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Factors Determining Differences in Soil pH in Adjacent Conifer and Alder-Conifer Stands

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ABSTRACT

Tree species may differ in their influence on biogeochemical cycles, leading to differing rates of soil acidification. Over time, quantitative and qualitative changes develop in the characteristics of the soil exchange complex. Three such characteristics regulate soil pH: (i) the quantity of acids present, which can be represented as the total cation-exchange capacity (CEC); (ii) the degree of dissociation of the acids, commonly called base saturation; and (iii) the affinity of the acids for H^+ , or acid strength, which represents the composite pK_a (negative log of the acid ionization constant) of the exchange complex. We examined the importance of these three factors in explaining the differences in soil pH between adjacent stands of conifers [primarily Douglas fir, *Pseudotsuga menziesii* (Mirbel) Franco] and conifers mixed with N-fixing red alder (*Alnus rubra* Bong.). At a low-productivity site (Wind River, WA), the pH of 0 to 0.15 m of soil from both alder-conifer and conifer stands averaged 4.3 in 0.01 M $CaCl_2$. The pH values were the same, however, only because higher base saturation in the alder-conifer stand was offset by greater acid strength. At a more productive site (Cascade Head, OR), soil pH (in 0.01 M $CaCl_2$) averaged 3.7 in the alder-conifer stand but 4.4 in the conifer stand. The difference in pH resulted primarily from greater acid strength of soil organic matter under alder, and secondarily from lower base saturation of the exchange complex. These results underscore the importance of considering qualitative changes in soil organic matter as factors driving changes in soil pH and other parameters.

DECLINES IN SOIL pH under red alder, a N-fixing tree species common in the Pacific Northwest, have been noted for more than two decades. The magnitudes of the declines have varied, ranging from essentially nil (e.g., Binkley, 1983; Binkley et al., 1984) to one unit in 50 yr (e.g., Franklin et al., 1968; Bormann and DeBell, 1981; Van Miegroet and Cole, 1984; Van Miegroet et al., 1989). Van Miegroet and Cole (1984) attributed the decrease in soil pH to decreased base saturation. They suggested that the lower base saturation resulted from the production of H^+ in nitrification, with H^+ displacing base cations, which then leached from the soil with NO_3^- .

Base saturation, however, is only one of three factors of the soil exchange complex that determine soil pH. Binkley et al. (1989) noted that the pH of a solution is determined by the quantity of weak acids (both protonated and dissociated), the degree of dissociation of the acids, and the strength of the acids (the pK_a). In soils, stabilized weak acids are composed of organic matter and crystalline and amorphous clays (Truog, 1945; Perdue, 1985). The quantity of acid can be represented by the total CEC of the soil. The degree of dissociation of the exchange complex is gauged by base

saturation (proportion of the exchange sites occupied by so-called base cations). Although cations are not bases in any chemical sense (Leeper, 1948), base cations represent the dissociated portion of the exchange complex, just as the undissociated portion is represented by H^+ and Al. Acid strength in soils derives from the composite contribution of many types of acids of varying pK_a .

The relative importance of these three factors can be examined with empirical titration curves (Binkley et al., 1989). The total quantity of acids present in the soil is represented by the quantity of acid or base needed to lower or raise the pH of the suspension to a defined end point. The quantity of acid required to reach an end point is defined as the acid-neutralizing capacity (ANC), and the quantity of base required is defined similarly as the base-neutralizing capacity (BNC; Stumm and Morgan, 1981). The degree of dissociation of the soil acids can be represented by the sum of the positive charge contributed by K, Na, Ca, and Mg. The cumulative acid strength is described by the shape of the titration curve. As described below, sensitivity analysis can be used to judge the contribution from each factor to the difference in pH between two soils.

In this project, we applied this empirical model to soil samples from two pairs of conifer and alder-conifer stands to determine the relative importance of each factor in determining soil pH.

METHODS

Site Description

The study sites are described in detail in Tarrant (1961) and Franklin et al. (1968). Briefly, the low-productivity Wind River site in western Washington has a site index for Douglas fir (without alder) of 25 m at 50 yr. The ecosystem N capital (biomass + soil to 0.9 m) was about 153 kmol/ha (2140 kg/ha) in a pure Douglas fir stand and about 353 kmol/ha (4940 kg/ha) in an adjacent alder-Douglas fir stand. Nitrogen mineralization in resin cores (Binkley and Hart, 1989) was almost undetectable in the Douglas fir stand, but averaged 12.5 kmol $ha^{-1} yr^{-1}$ (175 kg $ha^{-1} yr^{-1}$) annually in the alder-Douglas fir stand. Only about 0.03 kmol $ha^{-1} yr^{-1}$ of NO_3^- (0.4 kg $N ha^{-1} yr^{-1}$) leached from the conifer stand (based on tensionless lysimeters at 0.8 m and an extrapolated site water balance), and 0.18 kmol/ha (2.5 kg $N ha^{-1} yr^{-1}$) from the alder-conifer stand. The annual rate of accumulation of K + Ca + Mg in biomass was 0.45 kmol/ha for the conifer stand, and 0.67 kmol/ha for the alder-conifer stand. The soil, an unclassified Andic Haplumbrept, has a silty clay loam texture, and developed in Tertiary andesitic or rhyolitic parent materials with some pumice and basaltic gravel of Pleistocene origin (Miller and Tarrant, 1983). The site experienced repeated wildfires before plantation establishment in 1929. The alder were planted in a 22-m-wide strip through a 1000-m portion of the Douglas fir plantation.

The Cascade Head study site on the coast of Oregon is very productive, with a site index for Douglas fir (without alder) of 40 m at 50 yr. In 1935, a 0.2-ha conifer plot was established by cutting all alders in an 8-yr-old, naturally regenerated stand containing red alder, Douglas fir, western

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hemlock [*Tsuga heterophylla* (Raf.) Sarg.], and Sitka spruce [*Picea sitchensis* (Bong.) Carrière]. The alders were retained in an adjacent 0.2-ha plot. In 1985, the total ecosystem N capital of the conifer stand was 747 kmol/ha (10 460 kg/ha), compared with 1033 kmol/ha (14 460 kg/ha) in the alder-conifer stand (Binkley et al., 1989, unpublished data). Nitrogen mineralization at 0 to 0.3 m was estimated to be about 2.9 kmol ha⁻¹ yr⁻¹ (41 kg ha⁻¹ yr⁻¹) in the conifer stand, compared with 12.5 kmol ha⁻¹ yr⁻¹ (175 kg N ha⁻¹ yr⁻¹) in the alder-conifer stand. Nitrate leaching was about 0.5 kmol ha⁻¹ yr⁻¹ (7 kg N ha⁻¹ yr⁻¹) from the conifer stand, and 2.3 kmol ha⁻¹ yr⁻¹ (32 kg N ha⁻¹ yr⁻¹) from the alder-conifer stand. The average annual rate of accumulation of K + Ca + Mg in biomass was 0.70 kmol/ha for the conifer stand and 0.55 kmol/ha for the alder-conifer stand. The soil is a well-drained Typic Dystrandept of the Astoria silty clay loam series, developed in tuffaceous siltstone over basalt.

Soil Sampling and Analysis

Ten soil pits were dug in each stand, located at random distances (on alternate sides) from random points on a transect through the middle of each plot. The pits were approximately 0.5 by 1.0 m, and >1 m deep. Soil samples for chemical analysis were taken from 0 to 0.15, 0.15 to 0.40, 0.40 to 0.65, and 0.65 to 0.90 m at Wind River, and from 0 to 0.15, 0.15 to 0.30, 0.30 to 0.60, and 0.60 to 0.90 m at Cascade Head. These depths corresponded roughly to the Ah, B1, B2, and C1 horizons in all stands. The volume of large rocks was estimated by weighing all rocks removed from each pit, with conversion to volume based on the density of a subset of rocks. Bulk density of the rock-free soil was determined by weighing samples of known volume taken from the walls at each depth interval in each pit.

Soil C was analyzed with a LECO 12 C analyzer (LECO Corp., St. Joseph, MI). Extractable soil cations were determined by atomic absorption spectrophotometry on 100-mL extracts (1 M NaCl) of 10-g samples. Extractable Al (which may be underestimated with extraction with NaCl) was assumed to have a charge of +3. Total K, Ca, and Mg were determined by inductively coupled plasma spectrophotometry on samples digested with HF, H₂SO₄, and HClO₄ (Lim and Jackson, 1982, Method 1-6).

Five methods were used to characterize soil acidity. Soil pH was measured in solutions of deionized water, 0.01 M CaCl₂, and 1 M KCl, with soil weight/solution volume of 1:5. The effect of ambient differences in ionic strength on pH was determined by comparing the pH of samples in deionized water and in 0.01 M CaCl₂, and by analyzing the anions present in water extracts (50 mL of deionized water and 5 g of dry soil, analyzed with a DIONEX anion chromatograph [DIONEX Corp., Sunnyvale, Ca]).

Titration curves were used to estimate the ANC and BNC of the soils. Three composite soil samples were prepared from the original 10 air-dry samples from each of the four horizons in each stand (resource limitations prevented using all 40 original samples per stand). A set of 50-g subsamples were placed into 125-mL specimen cups, and 50 mL of 1 M KCl were added to buffer the ionic strength of the suspension. This set received consecutive additions (in 0.5-mL increments) of 0.01 M HCl, for poorly buffered soils, or 0.05 M HCl for more highly buffered soils. The pH of the supernatant remained relatively stable between 12 and 36 h after addition of the acid or base; we, therefore, measured pH between 20 and 28 h after each addition. Acid additions were stopped when pH 3.0 was reached. A second set of subsamples received similar increments of 0.01 or 0.05 M NaOH, stopping when the pH passed 8.2.

The empirical method of Binkley et al. (1989) was used to examine the relative importance of mechanisms (acid quantity, acid dissociation, and acid strength) in determining

the difference in pH between conifer and alder-conifer soils. The importance of differences in the quantity of acids present in the soil was evaluated by taking the titration curve for one soil, holding the content of K + Ca + Mg constant, and stretching the curve to match the greater ANC + BNC of another soil. The equation used to derive the adjusted curve was:

$$(\text{ANC})_{\text{new}} = (\text{ANC})_{\text{original}} \frac{[\text{ANC} + \text{BNC}]_{\text{original}}}{[\text{ANC} + \text{BNC}]_{\text{new}}} \quad [1]$$

where (ANC)_{new} gives the new *x* coordinates for each *y* coordinate on the shifted curve, (equivalent to the concentration of base cations that balance the charge); (ANC)_{original} is the base-cation concentration for the original curve, and [ANC + BNC]_{new} and [ANC + BNC]_{original} are the total quantities of acid present in the new soil and in the original soil. The pH of the new curve at the point of zero addition of acid or base equals the expected pH of the new soil if the ANC + BNC were shifted to match that of another soil (see Binkley et al., 1989, for graphical illustrations of this empirical method).

The importance of changes in the dissociation of the soil acids (equal to changing the content of base cations) was assessed by adding or removing a quantity of OH from the titration curve to match the desired change in dissociation of the exchange complex.

The importance of changes in acid strength was determined by adjusting the titration curves for the alder-conifer soil with the above equation to match the acid quantity of the conifer soil, and then adjusting the dissociation of the exchange complex (OH added) to match the conifer soil. The residual difference in pH after these adjustments represents the importance of the difference in acid strength.

Analyses of variance, used to examine differences in means, were calculated with SYSTAT (SYSTAT, 1985) with a probability of a Type I error set at 0.10.

RESULTS AND DISCUSSION

Characteristics of the Soil Exchange Complex

For soil samples from Wind River, pH in water was significantly lower (at *P* ≤ 0.10) in the alder-conifer than in the conifer soils. For pH in salt solutions, the only significant difference was a greater pH in the alder-conifer soils at 0.40 to 0.90 m (Table 1). Acid-neutralizing capacity of the alder-conifer soils exceeded that of the conifer soils only at 0 to 0.15 m (Table 1, Fig. 1). Base-neutralizing capacity at pH 5.5 (BNC_{pH 5.5}) was about 1.35 times higher in the conifer soils at 0.65- to 0.90-m depth than in the corresponding alder-conifer soils. The BNC_{pH 8.2} was higher in the alder-conifer soil at 0 to 0.15 m, but lower at 0.40 to 0.60 m. The buffer-intensity distribution (change in pH per unit of OH added as a function of pH; Stumm and Morgan, 1981, p. 160) showed that the alder-conifer soils were buffered better at any pH with respect to additions of OH than the conifer soils, but less buffered against additions of H⁺ (Fig. 2).

Concentrations of extractable cations were generally higher at 0 to 0.40 m in the alder-conifer soils at Wind River than in the conifer stand (Table 2). Although no differences were significant for the lower depths, the apparent decrease in extractable cations at 0.40 to 0.90 m in the alder soils roughly balanced the increases at 0 to 0.40 m (Table 3). The content of extractable base cations was significantly greater in the alder-con-

ifer soils at 0 to 0.40 m, but significantly smaller at the 0.40- to 0.65-m depth. The net difference in ex-

tractable K + Ca + Mg was only 9 kmol./ha at the 0- to 0.90-m depth, which is too slight to be statistically

Table 1. Means of soil pH and acid- and base-neutralizing capacities (ANC and BNC). Standard deviations are given in parentheses; $n = 10/\text{stand}$.

Location, stand depth	pH			ANC to pH 3		BNC			
	Water	0.01 M CaCl ₂	1 M KCl			to pH 5		to pH 8.2	
						mmol OH/kg	kmol OH/ha	mmol OH/kg	kmol OH/ha
m				mmol H/kg	kmol H/ha				
Wind River									
Conifer									
0-0.15	5.4 (0.1)†	4.3 (0.1)	4.0 (0.0)	259 (31)†	201	62 (9)	48	283 (29)†	220
0.15-0.40	5.3 (0.1)†	4.3 (0.1)	4.1 (0.1)	317 (36)†	563	66 (14)	117	248 (17)	440
0.40-0.65	5.2 (0.1)†	4.1 (0.1)	3.8 (0.1)†	187 (12)	360	167 (53)	321	329 (39)†	633
0.65-0.90	5.2 (0.1)†	4.1 (0.1)	3.6 (0.1)†	141 (17)	263	218 (30)†	407	361 (34)†	673
Sum					1 387		893		1 966
Alder-conifer									
0-0.15	5.1 (0.3)†	4.3 (0.2)	4.0 (0.1)	220 (31)†	150	87 (24)	59	377 (69)†	257
0.15-0.40	5.1 (0.2)†	4.2 (0.1)	4.1 (0.1)	270 (34)†	468	61 (8)	106	247 (20)	428
0.40-0.65	5.0 (0.2)†	4.1 (0.1)	3.9 (0.1)†	200 (33)	385	111 (23)	214	264 (10)†	508
0.65-0.90	4.9 (0.2)†	4.0 (0.1)	3.7 (0.0)†	161 (16)	311	159 (16)†	308	306 (16)†	592
Sum					1 314		687		1 785
Cascade Head									
Conifer									
0-0.15	5.4 (0.4)†	4.4 (0.4)†	4.0 (0.2)	429 (60)†	270	167 (48)	105	686 (50)†	433
0.15-0.30	5.4 (0.2)†	4.4 (0.2)†	4.1 (0.1)	736 (95)†	545	144 (32)	107	592 (24)†	439
0.30-0.60	5.2 (0.2)†	4.3 (0.2)	4.0 (0.0)	671 (39)	1 026	126 (17)	193	520 (27)	796
0.60-0.90	4.9 (0.2)†	4.1 (0.1)	3.9 (0.0)	384 (25)	578	189 (22)	285	447 (22)	673
Sum					2 419		690		2 341
Alder-conifer									
0-0.15	4.3 (0.4)†	3.7 (0.3)†	3.6 (0.3)	227 (118)†	180	298 (115)	194	825 (97)†	537
0.15-0.30	4.8 (0.4)†	4.1 (0.1)†	4.0 (0.0)	594 (36)†	440	181 (28)	134	689 (52)†	510
0.30-0.60	4.8 (0.3)†	4.2 (0.1)	4.0 (0.0)	665 (26)	1 125	137 (1)	232	537 (27)	907
0.60-0.90	4.7 (0.2)†	4.1 (0.1)	3.9 (0.0)	415 (69)	735	168 (20)	297	430 (20)	761
Sum					2 480		857		2 715

† Means differ at $P \leq 0.10$ between stands at each depth and location.

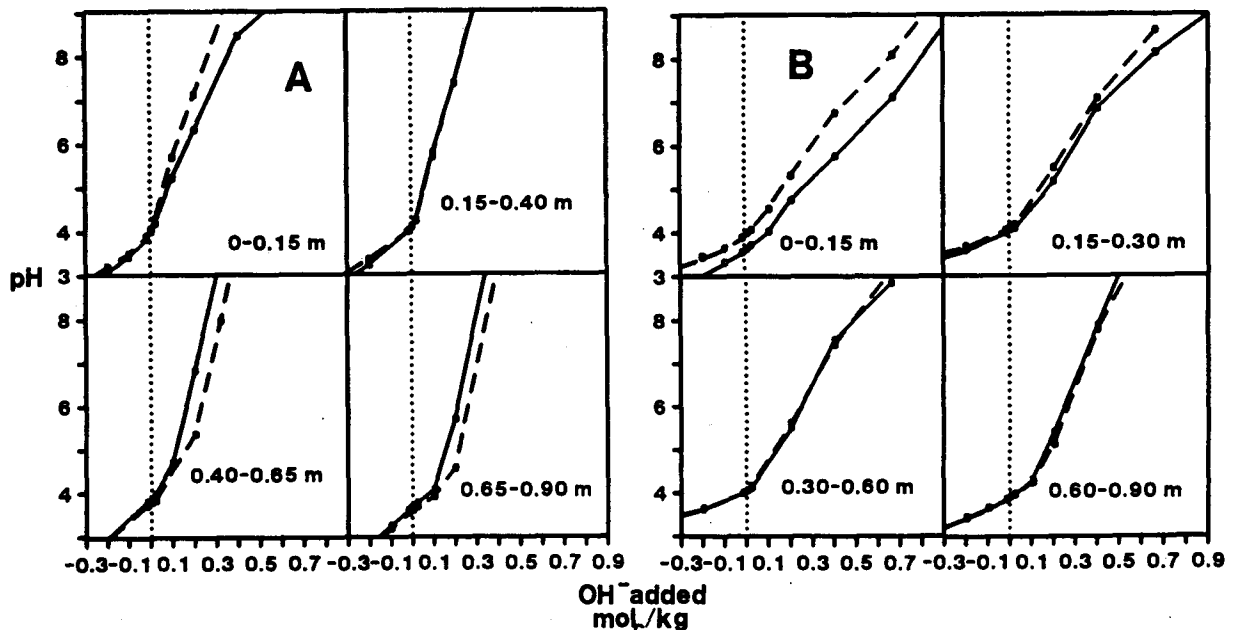


Fig. 1. Titration curves showing pH of supernatant 20 to 28 hr after addition of HCl or NaOH to soils from four depths. A = Wind River, B = Cascade Head; dashed line = conifer soil, solid line = alder-conifer soil.

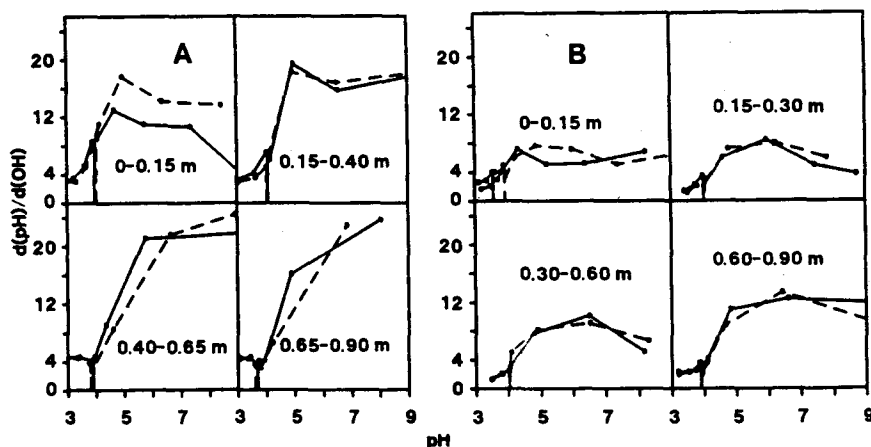
Table 2. Concentrations of total C and exchangeable (Exch.) cations and base saturation. Standard deviations are given in parentheses; $n = 10/\text{stand}$.

Location, stand, depth		Ca		Mg		K		Al	Base saturation	
Total C		Total	Exch.	Total	Exch.	Total	Exch.	Exch.		
m	mmol/kg	mmol/kg								
Wind River										
Conifer										
0-0.15	3 650 (300)†	890	8.3 (0.5)†	790	3.2 (0.6)†	230	3.7 (0.4)	32.4 (7.3)	0.32†	
0.15-0.40	1 290 (90)†	635	2.5 (0.5)†	770	1.9 (0.6)†	225	3.2 (0.3)	28.0 (7.1)†	0.22†	
0.40-0.65	450 (50)†	345	13.0 (0.6)	740	9.9 (1.2)	174	2.3 (0.5)	83.0 (29.9)	0.24†	
0.60-0.90	230 (30)†	215	15.2 (0.6)	725	11.5 (1.3)	130	1.7 (0.3)	150.2 (18.5)	0.16	
Alder-conifer										
0-0.15 m	5 580 (750)†	915	22.5 (0.7)†	725	8.1 (1.7)†	215	3.4 (0.3)	41.9 (5.0)	0.45†	
0.15-0.40	1 690 (160)†	725	6.6 (0.7)†	740	5.9 (0.9)†	225	3.1 (0.1)	45.5 (3.3)	0.26†	
0.40-0.65	660 (80)†	515	6.4 (0.8)	770	6.6 (1.2)	215	1.7 (0.2)	80.9 (10.0)	0.16†	
0.60-0.90	420 (40)†	400	12.7 (0.8)	770	10.4 (2.5)	170	1.2 (0.0)	124.3 (22.7)	0.17	
Cascade Head										
Conifer										
0-0.15	9 810 (730)	120	12.1 (0.1)†	510	19.7 (6.7)†	130	2.0 (0.2)	88.6 (6.0)†	0.29†	
0.15-0.30	6 400 (470)	100	5.5 (0.1)	590	11.8 (5.0)	150	1.1 (0.2)	50.6 (15.7)	0.29†	
0.30-0.60	3 870 (360)	95	2.3 (0.2)†	625	6.4 (2.1)†	160	0.6 (0.1)	52.9 (11.6)	0.17†	
0.60-0.90	1 760 (160)	65	2.1 (0.2)	690	4.8 (0.7)	185	0.6 (0.1)	118.2 (27.5)	0.07	
Alder-conifer										
0-0.15	9 850 (640)	115	6.2 (0.3)	500	4.1 (0.8)	130	2.1 (0.5)	138.0 (3.7)†	0.09†	
0.15-0.30	6 930 (300)	100	5.7 (0.3)	530	5.9 (3.4)	145	3.2 (0.3)	75.9 (17.4)	0.18†	
0.30-0.60	4 080 (400)	85	1.4 (0.4)	620	2.2 (1.2)	170	0.7 (0.1)	48.6 (9.0)	0.09†	
0.60-0.90	1 730 (180)	80	1.6 (0.4)	670	2.7 (0.9)	185	0.7 (0.2)	61.1 (19.3)	0.08	

† Means differ at $P \leq 0.10$ between stands at each depth and location.

Table 3. Total and exchangeable (Exch.) soil element pools at the 0- to 0.9-m depth.

Location, stand	Total C	Ca		Mg		K		Al
		Total	Exch.	Total	Exch.	Total	Exch.	Exch.
		kmol/ha						
Wind River								
Conifer	6 490	21 280	641	38 400	458	8 950	163	5 150
Alder-conifer	8 825	31 080	636	39 200	481	10 400	136	5 050
Cascade Head								
Conifer	19 495	40 200	184	28 000	377	7 400	41	3 530
Alder-conifer	21 580	43 900	126	29 650	147	7 970	45	3 210

Fig. 2. Buffer-intensity distribution, representing change in pH/OH as a function of pH . A high value indicates low buffer intensity. A = Wind River, B = Cascade Head; dashed line = conifer soil, solid line = alder-conifer soil.

or ecologically significant. The extractable pools composed a small fraction of the total pool of K, Ca, and Mg (Table 3).

For soil samples from Cascade Head, pH in water

was significantly lower at all depths in the alder-conifer than in the conifer soils (Table 1). The alder-conifer soils also showed lower pH in dilute salt solutions at 0- to 0.30-m depth, but not in 1 M KCl; ANC and

Table 4. Water-soluble anions, H⁺ concentrations, and pH for three composited samples for 0- to 0.15-m-depth soil from each stand. Standard deviations are given in parentheses.

Location, stand	pH	H	Cl	NO ₃	SO ₄	Alkalinity	Sum of anions
$\mu\text{mol/L}$							
Wind River							
Conifer	5.4 (0.1)	4.3 (0.8)†	56 (5)	10 (6)†	22 (2)†	72 (16)	175 (10)†
Alder-conifer	5.1 (0.1)†	7.9 (0.9)†	55 (13)	185 (12)†	13 (3)†	63 (46)	330 (45)†
Cascade Head							
Conifer	5.3 (0.1)	4.6 (0.8)†	66 (12)	100 (9)†	25 (3)†	53 (1)†	270 (10)†
Alder-conifer	4.6 (0.3)†	24.0 (9.1)†	50 (20)	350 (55)†	19 (2)†	11 (15)†	450 (20)†

† Means differ at $P \leq 0.10$ between stands at each depth and location.

Table 5. Measured and expected pH in 1 M KCl in the conifer stands if single factors were set equal to the value for the alder-conifer stands.

Location	Depth, m	Measured pH		Expected pH in conifer soil		
		Alder/conifer	Conifer	ANC + BNC†	Base cations	Acid strength
Wind River	0-0.15	4.0	4.0	4.0	4.3	3.9
	0.15-0.40	4.1	4.1	4.2	4.0	4.0
	0.40-0.65	3.9	3.8	3.8	3.8	3.8
	0.65-0.90	3.7	3.6	3.6	3.6	3.7
Cascade Head	0-0.15	3.6	3.9	4.0	3.8	3.7
	0.15-0.30	4.0	4.1	4.1	4.1	4.0
	0.30-0.60	4.0	4.0	4.1	4.0	4.0
	0.60-0.90	3.9	3.9	3.9	3.9	3.9

† Acid-neutralizing capacity plus base-neutralizing capacity.

BNC values differed significantly between stands at all depths (Table 1, Fig. 1). The buffer-intensity distribution differed markedly between stands (Fig. 2), especially at the 0- to 0.15-m depth, where the conifer soils were buffered better against change in pH near the ambient pH, but more poorly buffered between pH 5 and 7.

Contents of extractable K + Ca + Mg at Cascade Head were lower at the 0- to 0.15-m depth in the alder-conifer stand than in the conifer stand (Table 2), and the base saturation was also lower at the 0- to 0.60-m depth. In contrast to the Wind River site, the differences in K + Ca + Mg appeared to result from removal from the profile rather than from redistribution among horizons. The difference of 284 kmol_e/ha (0-0.90-m depth) represents almost one-half of the extractable K + Ca + Mg present in the conifer soil. If the alder-conifer soil originally had the K + Ca + Mg content of the conifer soil, the average annual rate of removal for 55 yr would have been about 5.2 kmol_e/ha. The apparent depletion of extractable cations represents a very small fraction (<0.05) of the total amount in the soil (Table 3).

Factors Determining Soil pH

Soil pH in water was lower under the alder-conifer stand at both locations, caused in part by the greater ionic strength in the water suspensions. The greater ionic strength resulted primarily from the greater concentrations of NO₃ in the alder-conifer soils (Table 4). For example, the concentration of water-soluble anions from the alder-conifer stand (0-0.15 m) at Wind River exceeded that of the conifer stand by about 160 $\mu\text{mol/L}$. Of this extra charge, H⁺ balanced only 3.6 $\mu\text{mol/L}$, but this difference in H⁺ concentrations was sufficient to drop solution pH by 0.3 units. The difference in anion concentrations between stands

at Cascade Head was about 180 $\mu\text{mol/L}$, and H⁺ balanced about 20 $\mu\text{mol/L}$ of the charge and lowered pH by 0.6 units. These patterns are an example of the tendency of increased ionic strength to lower solution pH in soils with significant exchangeable acidity (see Reuss and Johnson, 1986; Richter et al., 1988), without any substantial change in the exchange complex.

The evaluation of the relative importance of acid quantity, dissociation, and strength can be illustrated with data for the 0.15- to 0.40-m depth from the Wind River stands. Within this depth interval, the conifer soil contained 7.5 mmol_e/kg of K + Ca + Mg (Table 2), with ANC + BNC (between pH 3 and 5.5) of 383 mmol_e/kg (Table 3). The acid quantity for the 0.15- to 0.40-m soil from the alder-conifer stand at Wind River was 331 mmol_e/kg. If the acid quantity of the conifer soil was reduced to match that of the alder-conifer soil (a 14% reduction), the resulting increase in based saturation would increase soil pH from the observed 4.1 to 4.2 (Table 5). This rise was calculated by proportionally shortening the conifer soil's titration curve by 14% at each point, and then reading the pH at the level of zero addition of acid or base.

The 0.15- to 0.40-m soil samples from the Wind River conifer stand contained 7.5 mmol_e/kg of K + Ca + Mg, compared with 15.6 mmol_e/kg for the alder-conifer soil. The addition of 8.1 mmol_e/kg of K + Ca + Mg to the conifer soil would be equivalent to titrating the soil with 8.1 mmol_e/kg of OH⁻; therefore, the predicted pH can be read from the original titration curve by moving up the curve a distance corresponding to the 8.1 mmol_e/kg of OH⁻ added. The pH of the conifer soil that would be expected if it contained the quantity of base cations found in the alder-conifer soil would be essentially unchanged (<0.1 units).

The importance of differences in acid strength were evaluated by adjusting the curve (samples from 0.15 to 0.40 m in the alder-conifer stand) to have the ANC

+ BNC and the content of K + Ca + Mg of the soils from the conifer stand. After these adjustments, the pH at the zero point of addition of acid or base represents the pH expected for the conifer soil if it had the acid strength of the alder-conifer soil. For this depth, differences in acid strength appeared to be unimportant (Table 5).

At Wind River in general, acid quantity did not differ enough between stands to be important, but dissociation of the exchange complex (base saturation) and acid strength differed substantially in the upper soil (Table 5). If the 0- to 0.15-m conifer soil had the higher concentrations of K + Ca + Mg found in the alder-conifer stand, the expected pH in KCl would have been 4.3 rather than the observed 4.0. If the conifer soil were altered to have the acid strength of the alder-conifer soil (but retaining the original ANC + BNC and K + Ca + Mg), the expected pH (0-0.15 m) would have been only 3.9.

The most important difference in acidity factors between soil from the Cascade Head stands was the greater acid strength under the alder-conifer stand (Table 5). If only the acid strength of the conifer soil were changed to match the alder-conifer soil, the pH would have been 3.7 rather than the observed 3.9. Changing the concentrations of base cations alone would have lowered pH to 3.8. The difference in acid quantity was not important. The stronger acidity and lower concentrations of base cations in the alder-conifer stand combined to produce the observed pH of 3.6. In deeper horizons, pH differed little between stands, thus all factors were of marginal importance (Table 5).

Our results indicate that the hypothesis that decreased base saturation under alder is driven by H^+ production during nitrification may be correct in some cases, but it may not be a complete explanation. The lack of difference in soil pH at Wind River, where nitrification was roughly balanced by NO_3 assimilation (as gauged by the low rate of NO_3 leaching), appears consistent with the hypothesis. However, our results indicate that soil pH at 0 to 0.30 m would have been lower in the alder-conifer stand if the increase in acid strength had not been offset by an increase in base saturation. At Cascade Head, the low base saturation in soils from the alder-conifer stand relative to those from the conifer stand was consistent with the hypothesis, but the large difference in base saturation appeared less important than the greater acid strength of the exchange complex. The importance of differences in acid strength in controlling pH was also demonstrated by Binkley and Valentine (1990), who reported that greater acid strength accounted for the majority of difference in pH between soils under Norway spruce [*Picea abies* (L.) Karsten], white pine [*Pinus strobus* L.] and green ash [*Fraxinus pennsylvanica* Marshall]. Binkley et al. (1989) found that a drop in acid strength partially offset the 20-yr decline in soil pH in a loblolly pine (*Pinus taeda* L.) stand that accompanied a decrease in base saturation (driven by H^+ production associated with accumulation of Ca, Mg, and K in the biomass). The important role played by changes in the strength of soil acids across time and under the influence of plant species underscores the

importance of considering changes in soil acid strength in long-term assessments of soil acidification.

The low pH of the upper soil in the alder-conifer stand at Cascade Head relative to the conifer stand may result in substantially higher concentrations of Al in soil solutions. The low base saturation would make the soil-solution concentrations of Al especially responsive to changes in ionic strength (Reuss and Johnson, 1986; Reuss, 1989). Further, a reduction of one pH unit from 5.4 to 4.4 might increase 1000-fold the concentration of dissolved Al in equilibrium with Al minerals (Lindsay, 1979). These implications warrant direct assessment of the effects of alders on Al biogeochemistry.

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REFERENCES

- Binkley, D. 1983. Interaction of site fertility and red alder on ecosystem production in Douglas-fir plantations. *For. Ecol. Manage.* 5:215-227.
- Binkley, D., and S.C. Hart. 1989. The components of nitrogen availability assessments in forest soils. *Adv. Soil Sci.* 10:57-116.
- Binkley, D., J.D. Lousier, and K. Cromack, Jr. 1984. Ecosystem effects of Sitka alder in a Douglas-fir plantation. *For. Sci.* 30:26-35.
- Binkley, D., and D. Valentine. 1990. Fifty-year biogeochemical effects of green ash, white pine, and Norway spruce in a replicated experiment. *For. Ecol. Manage.* (in press).
- Binkley, D., D. Valentine, C. Wells, and U. Valentine. 1989. An empirical analysis of the factors contributing to 20-year decrease in soil pH in an old-field plantation of loblolly pine. *Biogeochem.* 7:39-54.
- Bormann, B., and D. DeBell. 1981. Nitrogen content and other soil properties related to age of red alder stands. *Soil Sci. Soc. Am. J.* 45:428-431.
- Franklin, J., C. Dyrness, D. Moore, and R. Tarrant. 1968. Chemical properties under coastal Oregon stands of alder and conifers. p. 157-172. *In* J. Trappe et al. (ed.) *Biology of alder*. USDA For. Serv., Portland, OR.
- Leeper, G.H. 1948. *Introduction to soil science*. Melbourne Univ. Press, Melbourne.
- Lim, C.H., and M. Jackson. 1982. Dissolution for total elemental analysis. p. 1-12. *In* A. Page et al. (ed.) *Methods of soil analysis*. Part 2. Chemical and microbiological properties. 2nd ed. ASA and SSSA, Madison, WI.
- Lindsay, W. 1979. *Chemical equilibria in soils*. John Wiley & Sons, New York.
- Miller, R., and R. Tarrant. 1983. Long-term response of Douglas-fir to ammonium nitrate fertilizer. *For. Sci.* 29:127-137.
- Perdue, E.M. 1985. Acidic functional groups of humic substances. p. 493-526. *In* G. Aiken et al. (ed.) *Humic substances in soil, sediment, and water*. John Wiley & Sons, New York.
- Reuss, J., and D. Johnson. 1986. *Acid deposition and acidification of soils and waters*. Springer-Verlag, New York.
- Reuss, J.O. 1989. Soil-solution equilibria in lysimeter leachates under red alder. p. 547-559. *In* R.K. Olson and A.S. LeFohn (ed.) *Effects of air pollution on western forests*. Air Waste Manage. Assoc., Pittsburgh, PA.
- Richter, D., P. Comer, K. King, H. Sawin, and D. Wright. 1988. Effects of low ionic strength solution of pH of acid forested soils. *Soil Sci. Soc. Am. J.* 52:261-264.
- Stumm, W., and J. Morgan. 1981. *Aquatic chemistry*. John Wiley & Sons, New York.
- SYSTAT. 1985. SYSTAT, the system for statistics. SYSTAT, Evanston, IL.
- Tarrant, R. 1961. Stand development and soil fertility in a Douglas-fir/red alder plantation. *For. Sci.* 7:238-247.
- Truog, E. 1945. A proposed system of names, abbreviations, symbols, and formulas for designating the soil base exchange substances and their acids and salts. *Soil Sci. Soc. Am. Proc.* 10:341-343.

Van Miegroet, H., and D. Cole. 1984. The impact of nitrification on soil acidification and cation leaching in a red alder forest. *J. Environ. Qual.* 13:585-590.

Van Miegroet, H., D. Cole, D. Binkley, and P. Sollins. 1989. The

effect of nitrogen accumulation and nitrification on soil chemical properties in alder forests. p. 515-528. *In* R.K. Olson and A.S. LeFohn (ed.) *Effects of air pollution on western forests*. Air Waste Manage. Assoc., Pittsburgh, PA.

