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Total soluble nitrogen in forest soils as determined by persulfate oxidation and by high temperature catalytic oxidation

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Abstract. Speedy and reliable measurements of soil soluble nitrogen (N) are critical for estimating N fluxes in forest ecosystems. The high temperature catalytic oxidation (HTCO) method was assessed and compared with persulfate oxidation (PO) to measure total soluble N in water, hot water, 2 M KCl, and 0.5 M K_2SO_4 extracts of 24 forest soils collected from south-east Queensland. All salt extracts were diluted 5-fold before measurement by the HTCO method to minimise the effects of salt precipitation on the surface of the Pt/Al_2O_3 catalysts that may impair oxidation efficiency. Drifts of sensitivity of signals in diluted KCl (0.4 M), K_2SO_4 (0.1 M), and water matrixes by the HTCO method were minor, with <2% in KCl matrix and <3% in K_2SO_4 and water matrices. Nitrogen recoveries from most standard N-containing compounds (5 mg/L) analysed by the HTCO method in all the matrices tested were >94%. The values of total soluble N in all extracts of soils obtained by both the PO and the HTCO methods were highly correlated. However, the HTCO method generally gave greater values than the PO method, particularly with high concentrations of N. We consider the HTCO method to be a simple, automated, rapid, quantitative, and reliable method for determining total soluble N in both water extracts and diluted salt extracts of forest soils.

Additional keywords: chemiluminescence, recovery, fumigation, water extracts, K_2SO_4 extracts, KCl extracts.

Introduction

Soil soluble nitrogen (N) pools, including mineral N (NH_4^+, NO_3^-, and NO_2^-) and soluble organic fractions (e.g. amino acids and peptides), play a vital role in N cycling in forest ecosystems and in global biogeochemical cycling of N at the broader scale (Qualls and Haines 1991; Jones *et al*. 2004). It has been suggested that boreal forest plants utilise not only mineral N from soil but also soil organic N directly (Näsholm *et al*. 1998) and about half or more of N in soil solution occurs in organic form in forest ecosystems (Currie *et al*. 1996; Qualls *et al*. 2000; Yu *et al*. 2002). Soil soluble N is used as a sensitive indicator for soil N status (Zhong and Makeschin 2003). Moreover, soil soluble N also represents major inputs of N to surface water in forested watersheds and affects water quality (Hedin *et al*. 1995). The measurement of total soil soluble N is thus critical both for accurately estimating N fluxes in forest ecosystems and for predicting the potential for N pollution in associated water bodies (e.g. eutrophication).

Water and a range of salt solutions (e.g. $CaCl_2$, KCl, K_2SO_4) have been used for extracting soluble N from soil (Murphy *et al*. 2000; Zhong and Makeschin 2003). Acid Kjeldahl digestion is the classical method for determining total N in water samples and soil extracts (Kjeldahl 1883; Bremner and Mulvaney 1982; Cornell *et al*. 2003). This method is based on the conversion of organic N to NH_4^+-N in hot and concentrated H_2SO_4 solution with selenium as catalyst. The NH_4^+-N is then distilled and determined by titration. However, this method is slow and cumbersome. Various persulfate ($K_2S_2O_8$) oxidation (PO) methods have been introduced as alternatives for measuring total N in water and soil extracts (Ebina *et al*. 1983; Keroleff 1983; Cabrera and Beare 1993; Yu *et al*. 2003; Doyle *et al*. 2004). Using this method, both NH_4^+-N and organic N are converted to NO_3^--N by the persulfate oxidising agent. The reaction takes place either in an autoclave or under the influence of ultraviolet light. The NO_3^--N is determined colourimetrically (Cabrera and Beare 1993; Williams *et al*. 1995; Sparling *et al*. 1996). This method is simple, sensitive, reliable, and suitable for processing a large number of samples. However, total soluble N at higher concentrations (>9 mg/L) may be underestimated compared with Kjeldahl

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digestion (Cabrera and Beare 1993). High temperature oxidation (HTO) and high temperature catalytic oxidation (HTCO) were originally developed to determine the total N in seawater (Suzuki *et al.* 1985; Badr *et al*. 2003; Cornell *et al*. 2003). These methods convert all forms of N to NO or NO_2 by oxidising the samples in a high-temperature furnace, and the NO is coupled with ozone (O_3) to produce NO_2*, which is measured subsequently by chemiluminescence. These methods are simple to perform and give excellent precision in water samples (Badr *et al*. 2003). Recently, the HTCO method has been used to measure dissolved soil N and throughfall N and N in diluted K_2SO_4 extracts of soil (Merriam *et al*. 1996; Alavoine and Nicolardot 2001). However, only 5 soils with similar chemical properties and a single salt extract (K_2SO_4) were tested for determination of soil soluble N by the HTCO method (Alavoine and Nicolardot 2001). In this paper we compared the PO and the HTCO methods for determination of total N in a wide range of water and salt extracts (2 M KCl and 0.5 M K_2SO_4) from forest soils.

Materials and methods

Soil sampling

Twenty-four surface forest soil samples (0–0.10 m) were collected from south-east Queensland, Australia (from 25°46″29′S, 151°56″41′E to 27°00″28′S, 153°08″26′E). These encompass a range of soil types, forest types, management practices and levels of fertility (Table 1). Ten soil cores (60 mm in diameter) at the depth of 0–0.10 m were randomly taken from an area of 10 m by 20 m of each location in March 2002 and bulked as a composite sample. Field moist soil samples were passed through a 2-mm sieve and stored at 4°C before analysis. A subsample of each soil was air-dried and stored at room temperature. Analyses of soil pH, total C, total N, CEC, conductivity, particle size, and hot-water-extractable total N were carried out on air-dried soils, whereas water-soluble total N and KCl- and K_2SO_4-extractable total N were measured on field-moist soils. All results are expressed on an oven-dry soil basis.

Preparation of soil extracts

Water extracts were prepared by mixing 20 g (dry weight equivalent) of field-moist soil samples with 50 mL of distilled water (soil : water ratio 1 : 2.5) in an end-to-end shaker for 1 h and filtering through a Whatman 42 paper and then a 0.45-µm filter membrane. Hot water extracts were obtained according to the method described by Sparling *et al*. (1998). In brief, 4.0 g (dry weight equivalent) of air-dried soil was incubated with 20 mL water in a capped test-tube at 70°C for 18 h. The test-tubes were then shaken on an end-to-end shaker for 5 min, and filtered through a Whatman 42 paper, followed by a 0.45-µm filter membrane. For the KCl extracts, 5 g (dry weight equivalent) of field-moist soil samples were extracted with 50 mL of 2 M KCl in an end-to-end shaker for 1 h and filtered through a Whatman 42 paper. The 0.5 M K_2SO_4 extracts of chloroform ($CHCl_3$)-fumigated and non-fumigated soil samples were prepared using the method described by Vance *et al*. (1987). In brief, 2 portions of 25 g of field-moist soils (dry weight equivalent) were weighed, and one of them was directly extracted with 100 mL 0.5 M K_2SO_4 in an end-to-end shaker for 30 min, and filtered through a Whatman 42 paper. The other portion of soil was fumigated with $CHCl_3$ vapour for 24 h, and then extracted as above. All above soil extracts were stored at −20°C before analysis.

Analysis of soluble N in soil extracts

Total soluble N in soil extracts was simultaneously measured by both the PO and the HTCO methods. The PO procedure described by Cabrera and Beare (1993) was adopted to convert all N in soil extracts (including water, hot water, 2 M KCl and 0.5 M K_2SO_4) to NO_3^--N, which was then determined colourimetrically using a LACHAT Quickchem Automated Ion Analyser (QuikChem Method 10107-04-1-H for NO_3^-/NO_2^-, Colorado, USA). All soil extracts with >10 mg N/L were diluted before measurement. Five standard urea solutions, each containing 5 mg N/L, were used to measure persulfate oxidising efficiency in each run. Recovery of urea N by the PO method was 92.8%, 98.2%, and 98.6% for 2 M KCl, 0.5 M K_2SO_4, and water matrices, respectively. For the HTCO method, soil extracts were combusted using medical grade O_2 (purity >99.6%) at 720°C, total N in the extracts being converted to NO. The gas stream containing the NO was then cooled and dehumidified by the electronic dehumidifier, and the NO detected by chemiluminesce gas analyser. We use a SHIMADZU TOC-$_{VCPH/CPN}$ analyser (fitted with a TN unit) (Kyoto, Japan) for this work. It generally takes 10–12 min to analyse one sample. Water and hot water extract samples were analysed without dilution, but 2 M KCl and 0.5 M K_2SO_4 extracts were diluted 5-fold before measurement to minimise the precipitation of salts on the surface of Pt/Al_2O_3 catalysts with resulting decrease in catalyst efficiency. Water and diluted salt solution blanks were checked in each run and were found to be <0.06 mg N/L. The repeatability and drift of sensitivity for the HTCO method was checked by the continuous analyses of 20 standard solutions (5 mg N/L KNO_3) in 0.4 M KCl, 0.1 M K_2SO_4, or water.

Standard solutions of N-(1-naphthyl) ethylenediamine dihydrochloride (NED), sulfanilamide, glycine, L-aspartic acid, sodium nitrite, urea, ethylenediaminetetraacetic acid disodium salt (EDTA), ammonium chloride, L-glutamic acid sodium salt and L-arginine, each containing 5 mg N/L, were used to determine N recovery (against KNO_3 standard solution) by the HTCO method. All the above analyses were carried out in triplicate.

Analysis of other soil properties

Soil total C and total N were analysed using an isotope ratio mass spectrometer with a Eurovector Elemental Analyser (Isoprime-EuroEA 3000, Milan, Italy). Soil particle size, pH, CEC, and conductivity were measured the methods reported by Xu *et al*. (1995).

Statistical analysis

Regression analyses on relationships between the values of total soluble N measured by the PO and the HTCO methods in various matrices were carried out in Statistix for Window, version 2.2. The *t*-tests to compare the slopes of regression equations with 1 (the slope when values of total soluble N determined by 2 methods are identical, namely $y = x$) were carried out according to the method described by Zar (1999). Paired *t*-tests for N recovery of N-containing compounds in different matrices were carried out in Microsoft Excel 2000.

Results and discussion

Soil characteristics

Because the chemical and physical properties of the soils in Table 1 vary so widely, they make a good test-bed for comparing the HTCO and the PO methods. Soil pH ranged from 3.6 to 7.0, organic C from 0.609 to 8.295%, total N from 0.02 to 0.71%, CEC from 2.2 to 57.9 cmol/kg, conductivity from 0.013 to 0.773 dS/m, clay content from <1.0% to 49.2%, silt from <1.0% to 29.3%, and sand from 27.7% to 97.9%.

Table 1. Chemical and physical properties determined for the forest soils (0–0.10 m) collected

Locations	Soil type[A]	Vegetations and/or management	Soil pH	Organic C (%)	Total N (%)	CEC (cmol/kg)	Conductivity (dS/m)	Clay (%)	Silt (%)	Sand (%)
1. Toolara	Grey Kandosol	*Pinus elliottii* var. *elliottii*	5.1	2.39	0.12	12.9	0.031	12.4	22.1	65.6
2. Toolara	Grey Kandosol	6-year-old F_1 hybrid *Pinus elliottii* × *Pinus caribaea*, double residue retention	4.6	2.45	0.06	6.8	0.035	4.4	7.6	88
3. Toolara	Grey Kandosol	6-year-old F_1 hybrid *Pinus elliottii* × *Pinus caribaea*, all residue removed	5.1	1.00	0.03	4.4	0.015	4.2	7.4	88.4
4. Toolara	Red Kurosol	Native eucalypt (*E. racemosa*, *E. tindaliae*, *E. intermedia*, *E. acmenioides*)	4.8	1.48	0.06	6.3	0.029	4.1	11.2	84.7
5. Toolara	Red Kurosol	31-year-old *Pinus elliottii* var. *elliottii*	4.7	1.94	0.05	8.4	0.032	5.2	11.9	82.9
6. Tuan	Podosol	7-year-old F_1 hybrid *Pinus elliottii* × *Pinus caribaea*	3.6	1.81	0.03	5.1	0.040	<1.0	1.8	97.9
7. Tuan	Podosol	Native eucalypt (*E. umbra*, *Banksia aemula*, *Allocasuarina littoralis*)	4.0	1.32	0.03	3.9	0.021	<1.0	1.9	97.8
8. Tuan	Podosol	14-year-old *Pinus caribaea* var. *hondurensis*	3.9	1.93	0.04	8.4	0.026	<1.0	4.6	95.4
9. Tuan	Red Kurosol	10-year-old hybrid F_1 hybrid *Pinus elliottii* × *Pinus caribaea*	4.8	0.61	0.02	2.2	0.012	3.2	6.3	90.5
10. Beerburrum	Yellow Kandosol	30-year-old *Pinus elliottii* var. *elliottii*	4.9	1.40	0.04	5.3	0.023	4.0	8.4	87.6
11. Beerburrum	Yellow Kandosol	1.2-year-old hybrid F_1 hybrid *Pinus elliottii* × *Pinus caribaea*	4.8	1.44	0.05	6.5	0.028	7.9	9.8	82
12. Imbil	Red Ferrosol	Dry subtropical rainforests	6.2	6.45	0.63	54.3	0.157	40.5	24.1	35.4
13. Imbil	Red Ferrosol	2-year-old *Araucaria cunninghamii*	7.0	8.30	0.69	57.9	0.285	38.9	20.1	41.0
14. Beerburrum	Red Kandosol	Native eucalypt (*E. racemosa*, *E. tindaliae*, *E. intermedia*, *Angophora floribunda*)	4.7	1.70	0.05	7.6	0.027	6.4	7.8	85.8
15. Beerburrum	Red Kandosol	13-year-old F_1 hybrid *Pinus elliottii* × *Pinus caribaea*	4.3	2.39	0.06	8.9	0.046	5.2	6.3	88.5
16. Beerburrum	Arenic Rudosol	1-year-old F_1 hybrid *Pinus elliottii* × *Pinus caribaea*	4.1	0.87	0.02	2.5	0.013	1.8	<1.0	98.0
17. Yarraman	Black Dermosol	Dry subtropical rainforests	5.4	4.11	0.25	24.9	0.065	14.6	29.3	56.1
18. Yarraman	Black Dermosol	2nd rotation *Araucaria cunninghamii*	6.1	4.09	0.24	26.0	0.057	19.2	6.3	74.6
19. Yarraman	Red Ferrosol	2nd rotation *Araucaria cunninghamii*	5.8	5.41	0.43	32.5	0.082	42.2	16.7	41.1
20. Yarraman	Red Ferrosol	Dry subtropical rainforests	5.3	7.26	0.62	41.4	0.115	49.2	23.1	27.7
21. Beerburrum	Yellow Kandosol	Native eucalypt (*E. microcorys*, *E. pilularis*, *E. racemosa*, *E. siderophloia*)	4.9	0.88	0.04	3.9	0.026	2.75	8.7	88.6
22. Toolara	Red Kurosol	Native eucalypt (*E. microcorys*, *E. pilularis*, *E. racemosa*, *E. siderophloia*)	3.9	2.13	0.08	9.4	0.037	8.9	8.9	82.2
23. Beerburrum	Podosol	*E. racemosa*, *E. intermedia*, *Melaleuca quinquenervia*	5.2	2.48	0.10	10.2	0.033	1.0	2.9	96.1
24. Yarraman	Red Ferrosol	Native *Araucaria cunninghamii*	5.7	7.14	0.71	45.3	0.773	32.4	36	31.7

[A]Soil type was classified according to Isbell (1996).

Table 2. Sensitivity drifts with standard solutions (5 mg N/L, KNO_3) in KCl, K_2SO_4, and water matrixes by the HTCO method

Test no.	KCl (mg/L)	KCl Recovery (%)	K_2SO_4 (mg/L)	K_2SO_4 Recovery (%)	Water (mg/L)	Water Recovery (%)
1	5.00	100.0	4.99	99.9	5.08	101.5
2	5.03	100.6	5.03	100.6	4.95	99.1
3	4.95	99.1	4.89	97.8	5.03	100.6
4	5.02	100.5	4.94	98.7	5.09	101.7
5	4.93	98.6	5.02	100.4	5.01	100.2
6	4.87	97.3	5.06	101.2	4.90	97.9
7	4.95	99.0	4.91	98.3	5.00	100.0
8	4.95	99.0	4.87	97.4	5.03	100.5
9	4.92	98.4	4.97	99.5	4.92	98.4
10	4.96	99.2	4.87	97.4	4.96	99.2
11	5.03	100.7	4.95	99.0	4.96	99.1
12	5.07	101.5	4.91	98.2	5.10	101.9
13	5.06	101.1	4.90	98.1	5.13	102.7
14	4.95	99.0	4.97	99.3	5.03	100.6
15	4.94	98.8	4.87	97.3	4.97	99.4
16	5.01	100.1	4.86	97.1	5.08	101.7
17	4.91	98.3	4.93	98.7	4.89	97.8
18	4.93	98.6	4.85	97.0	4.95	99.0
19	4.97	99.4	4.93	98.7	5.05	100.9
20	4.95	99.0	4.92	98.4	5.03	100.6
Mean	4.97	99.0	4.93	98.6	5.01	100.1
s.d.	0.05	1.1	0.06	1.20	0.07	1.4

Assessment of the HTCO method

Preliminary studies showed that without dilution (2 M KCl and 0.5 M K_2SO_4), large amounts of salts were deposited on the Pt/Al_2O_3 catalyst pellets, leading to poor reproducibility and to decreases in the oxidation efficiency by *c*. 30% for 2 M KCl matrix and by *c*. 10% for 0.5 M K_2SO_4 matrix in the first 20 samples (data not shown). Similar results were also reported by Alavoine and Nicolardot (2001). For this reason, all the 2 M KCl and 0.5 M K_2SO_4 soil extracts were diluted 5-fold (i.e. to final concentrations of 0.4 M KCl and 0.1 M K_2SO_4) before measurement of total soluble N by the HTCO method. The ranges of total soluble N measured by the HTCO method, with an injection volume of 50 µL, were 0.511–3.829 mg/L for diluted KCl extracts, 0.518–14.114 mg/L for diluted K_2SO_4 extracts of fumigated and non-fumigated soils, and 0.823–31.08 mg/L for water and hot water extracts of soils (without dilution). These were within the designated detection limits of total soluble N by the HTCO method using the SHIMADZU TOC-$_{VCPH/CPN}$ analyser (0.1–4000 mg/L), which were much wider than the detection limits of the PO method (Cabrera and Beare 1993).

Drifts of sensitivity of signals in diluted KCl (0.4 M), K_2SO_4 (0.1 M) and water matrices by the HTCO method were very minor, with <2% in KCl matrix and <3% in K_2SO_4 and water matrices (Table 2). This was consistent with the result of signal sensitivity tests for standard solution in a 0.025 M K_2SO_4 matrix by the HTCO method (Alavoine and Nicolardot 2001).

Nitrogen recoveries from different standard N-containing compounds (5 mg/L) analysed by the HTCO technique (against KNO_3 standard solution) in all matrices tested (water, K_2SO_4, and KCl) were >94% except for sulfanilamide (*c*. 85–89%) (Table 3). These N recoveries are comparable to those found in other studies (Walsh 1989; Merriam *et al*. 1996; Álvarez-Salgado and Miller 1998;

Table 3. Recoveries of N compounds (5 mg N/L) dissolved in water, 0.1 M K_2SO_4, and 0.4 M KCl matrix and measured by the HTCO method (standard deviations of the mean in parentheses)

N compound	Recovery (%) in: Water	K_2SO_4	KCl
N-(1-Naphthyl) ethylenediamine dihydrochloride	99.9 (0.11)	102.9 (1.16)	103.5 (1.26)
Sulfanilamide	84.6 (1.57)	85.3 (1.16)	88.8 (0.17)
Glycine, anminoacetic, glycocll	97.8 (0.91)	99.1 (0.34)	99.7 (0.23)
L-aspartic acid	103.3 (0.49)	102.1 (0.48)	104.9 (0.48)
Sodium nitrite	103.2 (0.14)	102.6 (1.33)	103.9 (0.14)
Urea	96.0 (1.12)	94.1 (0.34)	100.6 (1.62)
Ethylenediaminetetra-acetic acid disodium salt	99.1 (1.44)	98.2 (1.17)	99.3 (0.54)
Ammonium chloride	102.2 (0.08)	101.9 (0.74)	104.6 (0.48)
L-glutamic acid sodium salt	101.7 (0.49)	96.6 (1.91)	95.3 (0.49)
L-Arginine	94.6 (0.82)	96.2 (0.14)	94.2 (0.11)
Mean	98.2	97.9	99.5

Table 4. Soluble N pools extracted by KCl, K_2SO_4, cold water, and hot water and determined by persulfate oxidation (PO) and by high temperature catalytic oxidation (HTCO)

Soils	Total soluble N (mg/kg) in KCl extracts		Total soluble N (mg/kg) in K_2SO_4 extracts, unfumigated		Total soluble N (mg/kg) K_2SO_4 extracts, fumigated		N flush (mg/kg) in response to fumigation		Water soluble total N (mg/kg)		Hot water extractable total N (mg/kg)	
	PO	HTCO	PO	HTCO	PO	HTCO	PO	HTCO	PO	HTCO	PO	HTCO
1	52.5	74.6	22.3	27.0	44.3	56.7	21.9	29.7	20.1	21.2	41.6	50.9
2	19.8	31.2	14.2	17.9	24.6	34.0	10.4	16.1	8.9	10.4	32.8	36.2
3	13.7	20.4	9.4	11.4	16.7	18.8	7.3	7.4	4.4	5.3	18.6	20.1
4	34.3	48.7	21.4	26.4	32.2	43.8	10.8	17.4	9.5	10.2	36.1	43.3
5	19.0	34.0	12.9	16.0	23.8	33.0	10.8	17.1	6.3	6.8	26.2	32.2
6	17.5	23.0	10.1	11.8	18.6	22.9	8.5	11.0	7.4	6.9	24.0	26.5
7	17.0	24.9	12.0	14.0	21.3	26.6	9.4	12.5	5.8	5.7	29.7	30.1
8	21.9	31.5	13.9	17.5	22.8	28.6	8.9	11.1	7.5	7.7	29.0	28.5
9	14.2	22.0	12.1	13.8	15.5	19.7	3.4	5.9	4.5	4.5	16.5	16.6
10	25.3	26.1	9.9	10.1	18.0	22.5	8.1	12.4	11.0	11.4	24.4	23.6
11	13.6	40.0	25.5	25.5	35.8	40.9	10.3	15.4	16.4	16.0	33.3	33.4
12	164.2	173.6	96.1	99.9	196.3	261.3	100.2	161.4	156.5	189.6	177.6	209.5
13	249.7	255.4	179.3	187.2	308.0	375.2	128.7	187.9	205.6	271.4	154.5	222.7
14	15.9	31.8	11.8	14.6	22.5	25.7	10.6	11.1	4.2	4.9	22.3	20.2
15	27.0	46.7	21.8	27.2	33.3	45.8	11.5	18.6	10.4	11.9	38.5	38.2
16	8.8	14.0	11.1	10.3	11.4	13.3	0.4	2.9	4.9	3.5	18.1	16.7
17	17.8	25.8	18.4	23.8	30.9	41.2	12.4	17.3	16.9	16.1	77.9	84.6
18	22.2	38.1	19.3	24.7	35.3	48.0	16.0	23.3	17.0	13.3	57.4	72.6
19	59.9	70.7	52.9	70.4	69.3	95.4	16.4	25.0	34.6	35.3	126.6	141.7
20	83.8	94.7	70.9	86.1	100.8	125.4	29.9	39.3	51.5	51.6	183.7	236.8
21	18.7	31.1	15.9	19.7	19.4	28.8	3.5	9.1	9.7	9.6	27.6	25.9
22	39.3	61.9	26.4	35.2	38.5	52.1	12.1	17.0	15.6	15.4	48.5	51.9
23	27.9	45.7	14.4	16.2	26.8	35.4	12.4	19.2	11.7	11.2	40.9	39.9
24	177.3	183.9	82.6	89.4	166.8	218.9	84.3	129.5	107.5	113.3	435.4	658.9
Mean	48.4	60.4	32.7	37.3	55.5	71.4	22.8	34.1	31.1	35.5	71.7	90.0
CV%	20.3	25.9	24.6	22.7	26.1	25.5	29.2	29.9	33.8	37.6	26.4	31.4

Alavoine and Nicolardot 2001; Doyle *et al*. 2004). For example, Merriam *et al*. (1996) reported that N recoveries by the HTCO method for $NaNO_2$, EDTA, NED, caffeine, and glycine dissolved in water were >90%, for N concentrations of 0.5–10.0 mg/L. They also found that the HTCO method gained low recovery of sulfanilamide N (85.7% at 5 mg/L). Alavoine and Nicolardot (2001) observed nitrogen recoveries >98% for 12 different standard N compounds (at 10 mg/L) in 0.025 M K_2SO_4 matrix by the HTCO method. Doyle *et al*. (2004) also reported N recovery of >97% of N recoveries from glycine, lysine, urea, yeast extract, and nicotinamide by the HTCO method, all higher than the corresponding recoveries by the PO method (92–96%). The N recoveries from L-aspartic acid, $NaNO_2$, and NH_4Cl in all matrices tested exceeded 100% in our study, indicating that the N in these compounds was more completely oxidised to NO than the standard KNO_3 used to calibrate the analyser. Alavoine and Nicolardot (2001) also found that recovery of N from $NaNO_2$ in 0.025 M K_2SO_4 by HTCO was over 100%. A paired *t*-test showed that there were no significant differences observed in N recovery for N-containing compounds among different matrices in our study ($P > 0.05$) (Table 3). This further indicates that the HTCO method is suitable for determining total soluble N in both water and diluted salt extracts of forest soils.

Accumulated deposition of salts on the surface of catalyst can gradually reduce oxidation efficiency of the catalyst for the HTCO method. Dilution of salt extracts can reduce this impact and enhance the sensitivity of measurement. The performance of the catalyst can be checked by analysing a set of standard solutions. We suggest that it is necessary to perform the regeneration of the catalyst after each run on the SHIMADZU TOC-$_{VCPH/CPN}$ analyser and the catalyst needs to be replaced after measurement of about 1000–1500 samples in 0.4 M KCl matrix and 1500–2000 samples in 0.1 M K_2SO_4 matrix.

Comparing the PO and the HTCO methods for the determination of total soluble N

The results of total soluble N measured by the PO and the HTCO methods are shown in Table 4. The values of total soluble N in 2 M KCl extracts measured by 2 methods were well correlated ($r^2 = 0.989$, $P < 0.01$) (Fig. 1). The PO method tended to give lower values for total soluble N than the HTCO method, while the slope of the regression curve (0.975) was not significantly different from 1 (Fig. 1). Total soluble N in 0.5 M K_2SO_4 extracts of unfumigated soils determined by both methods was significantly correlated ($r^2 = 0.992$, $P < 0.01$), similarly for fumigated soils ($r^2 = 0.996$, $P < 0.01$) (Fig. 2). The slope of regression curve (1.051) for unfumigated soils was not significantly different from 1, whereas the slope of the regression curve (1.254) for fumigated soils was significantly different from 1 ($P < 0.05$) (Fig. 2). These results showed that the PO method underestimated total soluble N in K_2SO_4 extracts compared with the HTCO method, particularly with

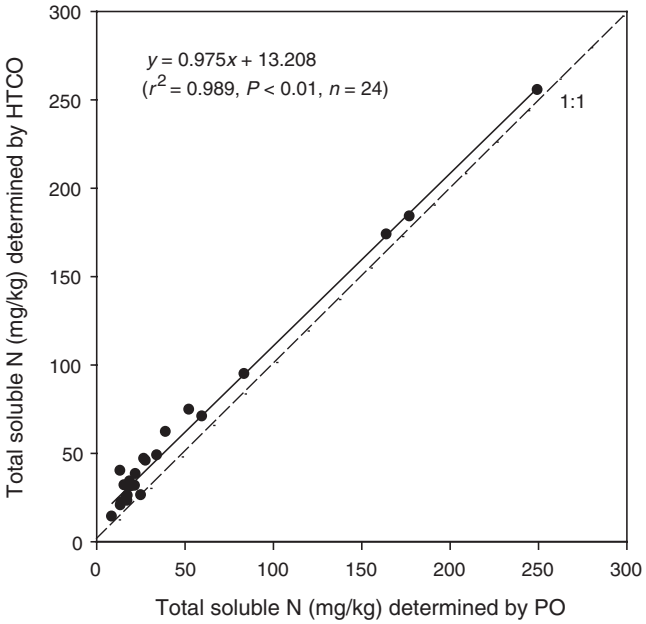

Fig. 1. Relationships between values of total soluble N in 2 M KCl extracts of forest soils, as determined by persulfate oxidation (PO) and by high temperature catalytic oxidation (HTCO). Solution diluted 5-fold before analysis.

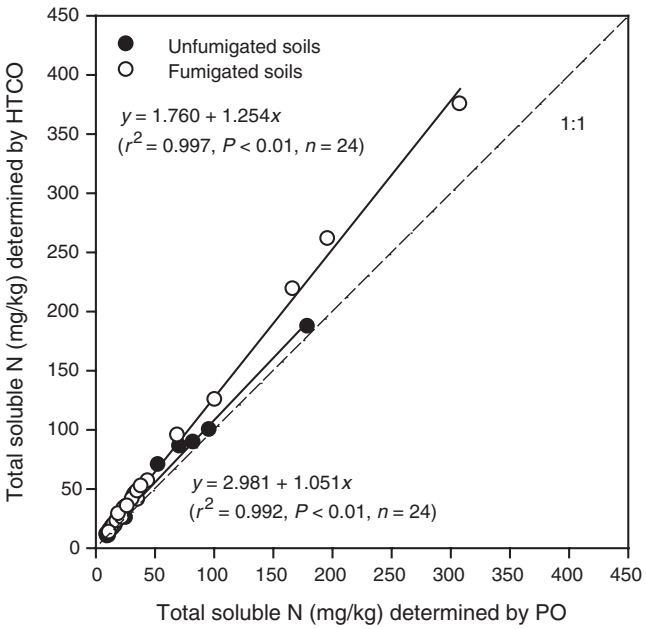

Fig. 2. Relationships between values of total soluble N in 0.5 M K_2SO_4 extracts of unfumigated and fumigated forest soils determined by persulfate oxidation (PO) and by high temperature catalytic oxidation (HTCO). Solution diluted 5-fold before analysis.

high concentrations of N (e.g. K_2SO_4 extracts of fumigated soils), even though dilution procedures were carried out when total N in the extracts was >10 mg/L. Doyle *et al*. (2004) also reported that the PO method recovered 95% of dissolved organic N in soil K_2SO_4 extracts compared with the HTCO method. More N released by fumigation was measured by the HTCO method than by the PO method (Table 4, Fig. 3). The regression slope was significantly different from 1 ($P < 0.05$) although the values obtained by 2 methods were significantly correlated (Fig. 3).

The values for total soluble N in water extracts obtained by the 2 methods were significantly correlated (Fig. 2), and similar when concentrations of total soluble N were low (<~115 mg/kg soil) (Table 2, Fig. 4). The regression slope was not significantly different from 1. The values of hot-water-extractable total N measured by the HTCO method were generally greater than by the PO method, particularly for high N concentrations (Table 2, Fig. 5). The regression slope was also significantly different from 1. Merriam *et al*. (1996) also found that the values of total soluble N measured by the HTCO and the PO methods in throughfall and soil solutions were highly correlated within a range from <0.5 to 110 mg/L, but that the HTCO method produced slightly greater values than the PO method. Maita and Yanada (1990) also reported a similar result with a range of N concentrations from 0 to 50 µg/L. The underestimation of total soluble N by the PO method compared with the HTCO method may be due to more complete oxidation of soluble N by the HTCO method. For some chemical compounds (such as amino-antipyrine caffeine), efficiency of N recovery by the PO method could be as low as *c*. 50–85%. (e.g. Zhu and Carreiro 2004). It is also possible that NH_4-N is lost through evolution of NH_3 under the alkaline condition of the persulfate oxidation (Ross 1992).

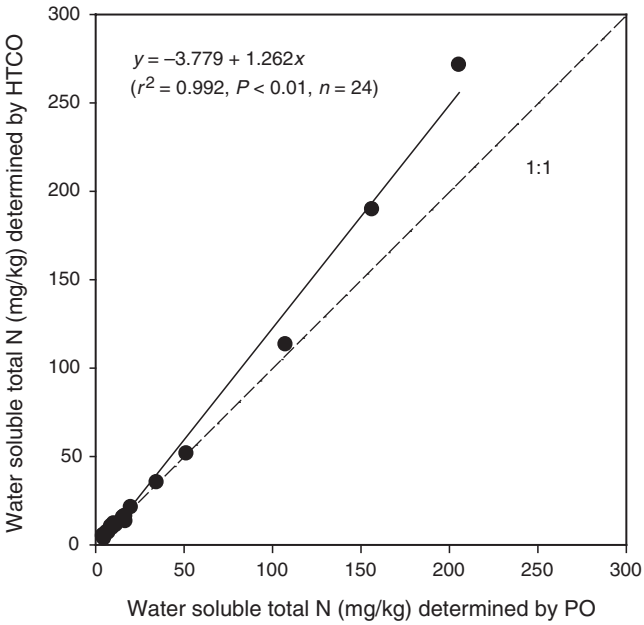

Fig. 4. Relationships between values of water-soluble total N in forest soils, as determined by persulfate oxidation (PO) and by high temperature catalytic oxidation (HTCO).

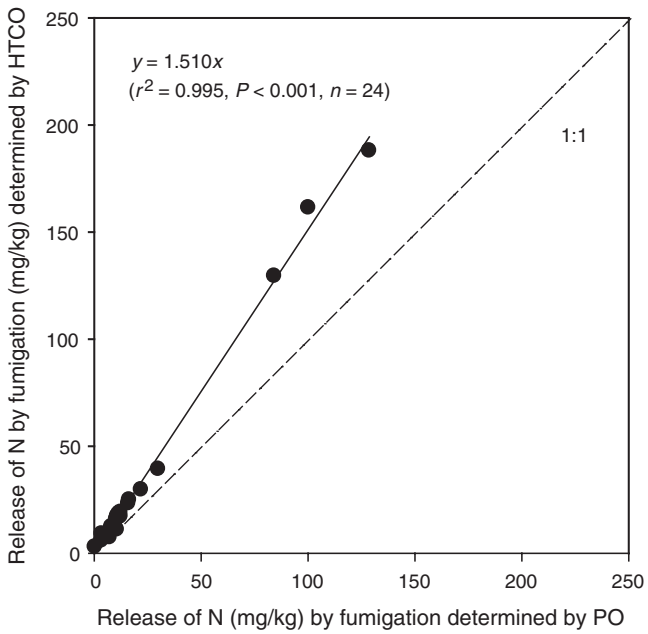

Fig. 3. Release of N by fumigation in forest soils, as determined by persulfate oxidation (PO) and by high temperature catalytic oxidation (HTCO). Solution diluted 5-fold before analysis.

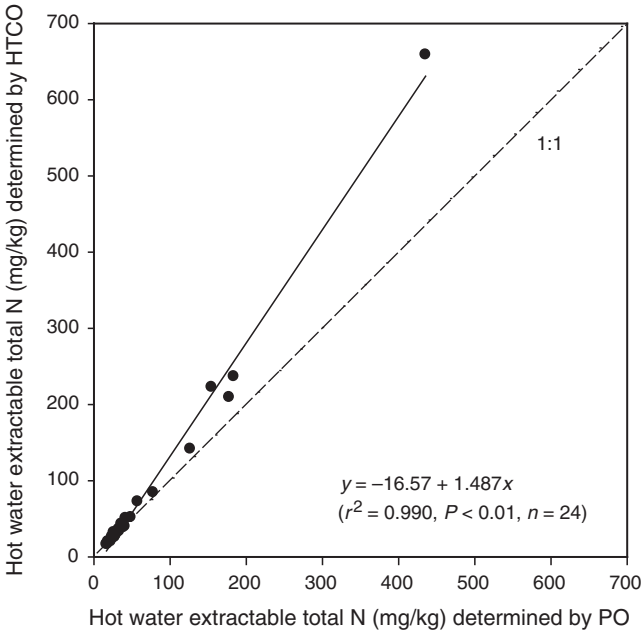

Fig. 5. Relationships between values of hot-water-extractable total N in forest soils, as determined by persulfate oxidation (PO) and by high temperature catalytic oxidation (HTCO).

Conclusions

The values of total soluble N in various extracts of forest soils measured by PO and HTCO methods were highly correlated, but the HTCO method gave more complete oxidation and thus appeared to give greater values for total soluble N than the PO method. We consider the HTCO method to be a simple, automated, rapid, quantitative, and reliable method, with a wider concentration range, for determining total soluble N in both water extracts and diluted salt extracts of forest soils. However, the HTCO method using the SHIMADZU TOC-$_{VCPH/CPN}$ analyser also has some constraints for concentrated salt extracts of soils. Salt extracts of soil require dilution before measurement and the catalysts have to be replaced more often. We suggest that the catalyst needs to be replaced after measurement of ~1000–1500 samples in 0.4 M KCl matrix and 1500–2000 samples in 0.1 M K_2SO_4 matrix.

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