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Redox Potentials and Denitrification in a Cropped Potato Processing Waste Water Disposal Field[1]

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ABSTRACT

Many potato processors apply processing waste water containing nitrogen and other plant nutrients to cropped land. More than 1 metric ton of N per hectare was applied each year when waste water application averaged 230 cm/year on one field for 2 years. Less than 300 kg N/ha was recovered in the harvested grass hay, and only about 15 kg N/ha leached each season. Redox measurements made at several depths from 5 to 150 cm showed poorly aerated zones in the soil profile because of a high water table during the summer. Under these conditions, nitrate leached into these poorly aerated zones would be denitrified. Sufficient decomposable organic matter was present to provide energy for denitrification.

Additional Index Words: flood irrigation, nitrate, chemical oxygen demand.

Potato processors are disposing of processing waste water by irrigating cropped land. The processing season and waste water irrigation begins with potato harvest in the fall and continues through the winter and part of the following summer. Irrigations following the end of processing were with canal water. The waste water contains relatively low concentrations of nitrogen, phosphorus, potassium, and other nutrients mostly associated with organic matter at concentrations of 1,000 to 2,000 ppm chemical oxygen demand (COD) (7). The organic matter and part of the inorganic constituents of the waste water are removed from the water by physical, biological, and chemical processes in the soil. These processes renovate the water, which becomes relatively pure before reaching the ground water beneath the treatment fields.

Kjeldahl nitrogen, in the 230 cm of waste water applied annually, averaged approximately 50 ppm N (nitrate-N was usually < 1 ppm), so that treatment fields received a yearly average of 1,300 kg N/ha, which is much more N than grass crops remove. Consequently, nitrate pollution of the ground water is a potential problem. However, water samples obtained by vacuum extraction from the soil profile contained nitrate concentrations usually < 2 ppm N (7). Redox potential measurements were made to determine if conditions existed in the field that would stimulate denitrification and account for the low nitrates observed.

Redox potentials (Eh) have been measured in soils for many years. Quispel (6) reported methods of making these measurements and showed redox values for aerated and inundated soils. He also reported a striking relationship between Eh and pH with lower values for Eh being observed with increasing pH values. Baas Becking et al. (1) reported several thousand Eh measurements in soils, microorganism cultures, waters, etc., and also showed a striking relationship between Eh and pH. Potentials for various redox reactions were reported by Bohn (2). He indicated that at pH 7, nitrate is reduced in soils at a redox potential of + 225 mV, or lower. He stated "To remove pH variability between soils, redox potentials are often adjusted to pH 7 by a factor, usually – 59 mV/pH." A series of papers by Gilbert et al. (3), Lance et al. (4), Linebarger et al. (5), and Whisler et al. (8) described redox measurements in soil columns and recharge basins where sewage waste water was applied for ground-water recharge. They discussed equipment design for reliable measurement of redox potentials with black platinum electrodes during wetting and drying cycles. Redox potentials low enough to induce denitrification were frequently found after wetting of the soils in the recharge basins or the soil columns in the laboratory.

MATERIALS AND METHODS

A site in a potato processing waste water treatment and disposal field was instrumented for redox measurements. The soil particle size distribution and pH are described in Table 1.

Redox measurements were made with platinized platinum electrodes with a calomel reference electrode in a salt bridge using a pH meter and a strip chart recorder (Fig. 1). The electrodes were made from No. 22 platinum wire, silver soldered into a short piece of

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Table 1—Soil mechanical analyses and pH of waste water treatment soil used for redox measurements

Sampling depth	Clay	Sand	Silt	Textural class	pH
cm	%				
0- 30	12	66	22	Sandy loam	7.7
30- 60	17	49	34	Loam	8.0
60- 90	14	57	29	Loamy sand/sandy loam	8.2
90-120	17	53	30	Sandy loam	8.1
120-150	16	51	33	Loam/sandy loam	8.0
150-178	26	24	50	Silt loam/loam	--

bronze welding rod and the solder joint and welding rod were waterproofed with epoxy resin and heat-shrink tubing (8). The platinum tip was then blacked by electroplating with platinum oxide, which decreased poisoning of the electrodes in soil. The electrodes were checked against a standard solution and any that varied by more than ± 10 mV were rejected. The platinum oxide coating is fragile and extreme care must be exercised in handling and placing the electrodes in the soil to prevent rubbing the coating off the electrodes. The electrodes were buried in the soil by excavating a pit, placing three electrodes in the pit wall in undisturbed soil at each depth at 150, 120, 90, 60, 30, 15, and 5 cm, refilling the pit, and covering it with grass sod. The wires from the electrodes were routed into an instrument shelter through 2-cm metal conduit and attached to a stepping switch. The stepping switch selected the electrodes in rotation, the redox potential was measured, and the potential recorded on a strip chart recorder. The salt bridge used with the reference electrode was constructed from a 250-ml Erlenmeyer flask with a 6-mm sidearm fused near the bottom. A 6-mm inside diameter (ID) tygon tube was attached to the sidearm of the flask and a 15-bar ceramic disc was attached to the other end of the tygon tube. The reservoir was filled with saturated KCl and the tygon tube with ceramic tip inserted into moist soil near the electrodes at the 15-cm depth (5). The calomel electrode was inserted into the KCl-containing reservoir and attached to the pH meter to complete the electrical circuit. Platinum electrode potential (Ept) was measured at 4-hour intervals from 16 May to 1 Nov. 1974 with few interruptions from equipment failures. The data were taken off the strip chart with a chart reader, punched on paper tape, and read by a computer and plotted. Individual electrode readings and the means of three replicates at each depth were plotted. When the three electrodes gave similar readings, means were used. A few of the electrodes became inoperative because of waterproofing failure and went off scale. When this happened, they were removed from the averages. At least one electrode at each depth remained operational throughout the experiment.

Waste water was metered onto the disposal field by the waste field operator. Water was sampled monthly for analyses from both the effluent stream and the soil profile. Ceramic cups attached to 3.8 cm PVC tubes were inserted into the soil at depths of 15, 30, 60, 90, 120, and 150 cm and soil water was sampled by applying approximately 0.75 bar tension to the tubes and pumping the water samples from the tubes later (7). Nitrate in the water samples was determined using a nitrate specific ion electrode, total nitrogen by a Kjeldahl procedure (7).

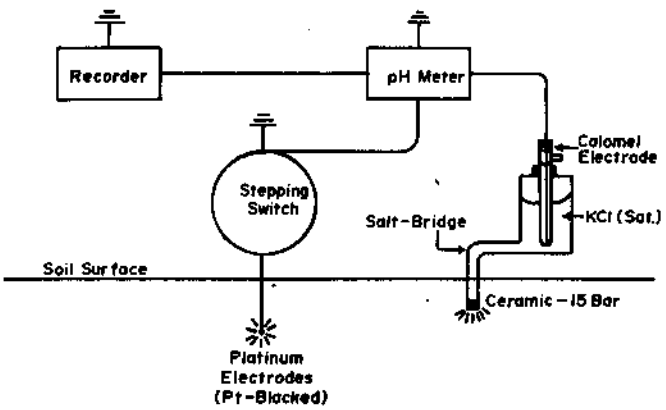

Fig. 1—Diagram of equipment used for measuring and recording redox potentials in the field.

Table 2—Waste water and nitrogen application and nitrate-N in water samples extracted from the 150-cm depth in a potato processing waste treatment field during two processing seasons

Month	Waste water applied 1972–73	Waste water applied 1973–74	Nitrogen applied† 1972–73	Nitrogen applied† 1973–74	Nitrate-N 1972–73	Nitrate-N 1973–74
	cm		kg/ha		mg/liter	
October	29	13	195	65	–	0.1
November	40	21	275	125	1.2	--
December	26	32	182	165	1.3	0
January	36	32	195	195	0.2	0.2
February	24	19	190	130	0	0.1
March	18	18	105	100	0.2	0.3
April	32	21	215	140	0.2	0.4
May	16	23	110	130	0	2.6
June	29	12	140	30	0	2.4
July	6	0	25	0	0	0.2
August	0	0	0	0	0	0
September	0	0	0	0	0	0
Total	266	201	1,635	1,080	Mean 0.3	0.7

† The organic matter in the waste water contained from 4 to 5% total nitrogen.

RESULTS AND DISCUSSION

Waste water applied to the treatment field for disposal is reported in Table 2. During the processing season, water applications ranged from 6 to 40 cm/month.

The nitrogen loading was calculated from the Kjeldahl analyses of the applied waste water (Table 2). During the processing seasons of 1972–73 and 1973–74, monthly applications of nitrogen in the waste water ranged from 25 to 275 kg N/ha with a total N application in the first season of 1,635 kg/ha, and in the second season of 1,080 kg/ha. Nitrate determined in the soil water at the 150-cm depth ranged from 0 to 2.6 ppm N during two processing seasons (Table 2) (7).

Redox measurements were made at seven soil depths but for this paper the 5-, 30-, 60-, and 120-cm depths are reported for a 5-month period in Fig. 2. The 5- and 30-cm depth electrodes were in relatively well-aerated soil most of the time. At both of these depths the addition of potato processing waste water caused sharp decreases in redox potential as shown in Fig. 2 and the recovery was relatively rapid. Rainfall was estimated from data available at weather stations a few miles away because rainfall incidents also caused the redox potential to decrease. Except for short time intervals, the redox potentials in the 5- and 30-cm depths were above the + 160-mV threshold for denitrification at pH 7.7. Grass growth was excellent with no indication of anaerobic conditions or growth problems in the root zone.

When the electrodes were installed, the water table was deeper than 320 cm. With the beginning of irrigation in the area outside the waste treatment field, the water table began to rise, and by early June was at 140 cm. By early July the water table stood at 65 to 80 cm, where it remained until October when the experiment was terminated. At the 60-cm depth, the redox potential was high early in the season with values ranging from + 300 to + 600 mV. These values are not corrected for pH but are corrected to the hydrogen electrode potential. As the water table rose, redox potentials decreased, reaching

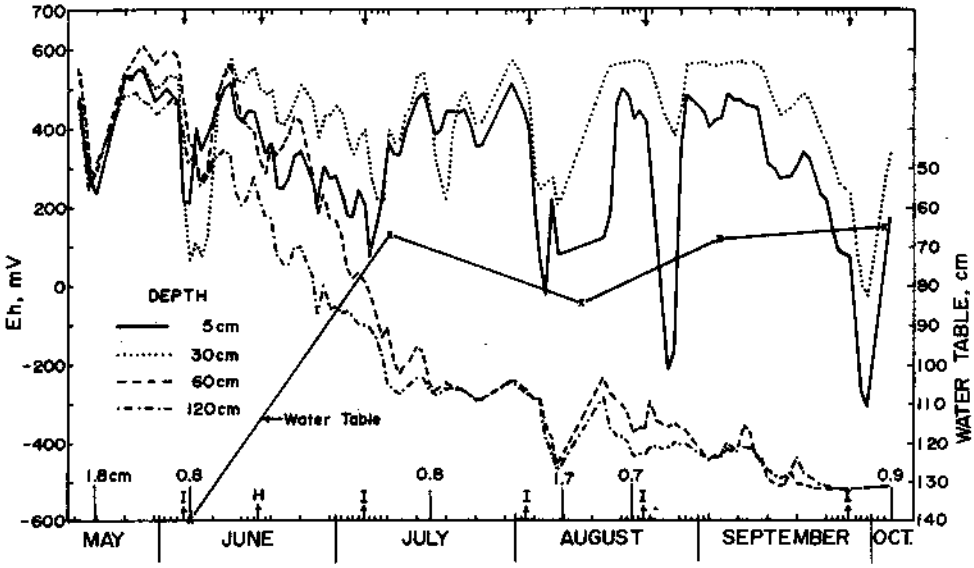

Fig. 2—Redox potentials in a potato processing waste treatment field at four depths resulting from a rising water table, irrigations (I), rainfall (1.8 cm, etc.) and at a forage harvest (H). Redox potentials are corrected to the hydrogen reference electrode.

values of approximately −400 mV. At this low redox potential, denitrification would be rapid and complete. Chemical oxygen demand in the water decreased rapidly with depth because of microbial utilization of the organic matter and soil filtration, but at 60 cm and deeper, an average of 45 mg COD/liter (7) remained after the microorganisms had utilized the soil oxygen and the nitrate oxygen. The microorganisms living in the highly reduced conditions utilized nitrate as a source of oxygen and almost quantitatively removed the nitrate, preventing groundwater pollution.

The 90- and 150-cm redox values (not shown) were similar to those shown for the 120-cm values (Fig. 2). The 15-cm redox values that are not shown in the figure are similar to the redox values at 5 and 30 cm.

During the winter months when there was no irrigation in the surrounding agricultural area, the water table lowered each year to approximately 320 cm below the soil surface. During this time, redox potentials in the soil increased, as measured in May and early June, and because of the increased redox potentials denitrification was not likely to be very rapid. During the winter months, when the water table was down the temperature was also low and nitrification was slow. The combination of these factors decreased the nitrate leaching in winter, but soil filtration removed organic matter from the waste water allowing excellent waste water cleanup throughout the year.

Redox measurements in soil are not quantitative, but they are a good indication of reducing and oxidizing conditions in the soil profile. With the low redox potentials found below 60 cm in this soil, it is reasonable to assume that the low nitrate values found in the soil water samples extracted from the 150-cm depth resulted from nitrate utilization by the grass crop and almost total denitrification of the nitrate that leached past the root zone. Leaching losses below the 150-cm depth were calculated to be approximately 15 kg N/ha as nitrate each year.

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