	23.3	1.0	2.7	17.2	6.1	1.5	0.2	11.6	4.9	0.6
	100°C	37.9	2.8	3.7	130.8	10.3	1.2	0.4	32.6	32.2	2.9
	150°C	46.2	11.1	10.5	1010.5	26.9	3.8	2.9	161.0	44.7	10.4
	200°C	13.7	8.4	21.2	841.8	70.4	3.9	4.3	189.8	72.5	21.7
	NaOH	4679.0	8.5	9.0	6937.1	391.7	135.8	16.8	212.6	3988.9	3.1
	$Na_4P_2O_7$	7443.6	9.5	13.8	8261.5	565.1	246.2	16.8	167.8	5084.1	3.4
Bw	H_2O	3.7	0.2	1.8	0.0	1.7	0.6	0.9	6.1	15.4	0.1
	50°C	1.0	0.6	1.0	0.2	2.5	0.3	0.2	2.3	9.7	0.4
	100°C	1.0	1.2	1.2	1.2	4.1	0.3	0.5	3.3	27.7	1.2
	150°C	2.3	5.1	3.2	22.3	13.5	0.8	3.4	15.3	51.4	5.8
	200°C	7.1	2.1	7.7	46.3	41.7	1.4	5.3	55.1	62.4	8.7
	NaOH	5124.3	0.6	0.9	26.5	106.9	0.5	0.6	194.8	214.3	0.2
	$Na_4P_2O_7$	7790.0	11.0	7.7	2613.8	581.1	265.3	482.6	126.3	5500.5	6.5

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Yields of inorganic cations obtained by the ASE exceeded the yields of conventional water extracts, in most cases even at a temperature of 50°C (Table VI). Only for the Bw material higher temperatures were required to achieve yields equal to or higher than the conventional water extract. In most cases ASE extracts did not even at 200°C reach the level of NaOH and $Na_4P_2O_7$ extracts. However, there were some exceptions especially for the Oh horizon and for the elements Ba and Zn.

For the ASE extracts, cations can be separated into two groups of a distinct behaviour. The yields of the first group (Ca, K, Mg, S, Si, Zn) increased with increasing temperature. The yields of the second group of cations (Fe, Al, Mn, Ba) increased up to 150°C and showed a decrease at an extraction temperature of 200°C. These trends were consistent for all horizons with only one exception (Al in the Bw horizon).

TABLE VII Yield of anions in liquid samples calculated in mg kg^{-1} soil

Sample	*Extraction*	*Oxalate*	*Chloride*	*Nitrate*	*Sulfate*
			mg/kg		
Oh	H_2O	58.0	10.9	6.3	87.0
	50°C	106.5	15.1	12.6	159.9
	100°C	190.6	19.5	16.7	176.1
	150°C	623.4	32.5	23.6	399.7
	200°C	623.9	31.0	23.1	501.9
E	H_2O	35.4	4.8	8.5	27.8
	50°C	33.9	4.2	3.0	28.0
	100°C	102.9	6.8	3.7	40.3
	150°C	259.1	2.6	2.7	107.6
	200°C	323.9	23.9	0.0	140.2
Bhs	H_2O	0.0	8.0	3.7	30.4
	50°C	29.6	10.9	5.9	20.9
	100°C	88.7	14.6	6.7	51.5
	150°C	192.2	34.2	5.4	141.9
	200°C	537.0	16.1	0.0	273.4
Bw	H_2O	0.0	6.5	4.1	22.1
	50°C	0.0	3.2	2.1	5.9
	100°C	0.6	4.2	2.8	8.6
	150°C	5.8	6.5	2.9	30.1
	200°C	32.4	1.0	1.9	107.0

For oxalate, as a representative of dissolved organic C with strong ionic character, already at 50° the yield from Oh and Bhs material was much higher than with the conventional water extract. Higher temperatures were needed for the E and Bw horizons (Table VII). Whereas the yield of oxalate from E, Bhs and Bw continued to rise with increasing temperature, a plateau was reached at 150°C for the Oh material, with no increase of yield with further rising temperature.

For the Oh horizon, the amounts of extracted chloride, sulfate and nitrate increased with temperature in a way similar to that of oxalate. Sulfate, however showed a further increase at 200°C. In mineral soil sulfate and to some extent also chloride behaved like oxalate, except that less chloride was extracted from the Bhs and Bw at 200°C than at 150°C. Here nitrate yields were mostly lower in ASE extracts than in the corresponding water extract and did not rise with temperature.

Reproducibility of the ASE extraction was estimated by measurement of extracted C after extraction of 11 samples each of E and Bhs material at a temperature of 100°C, and showed a coefficient of variance of 5.0 and 9.5 % respectively, which is in an acceptable range.

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DISCUSSION

The amount of organic C extracted from the soil by various extractants depends on the extractant itself, the extraction procedure and soil properties. High yields are usually obtained by NaOH and $Na_4P_2O_7$ because they effectively solubilize soil organic matter by deprotonation of functional groups or complexation of polyvalent cations which cause flocculation of organic macromolecules [3]. As expected, also in our experiments these two extractants were the most effective for the mineral soil horizons, showing comparable yield on the basis of extracted soil C. For the Oh, NaOH was more effective than $Na_4P_2O_7$ because here the flocculation of organic material by polyvalent cations is of minor importance. The extracts obtained by these two extractants, however, always had a high ash content, especially for the mineral soil. High ash contents are in most cases unfavourable for chemical analysis and were the reason why NaOH and $Na_4P_2O_7$ extracts had to be dialyzed prior to NMR analysis.

Solubility of soil organic matter during extraction depends on diffusion, desorption and chemical equilibria, which all are temperature-dependent. Elevated temperatures enhance diffusion, because of higher molecular movement. Endothermic reactions like dissolution processes and desorption are also favoured by elevated temperatures. Not only thermodynamics of chemical reactions are influ-

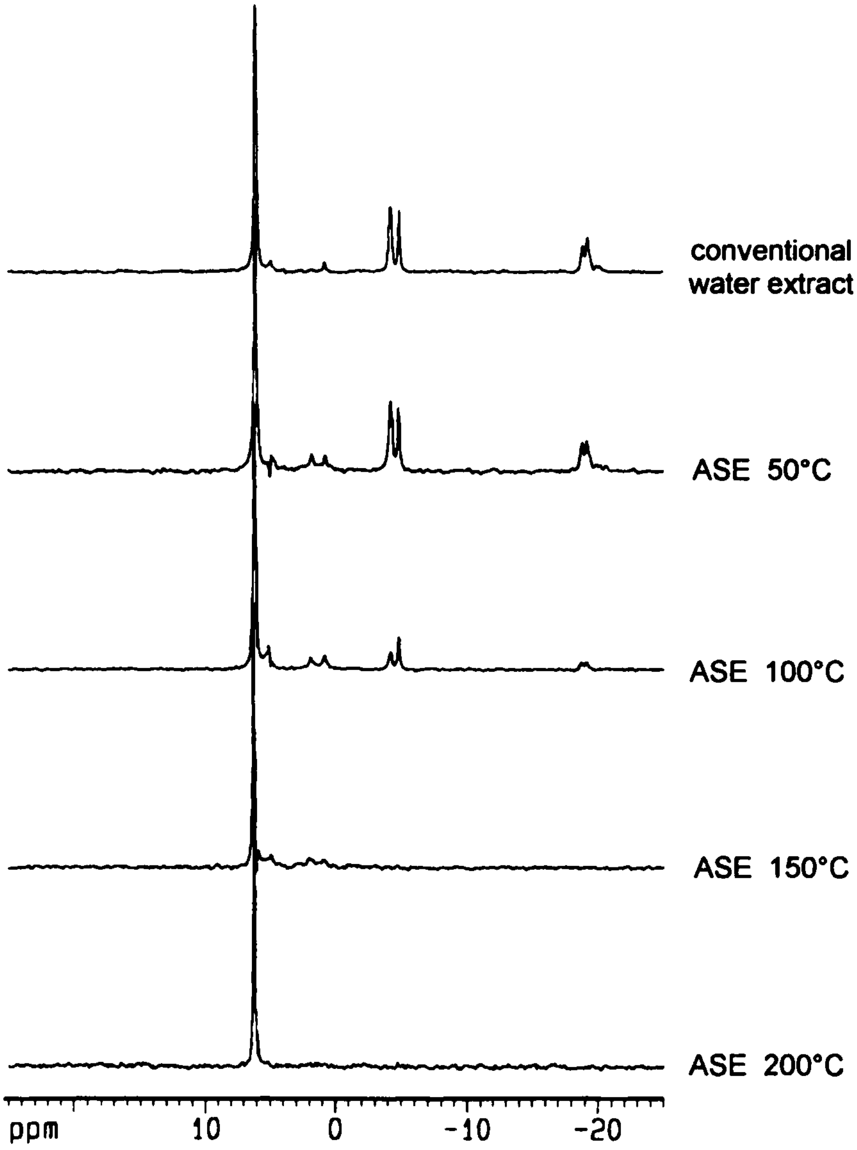

FIGURE 3 ^{31}P NMR spectra of the extracts obtained from the Oh horizon

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enced by temperature but also their kinetics. It is a general rule, that the rates of chemical reactions increase by a factor of 2 to 4 when temperature is raised by 10°C [10]. Considering all these temperature-dependent processes, a positive

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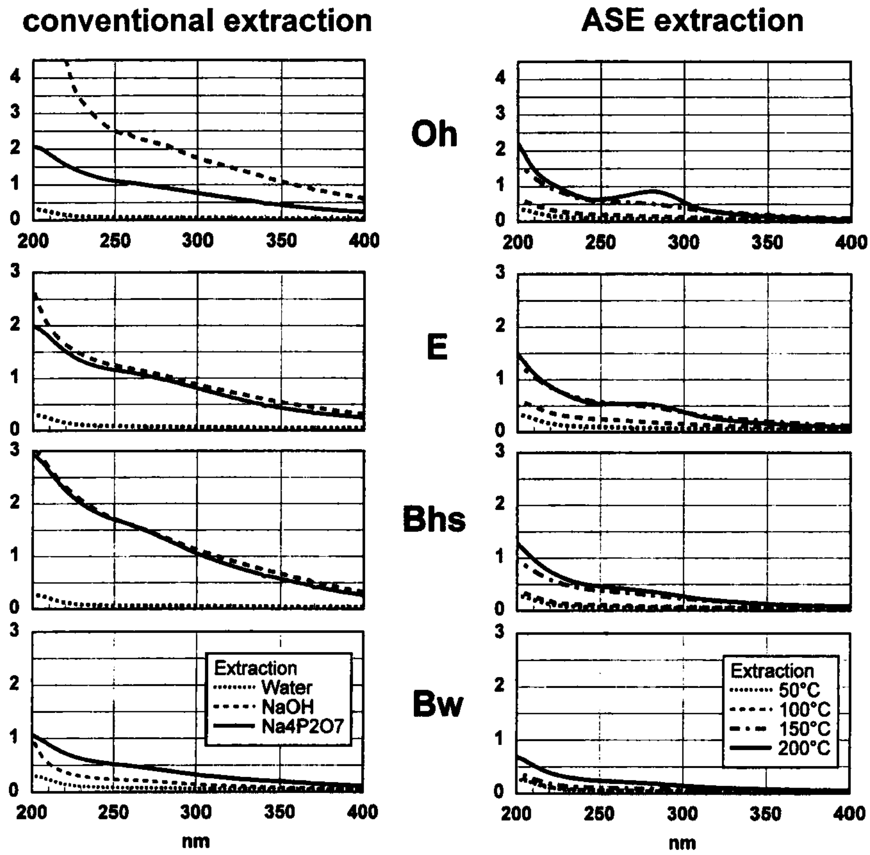

FIGURE 4 UV absorption spectra of all extracts

interdependence between extraction temperature and yield of extracted soil organic matter is expected. Because of some disproportional effects the increase of yield should be not linear. This was exactly observed in our study in the range up to 150°C. At 200°C in most cases there was no longer a disproportional increase of the yield, and thermal decomposition of the samples began, as indicated by a smell of the extract like roasted humus. Especially for the Oh horizon, where the interaction of soil organic matter with inorganic soil constituents (e.g. flocculation) is of minor importance, the ASE extraction at 150°C and higher was more effective than $Na_4P_2O_7$ and could even compete with NaOH.

To assess the quality of the extracted organic matter we used a variety of complementary analytical methods. UV absorption spectra of humic and fulvic acids are known not to show well defined maxima and minima [3]. This was also true

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for our extracts with the exception of the 200°C ASE extracts of the Oh and Ah horizons. The absorption maxima found in these two extracts in the region of 280 nm indicated the presence of phenolic compounds like derivatives of gallic and tannic acid [9]. This was confirmed by the higher proportion of aromatic structures detected by ^{1}H and ^{13}C NMR. Although also NaOH and $Na_4P_2O_7$ extracts had higher contents of aromatic structures they did not show such a clear maximum in their UV spectra but only a weak shoulder. Because the UV-active chromophores of organic molecules may be influenced by oxidation processes, pH and solvent characteristics [11] this probably was due to chemical alterations caused by these extraction solvents [2] as well as by their higher salt content.

The different composition of organic matter obtained at 200°C was confirmed by the decrease in yields of the elements Fe, Al and Mn at this temperature (Table VI). Dissolution of these elements from soils is known to depend mainly on complexation by organic compounds with specific functional groups [12,13]) and we interpret the decrease of these elements in the 200°C extracts as a hint for an alteration in the complexation properties of the obtained organic matter. This seems to be due to a higher amount of aromatic and alkylic compounds and a significant decrease of O-alkylic structures as detected by NMR (Tables IV and V).

Because the ranges of chemical shifts for several types of functional groups overlap [11], a quantitative evaluation of the complex NMR spectra of natural organic matter is not possible. Thus we used NMR as a fingerprint technique and compared the spectra by their peak patterns as well as by integration of commonly used regions of chemical shift [14]. Up to 150°C the integration of NMR spectra of the ASE extracts was very similar to the standard water extract. Also the fine structure of the spectra revealed only small shifts in the peak fingerprint. ^{1}H as well as ^{13}C NMR showed that the major structural element of the water and ASE extracts (up to 150°C) were O-alkyl structures, a fact that is often stated in literature for organic matter derived from forest soils [14,15].

The ASE extract at 200°C as well as the NaOH and $Na_4P_2O_7$ extracts had a clearly lower O-alkyl and a higher alkyl and aromatic character. For the ASE extract (200°C) this probably was due to thermal decomposition of organic matter under the conditions of high temperature and high pressure. Many sugars and their derivatives decompose at temperatures higher than 100°C – e.g. Fructose 105°C, Glucosamine 110°C, Glucose 146°C; [16] – which may have led to the observed decrease of O-alkyl C.

Organic and condensed phosphates are highly amenable to hydrolysis at elevated temperatures. They were hydrolyzed to a high degree at temperatures above 50°C. High-temperature water extraction therefore seems not suitable for the study of phosphorus species in soils.

CONCLUSIONS

High-temperature water extraction at elevated pressure is a suitable tool to obtain soil organic matter with little alteration of its chemical characteristics as compared to a conventional water extract. However, hydrolysis of labile components, such as organic phosphates, has to be taken into consideration. The optimal temperature for getting the best yield of chemical unaltered soil organic matter is between 100 and 150°C. At higher temperatures thermal degradation occurs leading to extracts enriched in aromatic and depleted in O-alkyl structures. Reproducibility of the ASE extraction is satisfactory. The different chemical composition of NaOH and $Na_4P_2O_7$ extracts probably is due to the different dissolution mechanisms at high pH.

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