Bull. Environ. Contam. Toxicol. (2004) 73:448–456

DOI: 10.1007/s00128-004-0450-9

Bulletin of Environmental Contamination and Toxicology

Characterization of California Rice Field Soils Susceptible to Delayed Phytotoxicity Syndrome

P. L. TenBrook,[1] M. R. Viant,[1] D. M. Holstege,[2] J. F. Williams,[3] R. S. Tjeerdema[1]

[1] Department of Environmental Toxicology, College of Agricultural and Environmental Sciences, University of California, Davis, CA 95616-8588, USA
[2] Division of Agriculture and Natural Resources Analytical Laboratory, University of California, Davis, CA 95616, USA
[3] University of California Cooperative Extension, Central Valley Region, Sutter/Yuba Counties, 142-A Garden Highway, Yuba City, CA 95991, USA

Received: 22 January 2004/Accepted: 14 July 2004

Thiobencarb (TB) has been used for many years to control weeds in California rice culture. In some instances, rice injury has occurred due to formation of deschlorothiobencarb (DTB), the product of reductive dechlorination of TB by anaerobic bacteria. Evidence suggests that delayed phytotoxicity syndrome (DPS), which causes stunting and discoloration in rice, results from exposure to DTB (Ishikawa *et al.*, 1980). DPS was first observed in California around the same time growers discontinued use of copper-based anti-fungal seed treatments (John Williams, *pers. comm.*). To date, DPS has been observed primarily in fields on the eastern side of the Sacramento Valley. Soils in this area are from alluvial terrace or fan terrace landforms, whose surface soils are typically sandy or sandy loam (USDA, 1988, 1998). In contrast, DPS has not been observed in soils from basin landforms on the western side of the Sacramento Valley. Basin surface soils have high clay content (USDA, 1988, 1998).

Little has been done to correlate physical-chemical soil characteristics with DPS. Moon and Kuwatsuka (1984) measured some 12 characteristics in conjunction with a study of TB dechlorination in Japanese rice field soils. However, limited replication precluded statistical analysis. Here, five replicate samples from each of 8 different California rice fields (3 of which have experienced DPS and 5 of which have not) facilitated statistical comparison.

MATERIALS AND METHODS

Soils were collected in the spring of 2002 from rice fields in Northern California. Three of the soils (from the Lauppe, Mathews and Vogt farms) have experienced DPS and are from the eastern part of the Sacramento Valley on alluvial terrace or fan terrace landforms (terrace soils). Four others (from the Dennis, Maltby, Maben and Swanner farms) have never experienced DPS (Table 1). These DPS-resistant soils are from the western part of the valley and are found on basin landforms (basin soils). The eighth soil, from the Lamalfa farm, which lies on the border between the basin and terrace landforms, has never experienced DPS. All soils were sieved to 2 mm and oven-dried at 55°C for at least 48 hours prior to submittal to the UC Davis Division of Agriculture and Natural Resources Analytical Laboratory for analysis.

Correspondence to: R. S. Tjeerdema

Table 1. Soil location, series, texture and taxonomy.

Field	County	Soil Series[1]	Texture (this study)[2]	Soil Taxonomy[3]
Dennis	Colusa	Willows	Clay	fine, smectitic, thermic Sodic Endoaquerts
Lamalfa	Sutter	Stockto n	Clay Loam	fine, smectitic, thermic Xeric Epiaquerts
Lauppe	Sutter	Galt	Loam	fine, smectitic, thermic Aquic Durixererts
Maben	Glenn	Willows	Loam	fine, smectitic, thermic Sodic Endoaquerts
Maltby	Colusa	Westfan	Silty Clay Loam	fine-loamy, mixed, superactive, thermic Pachic Haploxerolls
Mathews	Yuba	San Joaquin	Loam	fine, mixed, thermic Abruptic Durixeralfs
Swanner	Glenn	Plaza	Silty Clay Loam	fine-loamy, mixed, superactive, thermic Aeric Epiaqualfs
Vogt	Placer	Exeter	Sandy Loam	fine-loamy, mixed, thermic Typic Durixeralfs

1. USDA-NRCS (1968, 1980, 1988, 1998a, 1998b).
2. Hillel (1982).
3. USDA-NRCS web site (http://ortho.ftw.nrcs.usda.gov/cgi- bin/osd/osdname.cgi).

Total nitrogen and carbon were determined by the combustion method using a Carlo-Erba model 1500 series 2 (McGeehan and Naylor, 1988). Total Kjeldahl Nitrogen (TKN) was determined by wet oxidation of soil organic matter using a micro Kjeldahl procedure with sulfuric acid and digestion catalyst. Ammonium was determined by the diffusion-conductivity technique (Bremner and Mulvaney, 1982; Isaac and Johnson, 1976; Carlson *et al.*, 1990). Nitrate (NO_3-N) and ammonium (NH_4-N) were extracted using 2.0 N KCl and measured by the diffusion-conductivity method (Carlson *et al.*, 1990). Phosphate (P) was extracted using a dilute solution of HCl containing ammonium fluoride and was analyzed by flow injection analysis (Diamond, 1995; Horneck *et al.*, 1989). Exchangeable cations (K, Na, Ca, Mg) were determined by equilibrium extraction of soil using 1 N ammonium acetate (pH 7.0) and subsequent determination by atomic absorption/emission spectrometry (Thomas, 1982). Micronutrients (Zn, Mn, Cu, Fe) were determined by equilibrium extraction of soil using diethylenetriaminepentaacetic acid (DTPA) and subsequent analysis by atomic absorption spectrometry (Lindsay and Norvell, 1978). Cation-exchange capacity (CEC) was determined by the barium saturation and calcium replacement method (Janitzky, 1986). A modified Walkley-Black method was used to determine soil organic matter (OM) by calculation from organic carbon, based on organic matter containing 58% carbon (Nelson and Sommers, 1982). Soil pH was determined in

Table 2. Results of anlaysis of standard reference materials GRIDLEY2, NORD, UCD 004, UCD 005 and FARWELL

Parameter	Result	Acceptable Range	Parameter	Result	Acceptable Range
N (total; %)	0.09	0.097 ± 0.04	Fe (ppm)	52	53 ± 16
C (total; %)	0.880	0.886 ± 0.24	Mn (ppm)	55	58 ± 14
TKN (%)	0.148	0.153 ± 0.030	Zn (ppm)	8.4	8.4 ± 2.0
NO3-N (ppm)	70	68 ± 6	PH	6.5	6.5 ± 0.4
NH4-N (ppm)	5.6	5.1 ± 2.0	EC (mmos/cm)	0.29	0.29 ± 0.04
P (ppm)	39.1	39.1 ± 8.0	CEC (meq/100g)	31.8	31.0 ± 2.0
X-K (ppm)	1019	1053 ± 80	OM (%)	2.4	2.47 ± 0.2
X-Na (ppm)	15	23 ± 10	Sand (%)	17	15 ± 10
X-Ca (meq/100g)	21.4	20.6 ± 4.0	Silt (%)	41	45 ± 10
X-Mg (meq/100g)	8.9	9.1 ± 0.8	Clay (%)	42	40 ± 10
Cu (ppm)	1.9	2.0 ± 0.6			

saturated paste using a pH meter (U.S. Salinity Laboratory Staff, 1954). Electrical conductivity, (EC) was determined in saturated paste extract using a conductivity meter (Rhoades, 1982). Percent sand, silt and clay were determined in soil suspensions using the hydrometer method (Gee and Bauder, 1982). Standard reference materials were analyzed with each sample set. Results are shown in Table 2.

Principal component analysis (PCA) was accomplished using PLS_Toolbox 3.0 (Eigenvector Research, Manson, WA) running under MATLAB 6.1 (the MathWorks, Natick, MA). PCA was used to reduce the dimensionality of the soil data from 21 variables to just 2 principal components (PC), enabling the data to be visualized in a simple two-dimensional plot. This method is unsupervised and thus soils were not designated as DPS-susceptible vs. DPS-resistant or basin vs. terrace landform. Single-factor MANOVA and ANOVA, and Tukey-Kramer post-test analyses were accomplished using NCSS 2001 (NCSS, Kaysville, UT).

RESULTS AND DISCUSSION

Analytical results are summarized in Tables 3 and 4. Fig. 1 shows the output of the PCA analysis, including a scores plot, and loads plots. A plot of PC1 vs. PC2 (Fig. 1a) clearly illustrates the separation of DPS-susceptible (Lauppe, Mathews, Vogt) versus DPS-resistant soils (Dennis, Lamalfa, Maben, Maltby, Swanner)

Table 3. Summary of measured physical-chemical characteristics for DPS-susceptible soils (mean ± se).

Parameter	Lauppe	Mathews	Vogt	Mean
N total (%)	0.11 ± 0.00	0.12 ± 0.00	0.08 ± 0.00	0.10 ± 0.00
TKN (%)	0.095 ± 0.003	0.094 ± 0.004	0.065 ± 0.010	0.084 ± 0.005
NO3-N (mg/kg)	7.0 ± 0.7	4.2 ± 0.2	4.2 ± 0.1	5.1 ± 0.4
NH4-N (mg/kg)	12.7 ± 0.8	8.1 ± 0.4	6.2 ± 0.5	9.0 ± 0.8
C total (%)	1.32 ± 0.04	1.44 ± 0.03	0.80 ± 0.02	1.19 ± 0.08
OM (%)	1.81 ± 0.02	2.16 ± 0.05	1.07 ± 0.01	1.68 ± 0.12
P (mg/kg)	4.2 ± 0.2	3.5 ± 0.2	7.9 ± 0.4	5.2 ± 0.5
Ca (meq/100g)	7.9 ± 0.0	5.5 ± 0.1	2.9 ± 0.1	5.4 ± 0.6
K (mg/kg)	97 ± 0	79 ± 1	66 ± 3	81 ± 4
Mg (meq/100g)	6.32 ± 0.07	1.44 ± 0.05	1.56 ± 0.04	3.11 ± 0.61
Na (mg/kg)	56 ± 4	26 ± 2	98 ± 5	60 ± 8
Cu (mg/kg)	8.4 ± 0.3	10.9 ± 0.2	3.0 ± 0.1	7.5 ± 0.9
Fe (mg/kg)	223 ± 5	179 ± 5	136 ± 6	179 ± 10
Mn (mg/kg)	129 ± 4	182 ± 6	59 ± 5	123 ± 14
Zn (mg/kg)	3.9 ± 0.1	6.1 ± 0.2	5.2 ± 0.1	5.1 ± 0.3
CEC (meq/100g)	15.1 ± 0.1	7.6 ± 0.2	5.5 ± 0.1	9.4 ± 1.1
EC (dS/m)	0.44 ± 0.03	0.48 ± 0.03	0.63 ± 0.03	0.52 ± 0.03
pH	4.8 ± 0.1	5.2 ± 0.0	5.3 ± 0.2	5.1 ± 0.1
Clay (%)	24 ± 0	19 ± 0	11 ± 0	18 ± 1
Sand (%)	44 ± 1	35 ± 1	60 ± 0	46 ± 3
Silt (%)	32 ± 1	46 ± 1	29 ± 1	36 ± 2

along PC1. Terrace (Lauppe, Mathews, Vogt) and basin (Dennis, Maben, Maltby, Swanner) soils are also separated along PC1. Along PC2, Lamalfa soil is further separated from the rest of the soils. Contributions of the physical-chemical parameters to this separation are shown in the loads plots (Fig 1b and 1c). Together, PC1 and PC2 account for 71.92% of the total variance in the original data set.

Measured soil characteristics, together with the groupings and separations achieved by PCA, present a few possible explanations for the localized development of DPS in the eastern Sacramento Valley. Separation along PC1 is primarily due to textural differences, with the terrace, DPS-susceptible soils being characterized by high sand and low clay content (Fig. 1a, b). DPS-resistant soils, with higher OM and clay, may simply sorb TB making it unavailable to microbes for conversion to DTB. Any DTB formed in soils with high binding capacity would be less available to rice plants.

Separation of the LaMalfa soil from the others along PC2, together with the PC2 loads plot, suggests the possibility that either total Fe, Zn or total Cu, whose loads are of the highest magnitude, may contribute to DPS resistance. All of these elements are micronutrients that may be toxic to anaerobic bacteria at high levels.

Table 4. Summary of measured physical-cemical characteristics for DPS-resistant soils (mean ± se).

Parameter	Dennis	Lamalfa	Maben	Maltby	Swanner	Mean
N total (%)	0.21± 0.00	0.17 ± 0.00	0.15 ± 0.00	0.16 ± 0.00	0.20 ± 0.00	0.18 ± 0.00
TKN (%)	0.174 ± 0.005	0.168 ± 0.007	0.129 ± 0.004	0.135 ± 0.003	0.174 ± 0.003	0.156 ± 0.005
NO3-N (mg/kg)	12.8 ± 0.2	6.4 ± 0.1	9.6 ± 0.3	9.7 ± 0.2	8.0 ± 0.3	9.3 ± 0.4
NH4-N (mg/kg)	14.8 ± 0.4	17.1 ± 0.8	7.4 ± 0.4	11.9 ± 0.4	8.6 ± 0.2	12.0 ± 0.8
C total (%)	2.51 ± 0.04	2.04 ± 0.04	1.76 ± 0.06	1.89 ± 0.03	2.19 ± 0.05	2.08 ± 0.06
OM (%)	3.16 ± 0.05	3.16 ± 0.07	2.68 ± 0.03	2.56 ± 0.04	3.09 ± 0.03	2.93 ± 0.06
P (mg/kg)	1.5 ± 0.1	9.6 ± 0.3	1.8 ± 0.1	2.0 ± 0.1	13.4 ± 0.3	5.7 ± 1.0
Ca (meq/100g)	19.2 ± 0.2	11.4 ± 0.0	8.3 ± 0.0	12.1 ± 0.1	12.7 ± 0.0	12.9 ± 0.8
K (mg/kg)	358 ± 3	148 ± 5	127 ± 3	208 ± 7	186 ± 3	205 ± 17
Mg (meq/100g)	17.6 ± 0.5	6.82 ± 0.02	6.86 ± 0.04	10.0 ± 0.1	10.9 ± 0.0	10.4 ± 0.8
Na (mg/kg)	510 ± 74	68 ± 5	79 ± 7	259 ± 3	62 ± 1	196 ± 35
Cu (mg/kg)	12.6 ± 0.7	30.1 ± 4.3	16.9 ± 3.0	23.6 ± 2.1	15.2 ± 0.5	19.7 ± 1.7
Fe (mg/kg)	108 ± 4	179 ± 2	172 ± 18	183 ± 2	225 ± 6	174 ± 8
Mn (mg/kg)	101 ± 3	136 ± 2	33 ± 2	98 ± 1	65 ± 3	87 ± 7
Zn (mg/kg)	4.7 ± 0.2	35.7 ± 1.5	3.7 ± 0.2	6.8 ± 0.9	3.0 ± 0.3	10.8 ± 2.6
CEC (meq/100g)	40.9 ± 0.6	19.3 ± 0.0	16.1 ± 0.1	24.1 ± 0.0	24.7 ± 0.1	25.0 ± 1.8
EC (dS/m)	1.46 ± 0.03	0.63 ± 0.03	0.69 ± 0.02	0.84 ± 0.03	0.46 ± 0.01	0.81 ± 0.07
pH	5.9 ± 0.2	4.8 ± 0.2	5.3 ± 0.2	5.4 ± 0.0	5.6 ± 0.0	5.4 ± 0.1
Clay (%)	55 ± 1	38 ± 1	23 ± 0	40 ± 0	34 ± 0	38 ± 2
Sand (%)	9 ± 0	23± 1	30 ± 0	16 ± 0	18 ± 0	19 ± 1
Silt (%)	36 ± 1	39 ± 0	47 ± 1	44 ± 0	48 ± 0	43 ± 1

a.

b.

c.

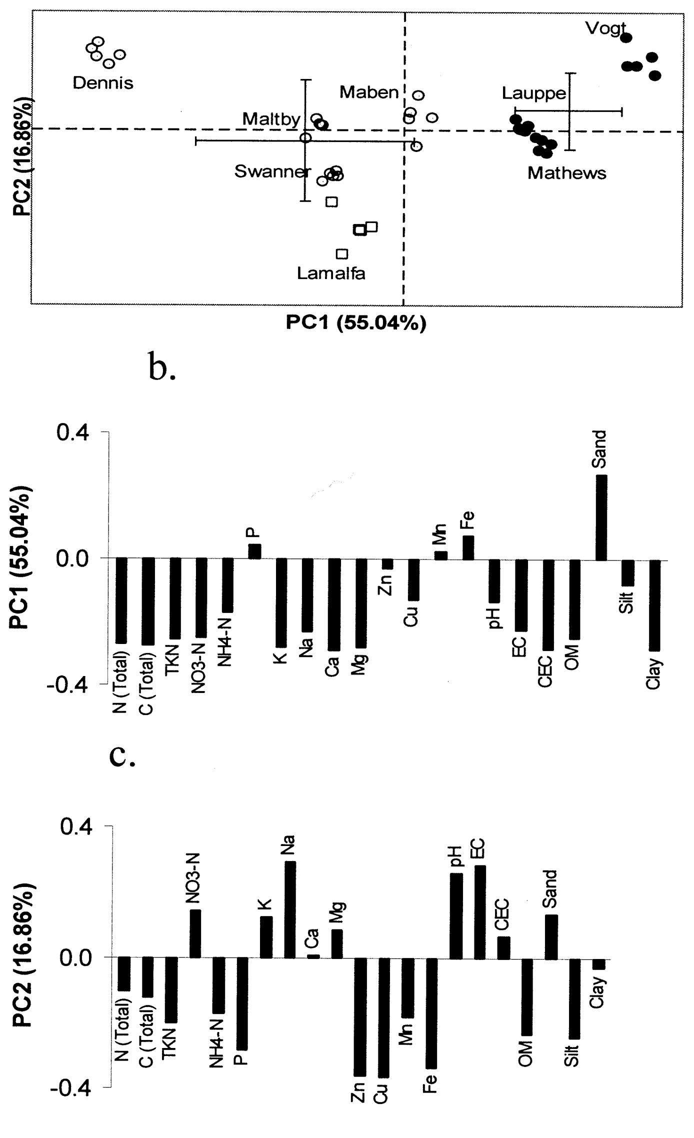

Figure 1. Results of PCA analysis; a. PCA scores plot showing classification of DPS-susceptible vs. DPS-resistant soils along PC1 with further separation of Lamalfa along PC2; O DPS-resistant basin soil; ● DPS-susceptible terrace soil; □ DPS-resistant soil of unknown origin; cross bars represent mean ± sd for DPS-susceptible and DPS-resistant groups. b. PCA loads plot for PC1; c. PCA loads plot for PC2.

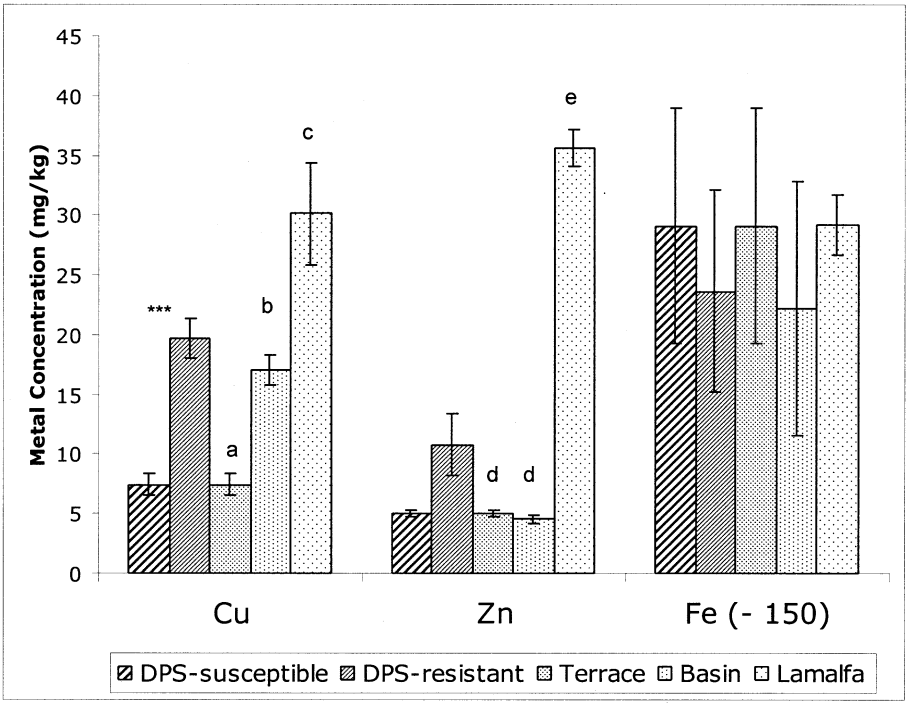

Figure 2. Cu, Zn and Fe results (mg/kg) for DPS-resistant vs. DPS-susceptible soils (*** indicates significant difference; $p \leq 0.001$), and for terrace vs. basin vs. Lamalfa soils (letters indicate groupings; $p \leq 0.001$); Fe values have been reduced by 150 mg/kg for scaling; bars represent mean $\pm$ se.

Ram *et al.* (2000) found that Fe (II) stimulated growth of sulfate-reducing and methane-producing bacteria suggesting that higher Fe levels in DPS-susceptible soils could actually enhance production of DTB. Fig. 2 indicates that Fe levels are not significantly different in DPS-resistant vs. DPS-susceptible soils, nor in terrace vs. basin vs. Lamalfa soils. Thus Fe is not likely to be a factor in differences in DPS susceptiblity. Kumar *et al.* (2001) found that sulfate-reducing bacteria, *Desulfovibrio desulfuricans*, may have some ability to detoxify Zn without suffering permanent damage. Zn toxicity in DPS-resistant soils is possible given the relatively high Zn levels (compared to those tested by Kumar *et al.*, 2001), but there were no significant differencse in Zn levels between DPS-resistant and DPS-susceptible soils ($p > 0.05$; Fig. 2) nor between terrace and basin soils ($p > 0.05$; Fig. 2). The Zn level in Lamalfa soil (Fig. 2) was significantly higher than all other soils tested ($p \leq 0.001$) and thus Zn cannot be ruled out as a possible microbial toxicant for Lamalfa soil. Cu (II) at 1.9 mg/L caused complete cessation of growth in *D. desulfuricans* (Kumar *et al.*, 2001). Levels of Cu measured in the present study are high enough to have the same effect. Cessation of bacterial growth would block the formation of DTB, thus preventing DPS.

This study has demonstrated that there are many measurable, significant differences between DPS-resistant and DPS-susceptible soils. A combination of multivariate and univariate statistical tools have led to two readily testable hypotheses: 1) that soil TB and DTB binding capacity are primarily responsible for differences in susceptibility to DPS; and 2) that Cu inhibits formation of DTB in DPS-resistant soils. If the first hypothesis is true, it may be possible to control DPS simply by reducing TB application rates to sandy soils. If the second is true, it may be possible to utilize Cu as a tool to prevent DPS in rice fields where TB is the herbicide of choice for weed control.

Acknowledgements. We thank Michael Hair for assistance with soil collection and Elizabeth Berg and Amanda Palumbo for assistance with sample preparation. Support was provided by the Donald G. Crosby Fellowship and the California Rice Research Board (Grant No.l RR02-6; Project No. RP-5).

REFERENCES

Bremner JM, Mulvaney CS (1982) Nitrogen-total. In: Page AL, Miller RH, Keeney DR (eds) Methods of Soil Analysis: Part 2. Chemical and Microbiological Properties. American Society of Agronomy Monograph Number 9. pp 595-624.

Carlson RM, Cabrera RI, Paul JL, Quick J, Evans RY (1990) Rapid direct determination of ammonium and nitrate in soil and plant tissue extracts. Commun Soil Sci Plant Anal 21:1519-1529.

Diamond D (1995) Phosphorus in soil extracts. QuikChem Method 10-115-01-1-A. Lachat Instruments, Milwaukee, WI.

Gee GW, Bauder JW (1982) Particle-size analysis. In: Klute A (ed.) Methods of Soil Analysis: Part 1. Physical and Mineralogical Methods. American Society of Agronomy Monograph Number 9. pp 383-411.

Hillel D (1982) Introduction to soil physics. Academic Press, San Diego, CA. p 29.

Horneck DA, Hart JM, Topper K, Koespell B (1989) Methods of soil analysis used in the soil testing laboratory at Oregon State University. Agric Exp Stn, Corvallis, OR, SM 89:4.

Isaac RA, Johnson WC (1976) Determination of total nitrogen in plant tissue, using a block digestor. J Assoc Off Anal Chem 59:98-100.

Ishikawa K, Shinohara R, Yagi A, Shigematsui S, Kimura I (1980) Identification of S-benzyl N,N-diethylthiocarbamate in paddy field soil applied with benthiocarb herbicide. J Pesticide Sci 5:107-109.

Janitzky P (1986) Cation exchange capacity. In: Singer MJ, Janitzky P (eds). Field and Laboratory Procedures Used in a Soil Chromosequence Study. U.S. Geological Survey Bulletin 1648. pp 21-23.

Kumar RS, Peyton BM, and Brown LT (2001) Copper-induced inhibition of growth of Desulfovibria desulfuricans G20: assessment of its toxicity and correlation with those of zinc and lead. Appl Environ Microbiol 67: 4765-4772.

Lindsay WL, Norvell WA (1978) Development of a DTPA soil test for zinc, iron,

manganese, and copper. Soil Sci Soc America J 42:421-428.
McGeehan SL, Naylor DV (1988) Automated instrumental analysis of carbon and nitrogen in plant and soil samples. Commun in Soil Sci Plant Anal 19: 493-505.
Moon HM, Kuwatsuka S (1984) Properties and conditions of soils causing the dechlorination of the herbicide benthiocarb (thiobencarb) in flooded fields. J Pesticide Sci 9: 745-754.
Nelson DW, Sommers LE (1982) Total carbon, organic carbon and organic matter. In: Page AL, Miller RH, Keeney DR (eds) Methods of Soil Analysis: Part 2. Chemical and Microbiological Properties. American Society of Agronomy Monograph Number 9. pp 539-579.
Ram SR, Singh L, Suryanarayana MVS, Alam SI (2000) Effect of iron, nickel and cobalt on bacterial activity and dynamics during anaerobic oxidation of organic matter. Water, Air Soil Pollut 117: 305-312.
Rhoades JD (1982) Soluble salts. In: Page AL, Miller RH, Keeney DR (eds) Methods of Soil Analysis: Part 2. Chemical and Microbiological Properties. American Society of Agronomy Monograph Number 9. pp 167-179.
Thomas GW (1982) Exchangeable cations. In: Page AL, Miller RH, Keeney DR (eds) Methods of Soil Analysis: Part 2. Chemical and Microbiological Properties. American Society of Agronomy Monograph Number 9. pp 159-165.
United States Department of Agriculture-National Resource Conservation Service (1968) Soil Survey of Glenn County, California.
United States Department of Agriculture-National Resource Conservation Service (1980) Soil Survey of Placer County, California.
United States Department of Agriculture-National Resource Conservation Service (1988) Soil Survey of Sutter County, California.
United States Department of Agriculture-National Resource Conservation Service (1998) Soil Survey of Colusa County, California.
United States Department of Agriculture-National Resource Conservation Service (1998) Soil Survey of Yuba County, California.
U.S. Salinity Laboratory Staff (1954) pH reading of saturated soil paste in Diagnosis and Improvement of Saline and Alkali Soils. L. A. Richards (ed.). USDA Agricultural Handbook 60. U.S. Government Printing Office, Washington, D.C. p. 102.