# Changes in Bicarbonate-extractable Inorganic and Organic Phosphorus by Drying Pasture Soils

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#### **ABSTRACT**

Soils are commonly dried in the laboratory prior to the determination of P fractions, but this can profoundly influence the results. We investigated the impact of soil drying on bicarbonate-extractable inorganic and organic P in 29 permanent lowland pasture soils from England and Wales (total C 29-80 g C kg<sup>-1</sup> soil, clay 219-681 g kg<sup>-1</sup> soil, pH 4.4-6.8) by extracting soils at approximate field moisture capacity and after air-drying at 30°C for 7 d. Air-drying increased the mean bicarbonate-extractable inorganic P from 14.8 to 22.5 mg P kg-1 soil, and the mean bicarbonate-extractable organic P from 17.4 to 25.7 mg P kg<sup>-1</sup> soil. Proportional increases for individual soils following drying were between 11 and 165% for inorganic P, and between -2 and 137% for organic P, being greatest in soils with low P concentrations. The results are unlikely to influence fests for plantavailable P, because these are derived from analyses of air-dried samples, but have important implications for attempts to relate bicarbonate-extractable P fractions to processes operating under field conditions.

DICARBONATE-EXTRACTION is amongst the most common soil-test P methods. Typically representing between 1 and 5% of the total soil P, this operationally defined extraction technique was originally developed for the estimation of plant-available soil P (Olsen et al., 1954), and is commonly used as an index of soil P status to determine fertilizer P requirements (Kamprath and Watson, 1980). It has proved a versatile extract being used to determine soil microbial P (Brookes et al., 1982), and recently to investigate the link between soil P and P transfer in runoff (Heckrath et al., 1995; Pote et al., 1996; Leinweber et al., 1999). Conventional procedures involve only the determination of inorganic orthophosphate in the bicarbonate extracts, but organic P compounds are also extracted and can be determined following a suitable digestion procedure. There is little information on the chemical composition of bicarbonate-extractable organic P. It may represent an active soil organic P fraction (Bowman and Cole, 1978; Dick and Tabatabai, 1978), although in some soils only small amounts are hydrolyzable by phosphatase enzymes (Otani and Ae, 1999; Hayes et al., 2000).

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We recently reported that soil drying causes significant changes in water-extractable P, in particular organic P, and that these changes appeared to be related to direct P release from lysed microbial cells (Turner and Haygarth, 2001; Turner et al., 2002). Similar changes were reported for inorganic P in bicarbonate extracts of New Zealand pasture soils (Sparling et al., 1985), and resin extracts of a range of mainly low organic matter European soils (Olsen and Court, 1982). However, no information is available on changes in bicarbonateextractable organic P induced by soil drying. The objectives of this work were to determine how soil drying affected the concentrations of bicarbonate-extractable inorganic and organic P in a wide range of soils under permanent pasture, and to investigate how these changes related to soils properties.

### MATERIALS AND METHODS Soil Sampling and Preparation

Twenty-nine lowland soils under permanent pasture were sampled during October 1998 from sites around England and Wales, selected from the National Soil Inventory database (National Soil Resources Institute, Cranfield University, UK) to give a wide range of organic matter, bicarbonate-extractable P, and textural characteristics. Soil blocks were taken to 10 cm from each site and transported to the laboratory in plastic trays. Soil moisture contents were standardized by saturating each turf with water and allowing drainage under cover for 48 h at ambient temperature. This moisture content, defined here as field moisture capacity, was determined by measuring the gravimetric water content of duplicate soil cores (dried at 105°C overnight). Each soil was sieved (<4 mm) to remove large roots, stones and macrofauna, then left to equilibrate for 1 wk at 10 to 15°C. These were designated as "moist" soils and were stored at 4°C for no more than 7 d prior to bicarbonate extraction. Subsamples were dried on shallow metal trays for 7 d at 30°C and were designated as "dry" soils.

### Determination of Bicarbonate-Extractable Phosphorus

Bicarbonate-extractable P was determined in moist and dry soils by extracting triplicate samples (2.50 g on an oven-dry soil basis) for 30 min with 50 mL of 0.5 M

Table 1. Physical, chemical, and biological properties of the 29 permanent lowland pasture soils from England and Wales. The soils are ranked in order of their moist-soil bicarbonate-extractable total P concentrations (see Table 2).

Soil No.	USDA class	Textural class†	pН	Clay	Total C	Total N	Oxalate- extraction		Total soil P			
									Total	Inorganic	Organic	Microbial
							AI	Fe	P	P	P	P
			g kg <sup>-1</sup> soil					mg kg <sup>-1</sup> soil				
1	Fluvaquents	clay	5.9	547	64.4	6.52	1.35	5.93	784	184	600	124
2	Dystrochrepts	clay loam	5.6	313	56.0	5.92	4.96	6.34	1004	222	<b>783</b>	56
3	Hapludalfs	clav	6.0	567	67.7	7.57	0.91	2.69	989	257	732	134
4	Hapludalfs	clay loam	5.5	328	40.1	4.05	0.80	3.22	568	124	444	97
5	Haplaquepts	cłay	5.0	362	47.2	5.04	1.85	6.60	854	117	737	108
6	Haplaquepts	clay	6.1	483	38.9	2.85	1.05	5.15	821	394	427	31
7	Hapludalfs	clay	5.2	629	68.8	7.33	1.51	4.35	1007	161	846	163
8	Paleudalfs	clay	6.8	541	69.2	5.49	3.30	9.60	1074	265	809	67
9	Haplaquepts	clav	5.8	579	66.3	6.99	1.09	7.09	900	190	710	158
10	Haplaquepts	sandy clay	4.8	430	39.8	3.40	1.07	4.29	376	33	343	68
11	Haplaquepts	sandy clay	5.0	359	49.6	4.66	3.24	9.01	626	140	486	65
12	Hapludalfs	silty clay	4.8	424	47.5	4.93	2.48	8.95	887	180	707	74
13	Haplaquepts	sandy clay	5.1	318	42.3	4.45	1.29	4.67	821	145	676	118
14	Dystrochrepts	clav	6.2	401	44.9	4.43	2.06	6.14	1321	489	832	76
15	Haplaquepts	sandy clay	4.8	338	36.9	3.63	1.02	3.66	585	74	511	121
16	Haplaquepts	clay loam	4.7	346	29.6	3.16	1.19	6.19	519	109	411	76
17	Hapludalfs	clay	5.1	338	43.7	4.73	1.00	4.69	988	361	627	81
18	Haplaquepts	day	4.7	484	48.4	5.37	1.60	9.96	997	272	725	138
19	Hapludalfs	clay loam	5.1	299	48.0	4.83	0.80	2.92	833	240	593	145
20	Haplaquepts	clay	4.4	457	45.4	4.08	1.46	5.53	571	86	486	103
21	Dystrochrepts	clay loam	5.5	273	30.8	3.40	2.44	3.44	1021	354	667	39
22	Dystrochrepts	sandy clay loam	5.5	219	30.6	3.25	0.85	4.48	834	350	485	80
23	Haplaquepts	clay	5.0	379	28.9	3.74	1.09	4.68	1020	351	669	97
24	Dystrochrepts	clay	4.5	445	58.7	6.35	1.44	7.65	1542	256	1286	118
25	Hapludalfs	clay loam	5.0	240	32.8	3.57	1.13	4.43	923	452	470	79
26	Haplaquepts	clay loam	4.8	335	46.0	4.83	1.53	5.33	1106	347	759	112
27	Dystrochrepts	sandy clay loam	5.9	261	47.2	4.61	1.95	6.30	1312	569	743	69
28	Fluvaquents	clay	5.0	681	80.4	8.70	2.44	12.88	1981	587	1394	239
29	Udipsamments	sandy clay loam	4.9	250	44.0	4.58	0.82	3.14	962	246	716	128

†Based on topsoil texture.

NaHCO<sub>3</sub> (adjusted to pH 8.5 with NaOH) on an endover-end shaker (Olsen et al., 1954). The exact volume of extractant was adjusted to account for soil moisture content to ensure equivalent solution/soil ratios for moist and dry soils. The extracts were filtered through Whatman No. 42 filter papers (Whatman Ltd, Clifton, NJ), and analyzed for inorganic P by acid-molybdate reaction (Murphy and Riley, 1962) following acidification with dilute H<sub>2</sub>SO<sub>4</sub> to remove carbonates. Total P in the extracts was determined by the same procedure following acid-persulphate digestion (Rowland and Haygarth, 1997). Organic P was calculated as the difference between total P and inorganic P. Inorganic P in bicarbonate extracts determined by molybdate-reaction includes only inorganic orthophosphate (Coventry et al., 2001), although this does not preclude some hydrolysis of acid-labile condensed and organic P compounds during pretreatment. In both procedures, the absorbance was read at 880 nm against a calibration from standards prepared in 0.5 M NaHCO<sub>3</sub>. Values were corrected for blanks (no soil) and are expressed on the basis of oven-dry weight of soil.

### **Determination of Soil Properties**

Total soil C and N were measured simultaneously using a Carlo-Erba NA2000 analyzer (Carlo-Erba, Milan, Italy). Total soil P fractions were determined by the ignition method with extraction in 0.5 M H<sub>2</sub>SO<sub>4</sub> (Saunders and Williams, 1955). Microbial P was determined by chloroform fumigation and bicarbonate extraction (Brookes et al., 1982). Soil texture was de-

termined by wet sieving followed by analysis using a Micromeritics Sedigraph 5100 with a Micromeritics Mastertech 51 automatic sampler (Micromeritics, Norcross, GA). Soil pH was determined in a 1:2.5 soil/deionized water ratio. Oxalate-extractable Fe and Al were determined by extraction with ammonium oxalate-oxalic acid for 2 h in the dark, with detection using inductively coupled plasma atomic emission spectrometry (ICP-AES) (Schoumans, 2000).

Some physical and chemical properties of the soils are presented in Table 1. Total C contents ranged from 28.9 to 80.4 g C kg<sup>-1</sup> soil, total N from 2.85 to 8.70 g N kg<sup>-1</sup> soil, total P from 376 to 1981 mg P kg<sup>-1</sup> soil, clay from 219 to 681 g kg<sup>-1</sup> soil, and pH from 4.4 to 6.8. Microbial P concentrations ranged between 31 and 239 mg P kg<sup>-1</sup> soil (Turner et al., 2001).

### RESULTS

### Changes in Bicarbonate-Extractable Phosphorus Following Soil Drying

Bicarbonate-extractable total P increased markedly in all soils after drying, from between 13.7 and 65.8 mg P kg<sup>-1</sup> soil (mean 32.2 mg P kg<sup>-1</sup>soil) in moist-soils, to between 22.2 and 88.1 mg P kg<sup>-1</sup> soil (mean 48.2 mg P kg<sup>-1</sup> soil) in dry soils (Table 2). This represented increases after drying of between 5.2 and 26.8 mg P kg<sup>-1</sup> soil (mean 16.0 mg P kg<sup>-1</sup> soil), equivalent to proportional increases of between 13 and 105% (mean increase of 57%).

Concentrations of bicarbonate-extractable inorganic

Table 2. Bicarbonate-extractable soil P fractions in 29 permanent pasture soils from England and Wales extracted at field capacity moisture and after air-drying at 30°C for 7 d. Values are means ± standard error of three extracts. Values in parentheses are the proportional increase (%) following soil drying.

Soil No.	Bicarbo	nate-Extractable	Total P	Bicarbona	te-Extractable In	organic P	Bicarbonate-Extractable Organic P		
	Moist	Air-dried	Change	Moist	Air-dried	Change	Moist	Air-dried	Change
					- mg P kg <sup>-1</sup> soil ·				
1	$13.7 \pm 0.62$	22.2 ± 0.46	8.5 (62)	6.6 ± 0.60	9.1 ± 0.39	2.5 (38)	7.1 ± 0.36	13.1 ± 0.42	6.0 (85)
2	15.9 ± 0.69	28.6 ± 0.17	12.7 (80)	5.8 ± 0.21	$11.3 \pm 0.11$	5.5 (95)	10.1 ± 0.48	17.3 ± 0.27	7.2 (71)
3	16.9 ± 0.85	$33.4 \pm 1.02$	16.5 (98)	8.3 ± 0.47	$14.0 \pm 0.35$	5.7 (68)	8.5 ± 0.38	19.4 ± 0.78	10.9 (127)
4	17.3 ± 0.56	$25.6 \pm 0.30$	8.3 (48)	8.8 ± 0.71	$11.3 \pm 0.47$	2.4 (28)	8.4 ± 0.40	$14.4 \pm 0.26$	6.0 (71)
5	$17.6 \pm 0.98$	36.1 ± 0.64	18.5 (105)	$6.1 \pm 0.45$	$14.3 \pm 0.49$	8.2 (134)	$11.5 \pm 0.65$	$21.8 \pm 0.26$	10.3 (90)
6	$17.9 \pm 0.58$	$28.3 \pm 0.61$	10.4 (58)	$12.3 \pm 0.56$	$17.5 \pm 0.35$	5.2 (42)	$5.6 \pm 0.07$	$10.8 \pm 0.37$	5.2 (93)
7	$18.8 \pm 0.33$	$32.6 \pm 2.38$	13.8 (73)	$7.5 \pm 0.32$	$12.5 \pm 1.04$	5.0 (67)	$11.3 \pm 0.08$	$20.2 \pm 1.34$	8.9 (79)
8	$18.9 \pm 1.57$	$36.2 \pm 0.57$	17.3 (92)	$10.2 \pm 1.42$	$15.6 \pm 0.46$	5.4 (53)	$8.7 \pm 2.62$	$20.6 \pm 0.72$	11.9 (137)
9	$19.5 \pm 0.36$	$32.0 \pm 0.56$	12.5 (64)	$7.6 \pm 0.30$	$13.7 \pm 0.76$	6.1 (80)	$11.8 \pm 0.46$	$18.3 \pm 0.24$	6.5 (55)
10	$20.1 \pm 0.48$	$31.8 \pm 0.44$	11.7 (58)	$6.2 \pm 0.31$	$12.9 \pm 0.23$	6.7 (108)	$13.9 \pm 0.20$	$18.9 \pm 0.21$	5.0 (36)
11	$22.8 \pm 0.30$	$38.5 \pm 0.95$	15.7 (69)	$7.9 \pm 0.13$	$14.5 \pm 0.13$	6.6 (84)	$14.9 \pm 0.27$	$24.0 \pm 1.08$	9.1 (61)
12	$23.6 \pm 0.70$	36.6 ± 0.19	13.0 (55)	$10.0 \pm 0.11$	$15.4 \pm 0.30$	5.4 (54)	$13.6 \pm 0.77$	$21.3 \pm 0.42$	7.7 (57)
13	$24.9 \pm 0.35$	44.8 ± 1.48	19.9 (80)	$9.3 \pm 0.17$	$17.3 \pm 0.45$	8.0 (86)	$15.7 \pm 0.48$	$27.5 \pm 1.09$	11.8 (75)
14	<b>29.2</b> ± <b>1.98</b>	$43.4 \pm 1.50$	14.2 (49)	$20.2 \pm 2.21$	$26.4 \pm 0.88$	6.2 (31)	8.9 ± 0.37	$17.0 \pm 0.63$	8.1 (91)
15	$31.2 \pm 0.93$	$52.1 \pm 1.11$	20.9 (67)	9.9 ± 1.23	$21.4 \pm 0.37$	11.5 (116)	21.3 ± 0.59	$30.7 \pm 0.88$	9.4 (44)
16	$31.4 \pm 1.15$	$53.5 \pm 0.79$	22.1 (70)	9.7 ± 1.10	$20.7 \pm 0.17$	11.0 (113)	$21.7 \pm 0.63$	$32.8 \pm 0.65$	11.1 (51)
17	$33.7 \pm 0.88$	$48.8 \pm 0.50$	15.1 (45)	19.9 ± 0.74	$25.7 \pm 0.72$	5.8 (29)	$13.8 \pm 0.19$	23.1 ± 0.23	9.3 (67)
18	$35.0 \pm 0.70$	54.4 ± 0.79	19.4 (55)	$11.2 \pm 0.19$	$22.1 \pm 0.21$	10.9 (97)	$23.9 \pm 0.51$	$32.3 \pm 0.81$	8.4 (35)
19	$37.4 \pm 0.50$	$61.6 \pm 1.87$	24.2 (65)	$18.4 \pm 0.07$	29.3 ± 1.08	10.9 (59)	$19.0 \pm 0.48$	$32.2 \pm 0.80$	13.2 (69)
20	$38.9 \pm 0.25$	$65.0 \pm 1.72$	26.1 (67)	$7.2 \pm 0.23$	<b>19.1</b> ± <b>0.7</b> 0	11.9 (165)	$31.7 \pm 0.10$	45.9 ± 1.04	14.2 (45)
21	$39.9 \pm 1.82$	$45.1 \pm 0.78$	5.2 (13)	$22.2 \pm 0.65$	$27.9 \pm 0.49$	5.7 (26)	$17.6 \pm 1.59$	$17.2 \pm 0.30$	-0.4(-2)
22	$41.7 \pm 0.56$	$57.7 \pm 0.47$	16.0 (38)	$27.2 \pm 0.22$	$34.9 \pm 0.59$	7.7 (28)	$14.5 \pm 0.58$	$22.8 \pm 0.16$	8.3 (57)
23	$41.9 \pm 1.08$	$53.3 \pm 1.38$	11.4 (27)	$18.7 \pm 0.58$	$24.1 \pm 0.76$	5.4 (29)	$23.2 \pm 0.55$	$29.2 \pm 0.66$	6.0 (26)
24	$42.6 \pm 0.14$	$69.4 \pm 0.98$	26.8 (63)	$12.0 \pm 0.09$	$23.6 \pm 0.48$	11.6 (97)	$30.6 \pm 0.15$	45.8 ± 1.19	15.2 (50)
25	$44.0 \pm 0.63$	$61.6 \pm 1.03$	17.6 (40)	$24.9 \pm 0.30$	$33.9 \pm 0.87$	9.1 (36)	$19.1 \pm 0.70$	$27.7 \pm 0.25$	8.6 (45)
26	$55.4 \pm 1.76$	$81.3 \pm 0.70$	25.9 (47)	$32.3 \pm 0.85$	$45.5 \pm 0.48$	13.2 (41)	$23.2 \pm 0.99$	35.9 ± 0.68	12.7 (55)
27	57.8 ± 2.23	66.8 ± 1.03	9.0 (16)	42.8 ± 0.14	47.4 ± 0.88	4.6 (11)	$15.0 \pm 2.16$	19.4 ± 0.93	4.4 (29)
28	59.4 ± 0.59	68.8 ± 0.44	9.4 (16)	$19.9 \pm 0.60$	$24.3 \pm 0.23$	4.4 (22)	39.5 ± 1.18	44.4 ± 0.21	4.9 (12)
29	65.8 ± 1.54	88.1 ± 0.93	22.3 (34)	26.2 ± 0.34	47.6 ± 0.31	21.4 (82)	$39.7 \pm 1.21$	40.6 ± 0.64	0.9 (2)

and organic P were similar for individual soils, although on average there was slightly more organic P in extracts of both moist and dry soils, and more organic P was released following soil drying (Table 2). Bicarbonateextractable inorganic P increased from between 5.8 and 42.8 mg P kg<sup>-1</sup> soil (mean 14.8 mg P kg<sup>-1</sup> soil) in moist soils, to between 9.1 and 47.6 mg P kg<sup>-1</sup> soil (mean 22.5 mg P kg<sup>-1</sup> soil) in dry soils. This represented increases after drying of between 2.5 and 21.4 mg P kg<sup>-1</sup> soil (mean 7.7 mg P kg<sup>-1</sup> soil), equivalent to proportional increases of between 11 and 165% (mean increase of 66%). Bicarbonate-extractable organic P increased from between 5.6 and 39.7 mg P kg<sup>-1</sup> soil (mean 17.4 mg P kg<sup>-1</sup> soil) in moist soils, to between 10.8 and 45.9 mg P kg<sup>-1</sup> soil (mean 25.7 mg P kg<sup>-1</sup> soil) in dry soils. This represented a decrease in bicarbonate-extractable organic P for one soil (0.4 mg P kg<sup>-1</sup> soil), but increases of up to 137% for the other soils (mean increase of 59%) (Table 2). The proportions of inorganic and organic P in bicarbonate extracts of individual soils changed little following soil drying. Thus, the proportion of inorganic P varied from between 18 and 74% (mean 45%) in moist soils, to between 29 and 71% (mean 46%) in dry soils, while the proportion of organic P varied from between 26 and 82% (mean 55%) in moist soils, to between 29 and 71% (mean 54%) in dry soils.

## Relationships Between Phosphorus Fractions and Soil Properties

There were strong correlations between bicarbonateextractable P concentrations in moist and dry soils, suggesting a consistent and proportional response to soil drying (Table 3). Bicarbonate-extractable inorganic P was strongly positively correlated with total soil inorganic P, and negatively correlated with clay content. Bicarbonate-extractable organic P was strongly negatively correlated with soil pH (Fig. 1), and positively correlated with total soil organic P (P < 0.05), and microbial P (P < 0.01).

The absolute changes in bicarbonate-extractable inorganic P following soil drying were strongly negatively correlated with soil pH (r = -0.55, P < 0.01). There were no significant relationships with oxalate-extractable Al or Fe, but soils with the greatest increases in bicarbonate-extractable inorganic P contained low concentrations of oxalate-extractable metals (Fig. 2). The proportional changes in bicarbonate-extractable inorganic P following soil drying were negatively correlated with soil pH (P < 0.01), total soil inorganic P (P < 0.001), and bicarbonate-extractable inorganic P in moist soils (P < 0.001). Therefore, the greatest proportional changes in bicarbonate-extractable inorganic P occurred in acidic soils with low inorganic P concentrations (Table 3, Fig. 3).

The absolute changes in bicarbonate-extractable organic P concentrations after soil drying were not significantly correlated with any of the soil properties measured. However, the proportional changes were positively correlated with soil pH (P < 0.001), and negatively correlated with the concentration of bicarbonate-extractable organic P in moist soil. Therefore, the greatest proportional changes in bicarbonate-extractable organic P occurred in neutral soils with low organic P concentrations (Table 3, Fig. 3).

Table 3. Correlation coefficients for relationships between soil properties and changes in bicarbonate-extractable P fractions following drying of 29 permanent grassland soils from England and Wales for 7 d at 30°C.

	Bicarbonate-extractable P										
		Inorg	ganic P		Organic P						
	Moist soil	Dry soil	Cha	inge		Dry soil	Change				
			mg P kg <sup>-1</sup>	%	Moist soil		mg P kg <sup>-1</sup>	%			
		Correlation coefficients									
Bicarbonate inorganic P											
Dry soil	0.94***				0.50**						
Change, mg P kg <sup>-1</sup>	0.22	0.55**	•		0.68***	0.70***					
Change, %	-0.60***	-0.35	0.46*		0.23	0.37	0.44*				
Bicarbonate organic P											
Dry soil	0.17	0.40*			0.93***						
Change, mg P kg <sup>-1</sup>	-0.27	-0.16	0.20		0.01	0.39*					
Change, %	-0.43*	-0.50**	-0.37	0.03	-0.70***	-0.46*	0.50**				
Soil properties											
Total C	-0.27	-0.32	-0.25	0.00	0.01	0.06	0.13	0.31			
Total N	-0.22	-0.26	-0.21	-0.03	0.09	0.13	0.12	0.21			
Clay	-0.49**	-0.55**	-0.35	0.10	-0.05	0.00	0.11	0.32			
pH	0.06	-0.14	-0.55**	0.51**	-0.66***	-0.71***	-0.25	0.58***			
Total soil P	0.42*	0.33	-0.08	-0.42*	0.35	0.31	-0.06	-0.13			
Total soil inorganic P	0.75***	0.58***	-0.17	-0.73***	0.15	0.03	-0.29	-0.18			
Total soil organic P	0.12	0.10	0.00	-0.13	0.40*	0.41*	0.11	-0.07			
Microbial P	-0.08	-0.02	0.14	0.08	0.47**	0.49**	0.15	-0.13			
Oxalate Al	-0.14	-0.22	-0.18	0.01	-0.14	-0.16	-0.07	0.10			
Oxalate Fe	-0.12	-0.17	-0.19	-0.02	-0.21	-0.23	0.09	-0.03			

<sup>\*</sup> Significant at the 0.05 probability level.

### **DISCUSSION**

The changes in bicarbonate-extractable P following soil drying revealed a similar trend to those reported previously for extraction with water, resin, and bicarbonate (Olsen and Court, 1982; Sparling et al., 1985; Turner and Haygarth, 2001). The increases in bicarbonate-extractable total P reported here (5.2–26.9 mg P kg<sup>-1</sup> soil) are several times greater than those reported for water-extracts of the same permanent pasture soils from England and Wales (1.1–7.6 mg P kg<sup>-1</sup> soil) and

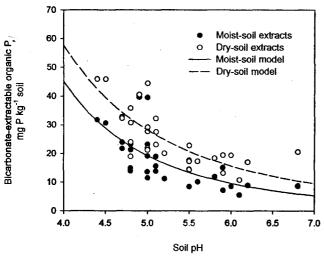
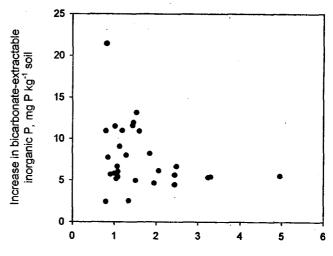


Fig. 1. The relationship between bicarbonate-extractable organic P (mg P kg<sup>-1</sup> soil) and soil pH for 29 permanent lowland pasture soils from England and Wales extracted at approximate field-capacity moisture content and after air-drying at 30°C for 7 d. The curves describe the following models: [Bicarbonate organic P from moist soil] = 9023[soil pH]<sup>-342</sup>,  $R^2$  = 0.49, P < 0.0001; and [Bicarbonate organic P from dry soil] = 5034[soil pH]<sup>-322</sup>,  $R^2$  = 0.60, P < 0.0001.

five Australian pasture soils (0.42–1.76 mg P kg<sup>-1</sup> soil) (Turner and Haygarth, 2001; Turner et al., 2002). Bicarbonate-extractable inorganic P in a range of New Zealand pasture soils increased by 2.7 to 21.7 mg P kg<sup>-1</sup> soil following air-drying, although concentrations decreased by 7.0 and 10.7 mg P kg<sup>-1</sup> for two soils (Sparling et al., 1985). Seasonal changes in the inorganic fraction were negatively correlated to soil moisture in sandy soils under grassland and arable cropping in Denmark (Magid and Nielsen, 1992).

Phosphorus released to water following soil drying is mainly organic, and appears to be derived from lysed



Oxalate-extractable Al, g Al kg<sup>-1</sup> soil

Fig. 2. The relationship between oxalate-extractable Al (g Al kg<sup>-1</sup> soil) and the increase in bicarbonate-extractable inorganic P (mg P kg<sup>-1</sup> soil) following air-drying at 30°C for 7 d in 29 permanent lowland pasture soils from England and Wales.

<sup>\*\*</sup> Significant at the 0.01 probability level.
\*\*\* Significant at the 0.001 probability level.

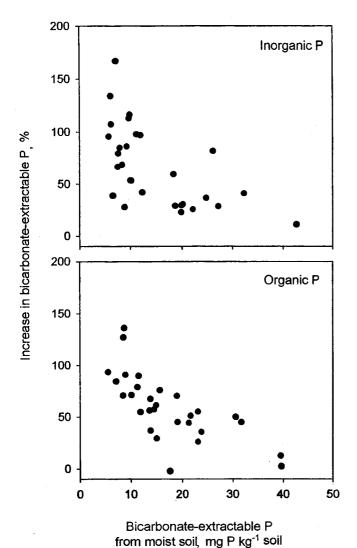


Fig. 3. The relationships between the proportional increase (%) in (top) bicarbonate-extractable inorganic P and (bottom) bicarbonate-extractable organic P following air-drying at 30°C for 7 d and the initial concentrations (mg P kg<sup>-1</sup> soil) in 29 permanent lowland pasture soils from England and Wales.

microbial cells (Salema et al., 1982; Turner and Haygarth, 2001). However, relatively similar amounts of inorganic and organic P were released to bicarbonate extracts, suggesting that for bicarbonate extractable P, changes in P solubility may be more important than direct release from the microbial biomass. A similar conclusion was reported by Magid and Nielsen (1992), who calculated that seasonal changes in bicarbonateextractable inorganic and organic P in sandy Danish soils were far greater than those expected on the basis of biological processes alone. Microbial cell death during the drying and rewetting process is primarily induced by osmotic shock and cell rupture upon rewetting with a solution of low ionic strength (Salema et al., 1982; Kieft et al., 1987). Therefore, the high ionic strength of bicarbonate solution may reduce this effect compared with water extraction (Sparling et al., 1985). The hypothesis that non-biomass organic P dominates in bicarbonate extracts is supported by <sup>31</sup>P nuclear magnetic resonance analysis of bicarbonate-extractable organic P in two Canadian (air-dried) soils under arable cropping (Zhang et al., 1999). This study revealed that the bicarbonate-extractable organic P was dominated by orthophosphate monoesters and was, therefore, similar to the whole-soil organic P extracted with NaOH. Orthophosphate diesters, the main organic P compounds in soil microorganisms, were present in only small concentrations.

The mechanisms by which soil drying could affect the solubility of nonbiomass inorganic and organic P are poorly understood, but probably include both physical and chemical changes. Rapid rehydration of dry soils commonly causes aggregate breakdown (Amézketa, 1999), which increases the surface area for desorption by exposing surfaces and associated P protected within aggregates (Nevo and Hagin, 1966). Such a process was linked to increases in resin-extractable inorganic P following soil drying (Olsen and Court, 1982). Aggregate breakdown would be exacerbated in sieved soils (Bartlett and James, 1980), but also occurs under field conditions (Kemper and Rosenau, 1984). A potentially more important process is the disruption of organic matter coatings on clay and mineral surfaces by the physical stresses induced during soil drying. This increases organic matter solubility, exposes formerly protected mineral surfaces, and was attributed to increases in oxalateextractable Si of up to 200% following drying of Swedish spodic B horizons (Simonsson et al., 1999). Soil drying also increases the crystallinity of pure Fe and Al oxides, which reduces the specific surface area and P sorption capacity of these minerals (McLaughlin et al., 1981). However, this is inconsistent with reports of increased sorption capacity of dried soils for P and S (Haynes and Swift, 1985; Comfort et al., 1991), which supports the hypothesis that physical disruption of organic matter coatings is the primary mechanism contributing to increases in bicarbonate-extractable P following soil drying.

The greatest increases in bicarbonate-extractable inorganic P occurred in low P pasture soils, as found in other studies (Olsen and Court, 1982; Sparling et al., 1985). This suggests that plant-available P tests might substantially overestimate the P status of such soils. However, these soils also contained relatively large concentrations of organic P in the bicarbonate extracts. This may contribute to plant nutrition in such soils, but little information exists on its chemical nature or biological availability. Some studies suggest that bicarbonate-extractable organic P is relatively active (Bowman and Cole, 1978; Guggenberger et al., 1996), while others indicate its resistance to hydrolysis by phosphatase enzymes (Otani and Ae, 1999; Hayes et al., 2000). The differences may be partly linked to pH, because most organic P compounds undergo reduced solubility in acidic soils, and become stabilized by association with clays and humic compounds (Goring and Bartholomew, 1952; Anderson and Arlidge, 1962). This is reflected in the negative correlations between bicarbonate-extractable organic P and soil pH (Tiessen et al., 1984), and almost certainly influences the relative bioavailability of bicarbonate-extractable organic P amongst different

soils. Clearly, more information on the chemical composition of bicarbonate-extractable organic P is needed to determine its potential as a biologically available pool of soil P.

Despite the possible errors in plant-available P tests induced by drying low P pasture soils, most soils are unlikely to be affected, because correlations between plant growth and soil P status are almost exclusively derived from analyses of air-dried soils. However, our results have important implications for attempts to understand patterns of P release and availability in the field, because seasonal changes in bicarbonate-extractable P tend to be small (e.g., Magid and Nielsen, 1992), and will almost certainly be masked by the relatively large changes induced by air-drying. Therefore, we suggest that such studies should use field moist samples, even though soil drying can greatly reduce the variability amongst replicate analyses.

### **CONCLUSIONS**

Concentrations of bicarbonate-extractable inorganic and organic P in permanent lowland pasture soils from England and Wales were substantially increased by airdrying prior to extraction. Similar proportions of inorganic and organic P were released following drying, which were proportionally greatest in soils with low initial bicarbonate-extractable P concentrations. The mechanisms underlying these changes remain poorly understood, but a combination of microbial lysis, aggregate breakdown, and disruption of organic matter coatings appear to be important. Organic P constituted a large proportion of the total extractable P, and more information is needed on the chemical composition of this potentially bioavailable fraction. The results have important implications for analytical procedures that involve soil drying prior to extraction, and for attempts to relate such measurements to seasonal patterns of soil P availability.

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