

RELATIONSHIP BETWEEN EXCHANGEABLE AND TOTAL MAGNESIUM IN PENNSYLVANIA SOILS¹

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Abstract—The particle size distribution, total and exchangeable Mg, and mineralogical compositions were determined on eight well-drained, noncultivated subsoils from Pennsylvania. No correlation was found between the clay content and total Mg ($r = .29$), or between the clay content and exchangeable Mg ($r = .35$). Serpentine, talc, and hypersthene were found in the very fine sand and silt fractions of soils having relatively high exchangeable Mg. Mica and 14-Å clay minerals were the only Mg-bearing minerals noted in the same fractions of soils having relatively low exchangeable Mg. Of the Mg-bearing clay minerals found in the clay fractions (smectite, vermiculite, chlorite, illite, and interstratified chlorite/vermiculite), only smectite decreased as the exchangeable Mg in the soils decreased. Two distinctly different distribution patterns of Mg were found for soils having relatively high and low exchangeable Mg. The former soils showed a decreasing Mg content as the particle size decreased, and the latter soils showed the opposite. Exchangeable Mg correlated significantly with the amount of Mg in whole soil, sand, and silt, but not with the amount of Mg in the clay, an indication that sand and silt but not clay were the important sources of exchangeable Mg in these soils.

Key Words—Cation exchange, Chlorite, Illite, Magnesium, Smectite, Soil, Vermiculite.

INTRODUCTION

Magnesium is a common constituent of various primary and secondary minerals found in rocks and soils and is one of the elements essential for living organisms. As a constituent of chlorophyll, it plays a vital role in photosynthesis by plants and hence is an essential factor in the existence of most living organisms. The source of magnesium used by plants is the soil.

Over a growing season, crops take up Mg mainly from the exchangeable sites on clays or from soil solution. In most soils, Mg in these easily available forms accounts for only a small portion (<10%) of the total soil Mg. The source of the extra solid-phase Mg is not fully understood. Salmon (1963) suggested that the main sources of such Mg that can be made available in soils are secondary minerals, particularly clay minerals, mica, and chlorite. Stahlberg (1960) determined the amount of nonexchangeable Mg released from 131 Swedish topsoils after boiling them in 1 N HCl. He found that vermiculite and chlorite were the main sources of this acid-soluble Mg. Prince *et al.* (1947), Stahlberg (1960), and Baker (1971), however, reported a poor correlation between exchangeable Mg and total or acid-soluble Mg in soils.

The objective of the present study was to determine

the source of exchangeable Mg in selected Pennsylvania soils with respect to soil texture and mineralogical composition and to contribute to the understanding of the behavior of Mg in such systems.

MATERIALS AND METHODS

Eight soils were selected to give a wide range of Mg saturation percentages, where % Mg saturation is defined as the exchangeable Mg content divided by the total cation-exchange capacity (CEC) (times 100) of the soil. The common characteristics of the soils are: (1) noncultivated—to avoid differences resulting from lime and fertilizer applications, cropping, and farm management, (2) well-drained—to eliminate the possibility of accumulation of Mg due to poor drainage and evaporation, and (3) subsoil—to reduce the effect of vegetation, organic matter accumulation and decomposition, and eolian deposits. Soil series, soil family, horizon, parent material, and location of the samples are shown in Table 1.

Exchangeable Ca, Mg, K, and Na were determined by ammonium acetate extraction. Five grams of soil were mixed with 30 ml of 1 N, pH 7.0 NH_4OAc solution in a 100-ml polypropylene centrifuge tube for 5 min using a vortex mixer. The sample was then centrifuged at 1000 rpm for 10 min, and the supernatant was decanted into a 200-ml volumetric flask. After five extractions, the combined supernatant was diluted to volume with deionized water. The elements were de-

¹ Paper No. 6753, Journal Series, Pennsylvania Agricultural Experiment Station, University Park, Pennsylvania 16802.

Table 1. Soil series, soil family, horizon, parent material, and sample location of eight soils from Pennsylvania.

Soil series	Soil family	Horizon	Parent material	Sample location
Chrome	Typic Hapludalf, fine, mixed, mesic	B2	Chlorite schist	Delaware Co., Pa.
Neshaminy	Ultic Hapludalf, fine-loamy, mixed, mesic	B22	Diabase	Montgomery Co., Pa.
Montalto	Ultic Hapludalf, fine, mixed, mesic	B22	Diabase	Lancaster Co., Pa.
Morrison (I)	Ultic Hapludalf, fine-loamy, mixed, mesic	B22t	Limestone, sandy	Centre Co., Pa.
Glenelg	Typic Hapludult, fine-loamy, mixed, mesic	B22	Mica schist	Chester Co., Pa.
Duffield	Ultic Hapludalf, fine-loamy, mixed, mesic	B22	Limestone, shaly	Lehigh Co., Pa.
Morrison (II)	Ultic Hapludalf, fine-loamy, mixed, mesic	B22	Sandstone, calcareous	Centre Co., Pa.
Elliber	Typic Hapludult, loamy-skeletal, mixed, mesic	B22	Limestone, very cherty	Perry Co., Pa.

Table 2. Exchangeable Mg (Ex. Mg), cation-exchange capacity (CEC), percentage of exchangeable Mg saturation (% Mg saturation), and particle size distribution of the eight soil samples.

Soil series	Ex. Mg (meq/100 g)	CEC (meq/100 g)	% Mg saturation	Sand (2-0.05 mm)	Silt (0.05-0.002 mm)	Clay (<0.002 mm)	Texture
Chrome	50.10	56.72	88.3	42.8	16.3	40.9	Clay
Neshaminy	8.70	14.20	61.3	36.7	35.7	27.6	Clay loam
Montalto	5.02	9.05	55.5	10.4	39.1	50.5	Clay
Morrison (I)	1.50	3.50	42.9	53.7	23.1	23.2	Sandy clay loam
Glenelg	2.20	6.25	35.2	23.5	57.8	18.6	Silt loam
Duffield	1.26	4.90	25.7	11.7	56.2	32.1	Silty clay loam
Morrison (II)	0.31	3.30	9.4	40.1	18.6	41.3	Clay
Elliber	0.07	3.90	1.8	37.2	55.2	7.6	Silt loam

Table 3. Chemical analysis (%) of whole soil (<2 mm) for the eight soil samples.

Soil series	SiO ₂	Al ₂ O ₃	MgO	CaO	Fe ₂ O ₃	TiO ₂	K ₂ O	Na ₂ O	H ₂ O ¹	Total
Chrome	47.84	3.14	19.59	0.55	16.03	0.13	0.20	0.09	10.71	98.28
Neshaminy	47.03	18.73	6.63	1.46	14.88	1.18	0.54	0.27	8.74	100.16
Montalto	48.68	22.91	0.72	0.13	14.78	1.56	0.79	0.17	10.02	99.76
Morrison (I)	77.19	10.34	0.95	0.09	3.91	0.58	3.99	0.09	2.87	100.01
Glenelg	68.24	15.00	0.99	0.26	6.80	1.31	2.34	0.81	3.95	99.70
Duffield	68.94	14.92	0.83	0.14	6.59	1.19	2.64	0.35	4.84	100.24
Morrison (II)	72.62	14.39	0.51	0.06	5.83	0.61	0.98	0.05	5.67	100.72
Elliber	89.19	3.92	0.20	0.09	1.60	0.68	0.58	0.12	3.30	99.68

¹ Ignition loss (110°-950°C).

terminated on a Perkin-Elmer model 106 atomic absorption spectrophotometer after diluting an aliquot of the extract with 2% SrCl₂ solution to avoid interferences.

Exchangeable Al and H were determined using the same extraction procedures as above except that a non-buffered extractant, 1 N KCl, was used (Yuan, 1959). The amount of Al in the extract was determined by atomic absorption analysis. H was measured by titration with standardized 0.1 N NaOH solution after adding NaF to prevent the interference of Al. The CEC

was estimated from the sum of the exchangeable cations.

Soil particle size fractions were separated by the procedure of Jackson (1958) and Edwards and Bremner (1967). It was not necessary to remove organic matter because the soils were from B2 horizons. The sand fraction (2-0.05 mm) was retained by a 300-mesh sieve, and the very fine sand fraction (0.1-0.05 mm) was separated for optical mineralogical study using a 140-mesh sieve. The <2-μm clay fraction was separated from the silt by centrifugation at 750 rpm for 2.9 min

Table 4. Mineralogical analysis of very fine sand and silt by X-ray powder diffraction and polarizing microscopy of the eight soil samples.

Soil series	Minerals ¹
Chrome	Serpentine, smectite, ² talc, ² quartz, chlorite
Neshaminy	Quartz, hypersthene, talc, halloysite, vermiculite, feldspar
Montalto	Quartz, kaolinite, talc, biotite, feldspar
Morrison (I)	Quartz, feldspar, mica, ² 14-Å mineral
Glenelg	Quartz, mica, feldspar, 14-Å mineral
Duffield	Quartz, feldspar, kaolinite, ² mica, 14-Å mineral
Morrison (II)	Quartz, feldspar, mica, ² 14-Å mineral
Elliber	Quartz, feldspar, mica, ² 14-Å mineral

¹ Listed in the order of decreasing abundance.

² Detectable amount present in silt fraction only.

using an International No. 2 centrifuge. Coarse silt (50–20 µm) was separated by sedimentation in a beaker and decantation. All fractions were washed free of salt and dried from acetone overnight at 110°C. Clays were lightly hand ground and stored in a desiccator.

The elemental composition of the whole soil and its size fractions was determined by LiBO₂ fusion (Medlin *et al.*, 1969). Samples containing particles larger than silt size (50 µm) were ground in a Spex mixer/mill to reduce the sampling error and to insure more complete fusion. A 5-min grinding period was found to be sufficient for a 2-g sample. Elements were analyzed by atomic absorption.

Prior to mineralogical analysis, all samples were treated with citrate-dithionite-bicarbonate to remove free iron oxides (Mehra and Jackson, 1960). Very fine sand and coarse silt were analyzed with a polarizing microscope after mounting on glass slides using the method described by Marshall and Jeffries (1946). X-ray powder diffraction (XRD) analyses were made for silt and ground samples of very fine sand using a Norelco diffractometer and Ni-filtered CuKα radiation. The procedures employed for clay analysis were: (1) X-ray powder diffraction—the specimen preparation fol-

Table 6. Percent MgO in the sand, silt, and clay fractions of the eight soil samples.

Soil series	Sand	Silt	Clay
Chrome	23.50	21.30	14.81
Neshaminy	14.50	2.82	1.09
Montalto	1.18	0.70	0.65
Morrison (I)	0.08	0.82	3.09
Glenelg	0.61	1.06	1.34
Duffield	0.48	0.62	1.33
Morrison (II)	0.02	0.42	1.02
Elliber	0.01	0.18	1.31

lowed the method described by Rich (1969, 1975) in which the sample was oriented on a ceramic tile with suction. The sample treatments included: (a) K-saturation and drying at room temperature, 300°, and 500°C, (b) Mg-saturation and drying at room temperature, (c) glycerol solvation of Mg-saturated sample, and (d) lithium dimethylsulfoxide (DMSO) treatment to differentiate kaolinite and chlorite (Abdel-Kader *et al.*, 1978); (2) Chemical quantitative clay mineral analysis—the methods of Alexiades and Jackson (1966) were followed with some modifications: (a) the CEC as determined by methylene blue adsorption (Phan Thi Hang and Brindley, 1970) was used for calculating the vermiculite and smectite content (Chu and Johnson, 1979), and (b) the lithium metaborate fusion technique (Medlin *et al.*, 1969) was used for elemental analysis; and (3) Final quantitative estimation of clay mineral content—the simultaneous linear equations (SLE) program of Hussey (1972) was used.

RESULTS AND DISCUSSION

In Table 2 the samples are arranged in the order of decreasing % Mg saturation. This order is similar to that of exchangeable Mg content except for two samples, Morrison (I) and Glenelg. The correlation coefficient between these two properties is .78 which is significant at the 5% level. Clay contents (Table 2) vary from 7.6% in the Elliber sample to 50.5% in the Mont-

Table 5. Mineralogical composition¹ (%) of clay (<2 µm) of the eight soil samples.

Soil series	Smec	Verm	Chlo	Illi	Kaol	Amor	Qtz	C/V	Feld	Talc	Total
Chrome	63	8	16	0	0	12	0	0	1	0	100
Neshaminy	19	8	0	3	48	9	0	5	1	5	98
Montalto	11	1	0	6	54	9	2	14	0	3	100
Morrison (I)	6	2	7	18	38	7	5	14	12	0	109
Glenelg	22	5	1	13	30	6	7	13	3	0	100
Duffield	9	2	3	17	37	10	7	14	1	0	100
Morrison (II)	3	2	4	16	62	3	6	1	0	0	97
Elliber	2	1	2	11	11	9	40	24	2	0	103

¹ Smec = smectite; Verm = vermiculite; Chlo = chlorite; Illi = illite; Kaol = kaolinite; Amor = noncrystalline material; Qtz = quartz; C/V = interstratified chlorite/vermiculite; Feld = feldspars; Talc = talc.

alto sample. No significant correlation between the clay content and the exchangeable Mg content ($r = .35$) was observed.

Chemical analyses of the whole soils (<2 mm) are given in Table 3. The sum of oxides and ignition loss is close to 100% except for the Chrome sample which has a high Cr_2O_3 (0.73%) and MnO (0.15%) content. No correlation was found between total soil Mg and clay contents of the samples ($r = .29$), i.e., the Mg content of the soil may affect the *type* of clay but not the *amount* of clay formed in the soil.

Inasmuch as major minerals found in the very fine sand and silt are similar, they were combined and listed in the order of decreasing abundance in Table 4. Various types of Mg-bearing primary minerals are present in the two samples that have higher MgO contents (Chrome, 19.59% and Neshaminy, 6.63%). The main source of Mg in the sand and silt fractions of the Chrome sample is serpentine, an unstable phase in the weathering environment, that alters to other minerals during soil formation (Dixon, 1977). The occurrence of smectite, talc, and quartz in the silt and the decreasing amount of serpentine from the sand to the silt fractions may indicate the alteration of serpentine in the sand. The majority of Mg in the sand and silt fractions of the Neshaminy sample is apparently from hypersthene. The XRD analysis shows a higher content of halloysite and vermiculite in the silt than in the sand fraction of the Neshaminy sample. The XRD patterns of the sand and silt are very similar for the soils with relatively low Mg content (<1.0% MgO). The source of Mg in these samples is mainly mica or 14-Å clay minerals.

The mineralogical composition of the clay fraction separated from each soil is shown in Table 5. Although smectite, vermiculite, chlorite, talc, and illite contain structural Mg, only smectite decreases in abundance as exchangeable Mg decreases. The lack of correspondence between the abundance of a Mg-bearing clay mineral and exchangeable Mg may be due to the stability of these minerals in the soil environment. Unless soil conditions, such as pH, composition of soil solution, etc., are changed considerably, the clay minerals will release very little Mg to their surroundings.

The Mg contents of the sand, silt, and clay fractions expressed as MgO are shown in Table 6. The sand and silt fractions of samples with high exchangeable Mg have higher Mg contents than similar fractions of samples with relatively low exchangeable Mg. The sand and silt fractions may be important sources of exchangeable Mg. Two distinctly different Mg distribution patterns were noted for samples with high and low exchangeable Mg. In the former, the MgO content decreased as the particle size decreased, and in the latter the opposite was true. The MgO contents of the clay fractions of six of the eight samples are in the range of $1.00 \pm 0.35\%$, despite a wide range of exchangeable Mg.

Table 7. Correlations between the MgO content and exchangeable Mg (r_1), the MgO content and exchangeable Mg with data from the Chrome sample deleted (r_2), and the MgO content and % exchangeable Mg (r_3).

	r_1	r_2	r_3
% MgO of whole soil	.98**	.87*	.63 ns
% MgO of sand \times % sand	.93**	.86*	.57 ns
% MgO of silt \times % silt	.99**	.83*	.67 ns
% MgO of clay \times % clay	.98**	-.10 ns	.27 ns

** Significant at 1% level.

* Significant at 5% level.

ns = nonsignificant.

Exchangeable Mg and the amount of MgO in the whole soil and the sand, silt, and clay fractions are highly correlated (Table 7, r_1). This relationship is somewhat misleading because of the unique characteristics of the Chrome sample. Its high exchangeable Mg plus the high MgO content of all of its size fractions resulted in a numerically large sum of products and, consequently, an erroneously high correlation coefficient (Steel and Torrie, 1960). If the data for the Chrome sample are excluded, the exchangeable Mg and the amount of MgO in whole soil, and the sand and silt fractions are positively correlated; however, a similar correlation does not exist for the clay fraction, thereby providing additional evidence that the sand and silt fractions may be the chief sources of exchangeable Mg.

No correlation was found between % Mg saturation and the amount of Mg in the whole soil or its particle size fractions (Table 7, r_3). Exchangeable Mg expressed as meq/100 g is thereby a better indicator of the Mg content in the solid phase of these soils than the % Mg saturation.

Thus, the mineralogical source of Mg for plant growth in these soils is from the sand and silt fractions. The clay fraction, being the most active inorganic portion of the soil because of its high surface area and charged nature, is the "retainer" but not the "supplier" of the exchangeable Mg.

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(Received 20 August 1983; accepted 14 November 1984; Ms. 1279)