Predicting the stage of decay of decomposing leaves by near infrared reflectance spectroscopy

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To study mineral cycling in forest ecosystems, it is essential to know the decomposition rate of the litter. This study attempted to predict directly, by near infrared reflectance spectroscopy, the stage of decomposition of leaf litter expressed as the percentage of ash-free litter mass remaining (LMR). Leaf litter of 10 different species, with varied initial compositions and at different stages of decomposition produced by incubation in the laboratory under controlled conditions, were used in this study. The LMR calibrations were carried out on half of the samples of the various populations (all species, woody species, broad-leaved species, trees, broad-leaved trees, oaks, deciduous trees, and evergreen trees). The standard error of cross validation varied between 1.69 and 3.01. Predictions were carried out on the other half of the samples of each population; the standard error of prediction varied between 2.35 and 3.77, with a r^2 (coefficient of determination) of 0.97 to 0.99. The calibration equations obtained from the laboratory samples were applied to samples that had decomposed in the field in litter bags. The standard error of prediction varied between 4.46 and 5.97, with a r^2 of 0.90 to 0.93. Near infrared reflectance spectroscopy thus provides a direct prediction of the LMR in leaf litter of different species, during the decomposition stage studied (i.e., between 100 and 20% of litter mass remaining). The possibilities of using near infrared reflectance spectroscopy in decomposition studies are discussed.

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Pour étudier le cycle des éléments minéraux dans les écosystèmes forestiers, il est nécessaire de connaître la vitesse de décomposition des litières. La présente étude tente de prédire directement, par spectroscopie proche infra rouge, le stade de décomposition de litières de feuilles, exprimé en pourcentage restant du poids initial, sans cendres (RML, reste de masse des litières). Des litières de feuilles de 10 espèces différentes, de composition chimique initiale variée et à différents stades de décomposition obtenus par incubation au laboratoire sous conditions contrôlées, ont été utilisées dans cette étude. Les calibrations pour le RML ont été effectuées sur la moitié des échantillons de différentes populations (toutes les espèces, espèces ligneuses, espèces feuillues, arbres, arbres feuillus, chênes, arbres décidus, arbres sempervirents). L'erreur standard de calibration varie de 1,69 à 3,01. Les prédictions ont été réalisées sur l'autre moitié des échantillons de chaque population; l'erreur standard de prédiction varie de 2,35 à 3,77, avec un r^2 (coefficient de détermination) de 0,97 à 0,99. Les équations de calibration obtenues à partir des échantillons de laboratoire ont été appliquées à des échantillons ayant décomposé sur le terrain dans des sachets. L'erreur standard de prédiction varie de 4,46 à 5,97 avec un r^2 de 0,90 à 0,93. La spectroscopie proche infra rouge permet donc de prédire directement le RML de litières de feuilles d'espèces différentes, au cours de la phase de décomposition étudiée, c'est à dire jusqu'à 80% de perte en poids. Les perspectives d'utilisation de la spectroscopie proche infra rouge dans les études de décomposition sont discutées.

Introduction

The understanding of nutrient cycling in forest ecosystems needs accurate prediction of decay rates of plant material. During decomposition processes, both weight and the biochemical characteristics of litter change with time (Swift et al. 1979; Berg and Staaf 1980; Taylor et al. 1989). Generally, curves of weight loss with time are fitted to an exponential decay model (Olson 1963). The decay constant k, can therefore be used to compare the decomposition of different species subjected to the same environmental conditions or of the same species along climatic gradients. The method that has usually been used for a considerable time (Falconer et al. 1933; Lunt 1933) is that of litter bags, but such studies are lengthy and time-consuming. In addition few studies have been able to measure long-term changes of litter. They are also adversely affected by bias because they involve the retention of the litter in bags that alter the microclimate and the macrofaunal activity (Witkamp and Olson 1963; Witkamp and Crossley 1966; St. John 1980).

Biochemical changes in litter during its decomposition follow a rather generalized pattern, with first the loss of the more soluble compounds, then degradation of cellulose, and finally attack of lignified compounds. The biochemical structure of the litter changes by passing through successive stages of immobilization and release of nutrients, and many models show that the release of nutrients depends on the stage of evolution of lignocelluloses (Berg 1986, 1988; Berg and McClaugherty 1989). In reality, each stage of decomposition is controlled by the current chemical structure of the litter. Melillo et al. (1989) and Aber et al. (1990) distinguished two major stages during litter decomposition. In stage 1, the litters lose a constant proportion of their weight per unit time, until the stage is reached where about 20% of the initial weight remains; at this stage all litters have a very similar chemical

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TABLE 1. Groupings of species for calibrations and predictions

	Tree	Shrub	Grass	Woody	Broad-leaved	Deciduous	Evergreen
Quercus pubescens	+			+	+	+	
Quercus ilex	+			+	+		+
Quercus coccifera	+			+	+		+
Castanea sativa	+			+	+	+	
Fagus sylvatica	+			+	+	+	
Pinus halepensis	+			+			+
Cistus albidus		+		+	+		
Cistus monspeliensis		+		+	+		
Brachypodium retusum			+				
Brachypodium phoenicoides			+				

composition (decay filter concept). During stage 2, litters only lose weight very slowly and change little chemically, while being incorporated into the soil. During the first stage, the litter weight loss is always strongly correlated with the increase in the concentration of nitrogen and of the lignocellulose index (lignin/(lignin + cellulose)). The speed at which this process takes place depends on environmental conditions such as soil moisture and temperature and air temperature, and on the initial litter quality. Several studies correlate the decomposition rate with the initial chemical composition of the litter: initial N concentration or C/N ratio (Aber and Melillo 1980; Taylor et al. 1989), concentration of N and water soluble compounds (Berg and Ekbohm 1991), lignin concentration (Fogel and Cromack 1977; Meentemeyer 1978; Berendse et al. 1987), lignin/N ratio (Melillo et al. 1982; Edmonds 1987; Stohlgren 1988; Blair 1988), lignin + cellulose (Aber et al. 1990), and holocellulose to lignocellulose quotient in late stages (McClaugherty and Berg 1987). In all these models the relative proportions of carbon, lignin, and nitrogen play a determinant role in the succession of processes and their speed.

However, all these studies are based on a rather rough understanding of the biochemical composition of litter and particularly of the organic fractions measured by classical chemical methods (Ryan et al. 1990). The methods measure the residues remaining at each stage, following successive attacks, and these residues in reality contain complex mixtures of different compounds. In addition, there is a constant exchange of compounds between the various fractions during decomposition. Thus Schlesinger and Hasey (1981), McClaugherty et al. (1985), Berg (1986, 1988), Maheswaran and Attiwill (1987), and Hart et al. (1992) noted that the organic fraction corresponding to "lignin" increased in absolute value during litter decomposition because the methods of chemical analysis used also include within this fraction those secondary compounds and humic substances that are formed during decomposition. This fraction was therefore called the "acid insoluble substance" by Berg (1986, 1988) or the "hard fraction" by Maheswaran and Attiwill (1987). For these reasons other types of approaches, of a physico-chemical nature, have recently been explored to study the biochemical structure of litter during decomposition. These include ^{13}C NMR spectroscopy (Zech et al. 1987; Norden and Berg 1989; Cogle et al. 1989), ^{13}C NMR spectroscopy and pyrolysis-field ionization mass spectroscopy (Kögel et al. 1988; Kögel-Knaber et al. 1988), differential scanning calorimetry and differential thermogravimetry (Reh et al. 1990), and infrared spectroscopy (Zech et al. 1987; Tam et al. 1991; McLellan et al. 1991*a*, 1991*b*; Joffre et al. 1992).

Recent works on the use of near infrared reflectance spectroscopy (NIRS) show that this is a powerful and quick method for predicting the biochemical composition of the canopy (Card et al. 1988; Wessman et al. 1988) and of forest litter (McLellan et al. 1991*a*, 1991*b*; Joffre et al. 1992). Preliminary results involving litter show in particular that the spectra are deformed in a regular manner as the decomposition progresses (McLellan et al. 1991*a*; Joffre et al. 1992). An attempt has therefore been made to relate this progressive spectral change, shared by all species, with the stage of decomposition of the litter, even if it is difficult to interpret these changes in terms of identified chemical constituents. This spectroscopic method seems to be able to answer the following questions:

(1) Since it is biochemical processes that control the changes in litter and its weight loss, could chemical properties, detectable by NIRS, be correlated with a given weight loss? In other words, can the stage of decomposition of a litter be determined directly, without having to undertake a litter bag type of experiment?
(2) Could this temporal change in chemical properties of leaf litter be general, irrespective of the speed at which it takes place and of the species or environmental conditions? In other words, does the precision of prediction of the stage of litter decomposition made by NIRS depend on the species and the speed of decomposition?

In this study an attempt has been made to determine the litter mass loss (or the litter mass remaining) directly using NIRS. This technique was first tested on samples of litter of various species and with varied initial chemical composition, at different stages of decomposition, in the laboratory under controlled conditions. Next, a check was made to test whether the calibrations thus obtained were applicable to litter that had decomposed in the field, under natural conditions.

Material and methods

Litter decomposition experiments

Two data sets collected from two experiments were used. The first experiment was conducted in the laboratory and involved 10 species (Table 1): 5 broad-leaved trees (*Quercus pubescens* L., *Quercus ilex* L., *Quercus coccifera* L., *Castanea sativa* Miller, and *Fagus sylvatica* L.), 1 conifer (*Pinus halepensis* Miller), 2 shrubs (*Cistus monspeliensis* L. and *Cistus albidus* L.), and 2 grasses (*Brachypodium retusum* (Pers.) Beauv. and *Brachypodium phoenicoides* Roem. & S.). Fresh fallen leaf litter of the woody species was collected at the leaf

TABLE 2. Initial chemical characteristics of leaf litters

	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)	C (%)	N (%)	C/N ratio	Lignin/N ratio
Quercus pubescens	25.2	14.4	17.3	6.4	50.4	0.98	51.4	17.7
Quercus ilex	22.6	15.2	14.9	6.0	51.9	1.02	50.9	14.6
Quercus coccifera	18.6	16.2	21.0	8.3	50.5	1.47	34.4	14.3
Castanea sativa	20.0	14.2	12.6	6.3	51.8	0.93	55.7	13.6
Fagus sylvatica	28.1	18.6	30.6	5.2	52.3	1.15	45.5	26.6
Pinus halepensis	21.7	10.4	16.5	5.6	56.6	0.80	70.7	20.6
Cistus albidus	25.2	11.0	21.9	9.1	46.6	0.75	62.1	29.2
Cistus monspeliensis	17.9	5.6	28.8	9.6	52.1	1.11	46.9	26.0
Brachypodium retusum	32.6	32.7	8.8	5.8	48.3	1.00	48.3	8.8
Brachypodium phoenicoides	32.8	33.1	10.1	7.4	46.6	1.06	44.0	9.5

fall period from near Montpellier. Dead leaves of the two grass species were cut during the summer. In the laboratory, a microcosm system, as described by Taylor and Parkinson (1988), was used. Air-dried samples of 7.00 ± 0.01 g were remoistened in water for 24 h and were put on a 2-mm nylon mesh on the soil surface of the microcosms. Microcosms were maintained at 22°C and were watered once a week to maintain soil moisture at 80% of field capacity. Five replicates of each litter were removed at 0.5, 1, 2, 4, 6, 10, and 14 months. The total number of samples thus obtained was 440.

The second experiment was conducted in the field in a *Q. pubescens* forest (50 km northeast of Marseille, 200 km east of Montpellier) and involved two species: *Q. pubescens* and *P. halepensis*. In this experiment, 5 mm mesh bags containing 10 g of air-dried litter, collected near this forest, were placed on the soil surface. Three replicates were removed after 5, 12, 19, and 26 months. The total number of samples thus obtained was 29.

All samples were dried in a ventilated oven at 60°C until constant weight, weighed, then ground in a cyclone mill through a 1-mm mesh.

Wet chemistry analyses for C, N, and proximate carbon fractions were carried out on the initial leaf litter (Table 2). C and N contents were determined with a Perkin–Elmer elemental analyser (PE 2400 CHN), and cellulose, hemicellulose, and lignin were determined using Van Soest (1963, 1965) procedures adjusted for Fibertec (Van Soest and Robertson 1985).

NIRS analysis

All samples were scanned with a near infrared reflectance spectrophotometer (NIRSystems 6500). Two replicate reflectance measurements of monochromatic light were made at 2-nm intervals over the range from 400 to 2500 nm, to produce an average spectrum with 1050 data points . Reflectance (R) was converted to absorbance (A) using the following equation: $A = \log(1/R)$. Data analysis was conducted using the ISI software system (Shenk and Westerhaus 1991*b*).

Determination of the litter mass remaining

The ash content of the litter samples was determined using NIRS (Joffre et al. 1992). A calibration equation was calculated from samples from the same batch of litter, on which the ash content was determined using wet chemistry methods. This allowed the ash content (%) in the leaf litter to be determined from the spectra, using modified partial least squares regression and scatter regression, with a standard error of cross validation of 1.52 and a coefficient of determination (r^2) of 0.99. The ash content of all the litter samples was thus predicted, which enabled the ash-free litter mass remaining to be determined for each. The ash-free, ovendried, litter mass remaining is hereafter denoted as LMR.

Population definition and calibration procedures

Calibrations were developed for LMR from laboratory samples. To test the influence of the homogeneity of the calibration set on the precision of the prediction, several sample populations were defined. Calibrations were then calculated for each of these populations. These populations involved the following groupings of species: all species, woody species, broad-leaved species, trees, broad-leaved trees, oaks, deciduous trees, and evergreen trees (Table 1). Calibrations were not calculated for each individual species, as the number of samples was insufficient (<40). For each population, all the samples were ranked and then divided into two sets on an every second sample basis.

The first set was the calibration set. A principal components analysis was carried out on each population in order to identify and eliminate samples that deviated too far from the sample mean. The principal component scores associated with the largest eigenvalues were multiplied by the spectral data to obtain sample loadings (Shenk and Westerhaus 1991*a*). Mahalanobis distances (H) (Mahalanobis 1936) from the average spectrum were then computed on the sample loadings. This procedure provides a ranking of the spectral data on the basis of the standardized H distance from the average spectrum. Spectra with standardized $H > 3$ were eliminated from the calibration set (Shenk and Westerhaus 1991*a*, 1991*b*). The calibration equations were then calculated using the modified partial least squares regression method (Martens and Jensen 1982; Shenk and Westerhaus 1991*b*). This uses all the spectral information, unlike stepwise regression type methods, which only use a small number of wavelengths (Windham et al. 1989). This method proved to be more powerful than the stepwise regression method for determining the chemical composition of the same sample set (Joffre et al. 1992). In addition, all the calibrations were obtained after correcting the spectra by a detrending method (Barnes et al. 1989). Two series of calibrations were produced, the first on the entire spectrum (400–2500 nm) and the second on the near infrared (1100–2500 nm). In both cases, that part of the spectrum corresponding to water (1948–1968 nm) was excluded. For each calibration, six mathematical treatments, corresponding to the first and second derivative and a gap of 8, 16, and 24 nm (4, 8, and 12 data points) were compared. After comparison of the results of various mathematical treatments, the calibration equation that gave the best results in terms of standard error of cross validation was selected.

The second microcosm set was used as the validation set. The LMR values were predicted using the calibration equations and compared with the measured values, allowing calculation of the standard error of prediction.

The last stage consisted of verifying that the calibrations based on laboratory samples were valid for making predictions about field samples. This was done by first checking that the field samples belonged to the same population as that defined by the laboratory samples by carrying out a principal components analysis and then calculating the H distances. Then the LMR values were predicted and the precision of this prediction (SE of prediction) for different calibration equations was calculated.

Results

Diversity of the leaf litter studied

The leaf litter of the 10 species used in this study showed great diversity in their initial chemical composition (Table 2).

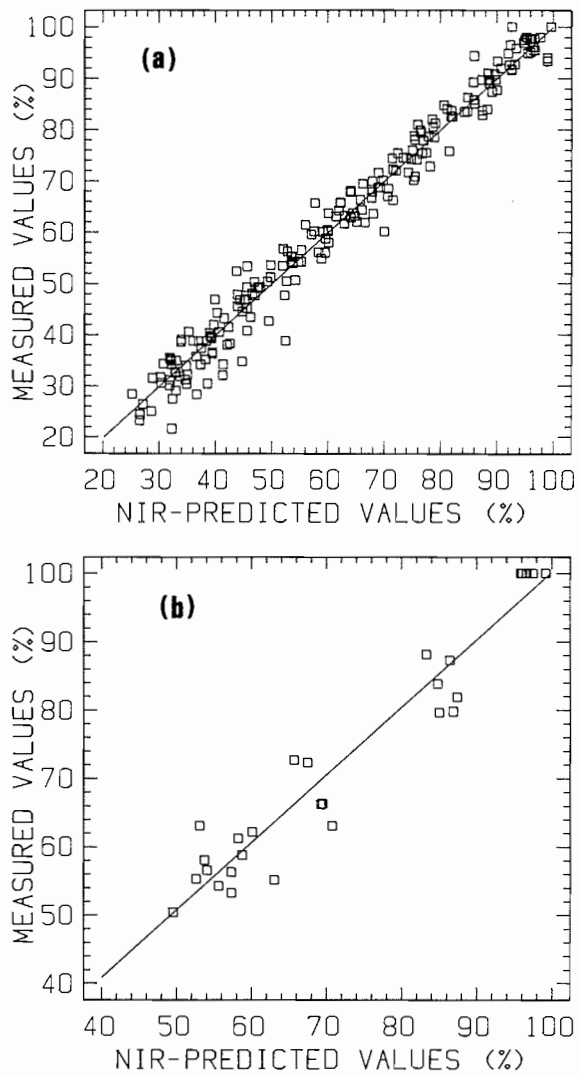

FIG. 1. Relationships between measured values of litter mass remaining (LMR) and near infrared (NIR-) predicted LMR values using the microcosm calibration equation carried out on all species and on the entire spectrum. (*a*) Microcosm samples (n = 216, r^2 = 0.98, SE of prediction = 3.53). (*b*) Field samples (n = 29, r^2 = 0.93, SE of prediction = 4.46).

The N concentrations varied by a factor of 2 (0.75 to 1.47%) and those of lignin by a factor of 3 (8.8–30.6%). The C/N and lignin/N ratios, which are the indices most commonly used as criteria of litter quality, varied from 34.4 to 70.7 and from 8.8 to 29.2, respectively. The stages of decomposition (LMR) varied from 100 to 22% and were distributed regularly over this entire range (Fig. 1*a*).

Calibrations

All the calibrations obtained showed that the absorbance spectra are closely correlated with LMR. The coefficients of determination were all equal to 0.99, and the standard error of cross validation varied from 1.69 to 3.01 (Table 3). When the calibrations were carried out on a limited number of species, the standard error of cross validation decreased (Table 3).

For equivalent groupings of species, the standard errors of calibration were very similar, whether the calibrations were carried out on the entire spectrum or only on the near infrared. In contrast, the standard error of cross validation values were always lower in the second case (Table 3).

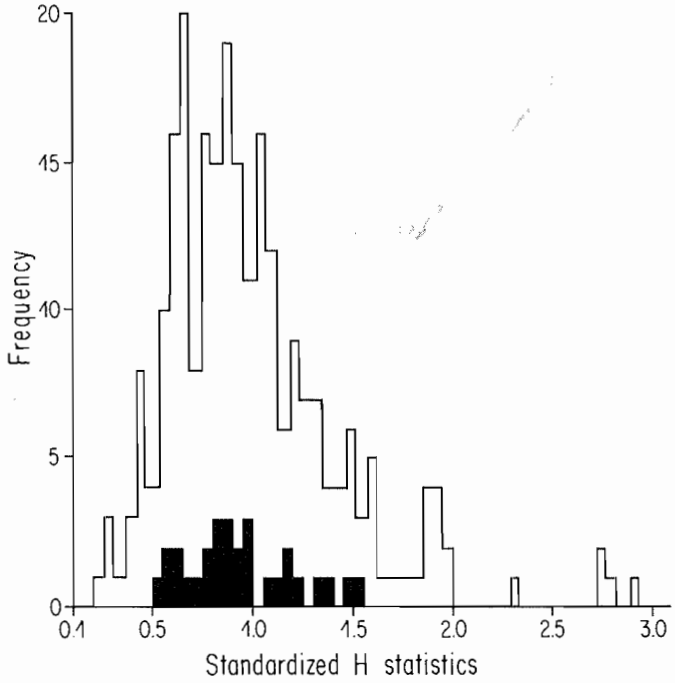

FIG. 2. Distribution of standardized Mahalanobis distance (H) from the mean for all microcosm calibration samples and field samples. Open area, all samples; black area, field samples.

Prediction of LMR in microcosm samples

The LMR values predicted from the various calibration equations were all close to the measured values (Fig. 1*a*): the standard error of prediction varied from 2.35 to 3.77, the coefficient of determination (r^2) from 0.97 to 0.99, and the bias from 0 to 0.78 (Table 4).

On the whole, the standard error of prediction tended to decrease when the predictions were carried out on a more limited group of species. It was also noted that in all cases of equivalent grouping of species, except for trees, the standard error of prediction was always lower when the calibration equation used all of the spectrum, rather than just the near infrared region (Table 4).

Prediction of LMR in field samples

The principal components analysis carried out on all the calibration sample set and the field samples showed that the field samples belonged to the same spectral family as the microcosm leaf litter calibration set (Fig. 2). When the calibration equations derived from the microcosm calibration set (all species, woody species, and trees) were applied to the field samples, the predicted LMR values were close to the measured values (Fig. 1*b*), but with a slightly greater error than for the microcosm samples: standard error of prediction between 4.46 and 5.97, r^2 between 0.90 and 0.93, and bias between 0.46 and 2.11 (Table 5).

The calibration equations derived from all species gave the best predictions (Table 5), and for two equations out of three, the prediction was better if the equations derived from the entire spectrum were used rather than just from the near infrared.

TABLE 3. Calibration statistics of LMR (% litter mass remaining), using the entire spectrum (400–2500 nm) or only the near infrared (1100–2500 nm)

Treatment	No. of species	*n*	Mean	Range	SEC	r^2	SECV	Math
400–2500 nm								
All species	10	217	62.75	100–24.76	2.39	0.99	3.01	1 4 4
Woody species	8	184	62.89	100–24.76	2.07	0.99	2.75	2 8 4
Broad-leaved species	7	150	62.79	100–24.76	2.15	0.99	2.52	1 12 8
Trees	6	148	64.44	100–24.76	1.78	0.99	2.44	2 8 4
Broad-leaved trees	5	115	63.93	100–24.76	1.87	0.99	2.49	1 12 8
Evergreen trees	3	88	63.57	100–25.80	1.12	0.99	1.77	2 12 8
Deciduous trees	3	62	65.80	100–24.76	1.22	0.99	2.12	1 8 4
Quercus	3	75	63.76	100–30.29	1.13	0.99	2.21	1 4 4
1100–2500 nm								
All species	10	214	62.49	100–24.76	2.40	0.99	2.81	1 4 4
Woody species	8	182	63.04	100–24.76	2.13	0.99	2.50	1 8 4
Broad-leaved species	7	148	62.50	100–24.76	2.23	0.99	2.47	1 12 8
Trees	6	150	64.32	100–24.76	1.90	0.99	2.36	1 4 4
Broad-leaved trees	5	114	64.42	100–24.76	1.61	0.99	2.27	1 8 4
Evergreen trees	3	88	63.57	100–25.80	1.30	0.99	1.69	2 8 4
Deciduous trees	3	61	66.24	100–24.76	0.82	0.99	1.82	1 4 4
Quercus	3	73	63.94	100–30.29	1.55	0.99	2.15	2 8 4

NOTE: Math treatment indicates the mathematical transformation of spectral data: the first number is the order of the derivative function, the second is the segment length in data points over which the derivative was taken, and the third is the segment length over which the function was smoothed. SEC, standard error of calibration; SECV, standard error of cross validation.

TABLE 4. Prediction statistics of LMR (% litter mass remaining) in microcosm samples, using the entire spectrum (400–2500 nm) or only the near infrared (1100–2500 nm)

	No. of species	*n*	Mean	Range	SEP	r^2	Bias
400–2500 nm							
All species	10	216	62.96	100–21.6	3.53	0.98	−0.18
Woody species	8	185	62.81	100–21.6	3.56	0.98	−0.14
Broad-leaved species	7	151	62.79	100–23.2	3.09	0.98	−0.33
Trees	6	149	64.34	100–23.2	3.12	0.98	−0.32
Broad-leaved trees	5	115	64.77	100–23.2	2.47	0.99	−0.22
Evergreen trees	3	88	63.03	100–24.4	3.12	0.98	−0.31
Deciduous trees	3	61	66.24	100–23.2	2.35	0.99	0.00
Quercus	3	74	64.84	100–30.3	2.60	0.99	−0.78
1100–2500 nm							
All species	10	216	62.96	100–21.6	3.76	0.97	−0.24
Woody species	8	185	62.52	100–21.6	3.77	0.97	−0.41
Broad-leaved species	7	151	62.79	100–23.2	3.54	0.98	−0.31
Trees	6	149	64.34	100–23.2	3.03	0.98	−0.20
Broad-leaved trees	5	115	64.77	100–23.2	2.90	0.98	−0.51
Evergreen trees	3	88	63.03	100–24.4	3.44	0.98	−0.42
Deciduous trees	3	61	66.24	100–23.2	2.70	0.99	−0.25
Quercus	3	74	64.84	100–30.3	2.93	0.98	−0.70

NOTE: SEP, standard error of prediction.

Discussion and conclusions

The species used in this study had a wide range of initial chemical compositions, particularly their N, cellulose, and lignin contents (Table 2). The types of decomposition observed were probably therefore representative of the various processes involved in decomposition of leaf material. The NIRS therefore enables the stage of decomposition to be predicted, in terms of LMR, irrespective of the species studied. It is interesting to note that the visible region (400–700 nm) of the absorption spectra provided useful predictive information. The predictions were thus almost always better when the entire spectrum was taken into account rather than just the near infrared region. Figure 3 shows that the correlations between the wavelengths and the LMR had high values in the visible region. This part of the spectrum thus provides valuable information for predicting the LMR. This result is not surprising, considering the major color changes that occur between fresh litter and advanced stages of decomposition.

TABLE 5. Prediction statistics of LMR (% litter mass remaining) in field samples (*Quercus pubescens* and *Pinus halepensis*) using different microcosm calibration equations carried out on all species, woody species, and trees and calculated on the entire spectrum (400–2500 nm) or only on the near infrared (1100–2500 nm)

Equation	No. of species	*n*	Mean	Range	SEP	r^2	Bias
			400–2500 nm				
All species	10	29	73.27	100–50.36	4.46	0.93	0.46
Woody species	8	29	73.27	100–50.36	5.74	0.90	−1.75
Trees	6	29	73.27	100–50.36	4.79	0.93	−0.86
			1100–2500 nm				
All species	10	29	73.27	100–50.36	5.30	0.91	−0.06
Woody species	8	29	73.27	100–50.36	5.38	0.91	−1.21
Trees	6	29	73.27	100–50.36	5.97	0.90	−2.11

NOTE: SEP, standard error of prediction.

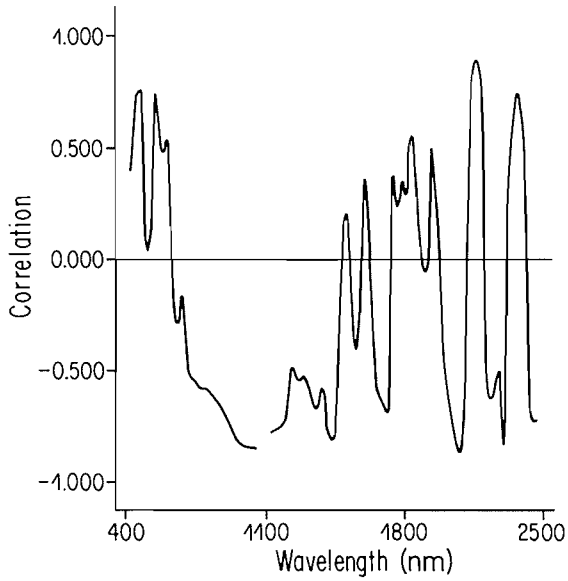

FIG. 3. Correlogram for percent litter mass remaining from microcosm calibration set (217 samples); math treatment: 1, 15, 15 (cf. Table 3).

The litter samples used in this study that were obtained by incubation in the laboratory showed a range of stages of decomposition varying up to 75–80% weight loss. This range is equivalent to phase 1 of Aber et al. (1990), during which the loss rate stays constant, and the lignin/cellulose ratio and N concentration increase in proportion to weight loss. It is therefore during this phase of decomposition that the stage of decomposition can be predicted from spectral information. Further experiments would be needed to test this method when considering more advanced stages of decomposition (phase 2 of Aber et al. 1990).

The calibrations and predictions of LMR in microcosm samples were more precise when fewer number of species were included. Thus, for material obtained under controlled laboratory conditions, the more homogeneous the initial material, the better the prediction of LMR during decomposition. However, for material decomposed under natural conditions, polluted by the earth and allochthonous compounds, it was the equations derived from the material that was the most heterogeneous at the start that provided the best prediction of LMR.

The field samples belonged to the same spectral family as the samples that were decomposed in the laboratory. However, the correlations between predicted LMR values and those actually measured were less good in field samples. This could be attributed to errors in measurement of the true weight remaining in field samples, as there was strong likelihood of loss of material or of external pollution during the long exposure times of samples on the forest floor. The calibration equations derived from samples incubated in the laboratory did, however, provide predictions, with a very acceptable level of precision, of the stage of decomposition of leaf litter that had decomposed under natural conditions in litter bags. It is thus possible to quickly produce a database in the laboratory (in the case of this study, in 14 months at 22°C) that is usable with samples collected in the field. NIRS has thus proved to be a method that can be used on all leaf litter samples, irrespective of the environmental conditions in which they have decomposed and irrespective of the duration of decomposition.

These results signify that the temporal changes in litter weights reflect a change in their chemical properties; a precise series of spectral information that cannot be identified at present, but that is shared by all stages of litter decomposition up to 80% weight loss, changes with weight loss during decomposition. For any given stage of decomposition, expressed as LMR, there is thus an equivalent precise state within this spectral information series, irrespective of species and initial chemical composition. What varies from one species to another, and with environmental conditions, is the time taken to reach the different stages in this temporal change in the chemical properties of the litter. These results do not contradict those concerning the biochemical changes (e.g., the increase in N or lignin concentration) of various species in relation to weight loss. These concentrations at each stage of decomposition do, however, depend on the original concentrations. They are not therefore good indicators of LMR, valid irrespective of species. Spectra reveal the existence of chemical bonds, certain of which vary directly and proportionately as a function of the stage of litter decomposition, in all species irrespective of their original chemical composition. Tam et al. (1991) also noted that precise absorption bands, interpreted as the C=O, C=C, C—O and C—OH bonds, revealing the

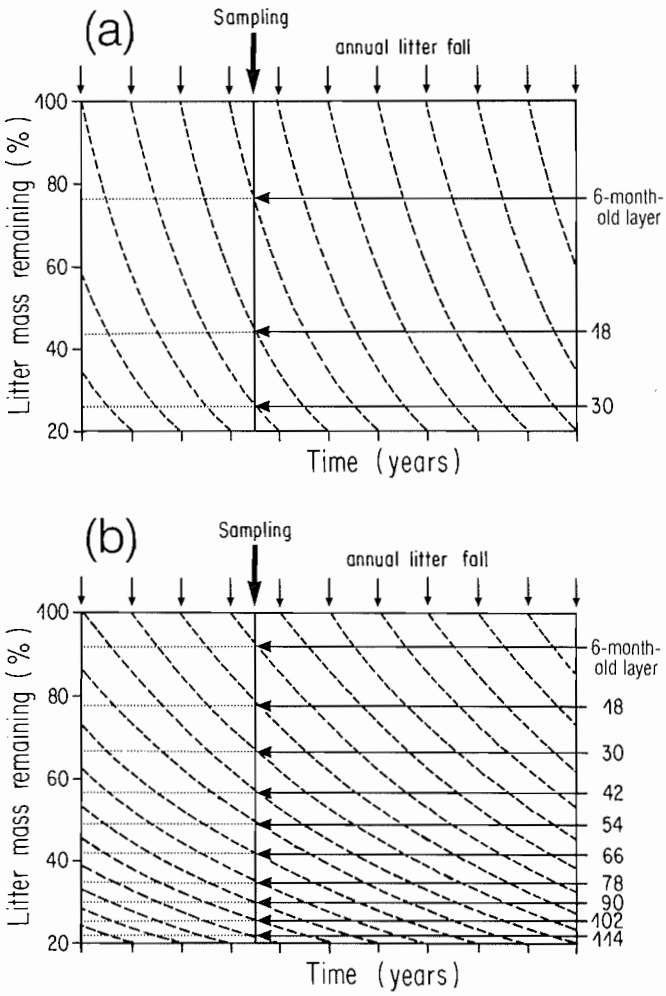

FIG. 4. Two theoretical scenarios of forest litter dynamics with contrasted decay rates: (*a*) high k, 80% weight loss in 3 years; (*b*) low k, 80% loss in 10 years. If a sampling of the forest floor is carried out 6 months after the maximum leaf fall period, the upper layer is 6 months old, the second one 18 months old, etc. By measuring the near infrared spectrum of each of the superimposed layers of litter, litter mass remaining (LMR) values can be predicted, which allows the decay constant (k) of the forest floor to be predicted. In scenario *a*, the LMR values of the three upper layers are 77, 45, and 26%, respectively, so $k = 0.54$; in scenario *b*, the LMR values of the three upper layers are 92, 79, and 67%, respectively, so $k = 0.16$.

aromatic and aliphatic structure, change with the depth at which the litter was collected and therefore with the stage of litter decomposition.

This possibility of directly and easily measuring the stage of litter decomposition (LMR) provides new perspectives. If, as several authors have shown, the decay constant (k) is a value that only depends on the initial litter quality and the environmental conditions, it should be possible to measure it directly in the field without undertaking long litter bag experiments. Figure 4 shows two simplified theoretical cases where litter either decomposes quickly (high k, 80% weight loss in 3 years) or slowly (low k, 80% loss in 10 years). By sampling from narrow layers of superimposed litter and measuring the stage of decomposition (LMR) of these different layers, it should be possible to estimate the value of k if the season of annual leaf fall is known for the deciduous species or the season of maximum leaf fall, for the evergreen species. If k stays constant up to 80% of weight loss from the litter, measuring the stage of decomposition of the most recent layers, which are the most distinct and therefore have the greatest differences in LMR values, should suffice for estimating k. As many studies have shown (Aber and Melillo 1980, 1982; Melillo et al. 1982, 1989; McClaugherty et al. 1985, Berg and Staaf 1987; Berg and McClaugherty 1987, 1989; Blair 1988), there is also usually an inverse linear relation between the percent LMR and the N concentration. The slope of this relation is specific and depends on the initial chemical characteristics of the litter (Melillo et al. 1982). According to Aber and Melillo (1980, 1982) and Aber et al. (1990), the inverse linear relation provides a way of directly calculating the timing of the switch from immobilization to mineralization of N. By just measuring the spectrum of the superimposed layers of litter in each vertical forest floor profile by NIRS, it should be possible to predict both the LMR and the N concentration (McLellan et al. 1991*a*, 1991*b*; Joffre et al. 1992), and therefore predict the decay rate and the inverse linear relation between LMR and N concentration.

This simple and quick approach to the study of vertical profiles of litter accumulated on the soil surface provides new perspectives. It should allow comparison of the speed of decomposition of various litters within the same forest community and to relate them to initial chemical composition of the leaves from which the litters are derived and thus confront the problems of spatial heterogeneity in the dynamics of organic matter and nutrient recycling. It should also provide an easy means of comparing the dynamics of litter decomposition between species and (or) environmental gradients.

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