Mine waste contamination limits soil respiration rates: a case study using quantile regression

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Abstract

We present an application of a statistical approach, quantile regression (QR), which identifies trends in soil processes otherwise masked by spatial and temporal variability. QR identifies limits on processes and changes in the variance of a response along an environmental gradient. We quantified in situ soil respiration, pH, and heavy metal concentrations across a mine waste contamination gradient that spanned greater than an order of magnitude of metal concentrations. Respiration values were monitored at study sites over 2 years. We used QR to show that soil respiration was limited with respect to both heavy metals and pH, and that both increased metals and increased acidity constrained variation in soil respiration values. Maximum respiration values declined by 48% over the Metals Contamination Index (MCI) range and by 72% over the pH range. The use of QR avoided the necessity of discriminating between multiple sources of variation in a spatially and temporally variable system. It is often unrealistic or too time consuming and expensive to attempt to measure all of the relevant predictor variables in the field. The simpler approach offered by QR is to explore factors that limit a process, recognizing that not all of the factors contributing to a soil function will be measured. An application of this approach to the evaluation of a mine waste remediation procedure is discussed.

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1. Introduction

The large natural variability of soil processes often makes it difficult or impossible to measure the effects of a soil perturbation (i.e. pollutant) on soil function (Klironomos et al., 1999). This impediment has been identified as a major challenge facing the field of soil ecology (Arnold and Wilding, 1991; Ettema and Wardle, 2002). We have studied the response of soil respiration to mine waste (heavy metal) contamination using a statistical approach that facilitates separating trends in soil processes from natural temporal and spatial variability. Soil respiration (CO_2 efflux), a common measure of soil health (Edwards et al., 1970; Hanson et al., 2000; Illeris et al., 2003), responds to contaminants but also to temporal

changes in moisture, temperature, light conditions, and spatial variation in soil fertility (Edwards, 1975; Edwards and Ross-Todd, 1983; Dörr and Münnich, 1987; Buchmann, 2000). In addition to concentration effects, most contaminants interact with the soil physiochemical structure to varying extents to impart additional variability (Dahlin et al., 1997; Vanhala, 1999). For instance, the toxicity of heavy metals depends on soil acidity and organic matter because these factors strongly influence metal/metalloid bioavailability (Lock and Janssen, 2001).

As a result of these complex interactions, bivariate scattergrams of soil respiration values versus contaminant concentrations often display a characteristic 'wedge-shape' pattern that suggests contaminants act to limit maximum respiration values (Terrell et al., 1996). Wedge-shaped data distributions, which are relatively common in ecological studies, occur when the measured factor limits the ultimate ceiling of the data distribution but unmeasured factors are limiting over

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portions of the predictor variable range (Thomson et al., 1996; Cade et al., 1999). The development of quantile regression (QR) has filled a need for a statistical method of analyzing the upper limit of a response variable distribution (Koenker and Bassett, 1978; Koenker and D'Orey, 1987). QR analysis can be used to estimate a rate of change for the upper limit of a response variable distribution instead of the mean (Cade and Noon, 2003). Functions are defined by finding the minimum sum of asymmetrically weighted residual errors (Koenker and Bassett, 1978; Cade et al., 1999). Function lines fit portions of the data set (quantiles (τ)) such that at any point along a predictor variable distribution a given portion of the response variable data falls below the described function. This means that at any given point along an independent axis 90% of the response variable data distribution lies below a line described by $\tau = 0.90$. Applications of QR to analyze limiting ecological relationships have been reviewed (Cade et al., 1999; Cade and Noon, 2003), but to our knowledge, this method has not yet been used in soil ecology.

We measured the response of in situ soil respiration to a wide range of heavy metal concentrations in soils that have been contaminated by fluvial mine waste for about 100 years (Moore and Luoma, 1990). QR was performed on respiration data using metal concentrations as well as pH as predictor variables. Soil pH was measured because soil acidity generated from the oxidation of sulfidic ores in mine wastes affects the bioavailability of heavy metals (Cavallaro and McBride, 1980; Harter, 1983). It has also been reported that metal toxicity in soils changes over time with changes in soil physiochemical characteristics (i.e. pH) further altering metal availability and metal speciation (Lock and Janssen, 2001).

Where heavy metal concentrations and pH are highly correlated, it is not possible to separate the effects of either on soil function (Speir et al., 1999). Our preliminary investigations indicated that pH and metal concentrations were not strongly correlated at our study site, thus allowing the interaction of the separate effects of heavy metals and pH on the suppression of soil function to be studied in a field setting. Below we report separately on the limiting effects of metals and pH. We also present soil organic matter content data for selected sites because cation exchange between organic materials and heavy metals is an important

mechanism of metal stabilization and detoxification, and therefore likely plays a role in determining the observed patterns (Doelman and Haanstra, 1984; Temminghoff et al., 1997; Kinniburgh et al., 1999; Ge et al., 2002).

2. Materials and methods

2.1. Study site description

Large-scale floods in the late 1800s and early 1900s near the historic mining and smelting districts of Butte and Anaconda, Montana deposited metal-rich mine wastes over the upper Clark Fork River floodplain (Moore and Luoma, 1990). Wastes were distributed heterogeneously and subsequently re-worked by later floods and channel migration such that contaminant concentrations vary over numerous spatial scales (Helgen and Moore, 1996). These turn of the century floods raised the level of the valley floor by more than a meter, thus all of the soils at the study sites are fluvial in origin and of approximately the same age (about 100 years). Over-bank flooding has been rare since the 1950s when upstream flood control structures were emplaced that have mitigated flooding and prevented the downstream migration of sediments. Subsequently, the channel has degraded through the deposited sediments resulting in an isolated channel (Moore and Luoma, 1990). The area receives an average of 33.7 cm of rain yr^{-1}.

The primary study area was located within the riparian zone of the Grant Kohrs Ranch National Historic Site, an active cattle ranch in Deerlodge, Montana, USA. Much of the riparian zone is fenced to restrict grazing by cattle and vegetation within the fenced area includes grasslands, willow thickets, sand bars, and slickens. All study sites were vegetated with the exception of slickens sites (Table 1).

Slickens, un-vegetated low pH tailings deposits, are visually identified by the presence of surface accumulations of heavy metal salts. Slickens are of special interest because metals washed from them by storms represent a source of acute toxicity to the aquatic ecosystem and dust blown from slickens is of human health concern (Nimick and Moore, 1991). Two of the study sites reported below were located entirely in slickens, while three others were located partially in slickens (see Table 1). Six less contaminated secondary

Table 1
pH, MCI, copper, organic matter content, and respiration (range) values for slicknes sites and two sites with the highest MCI values

Site	pH	MCI	Cu (mg kg^{-1})	OM (%)	Respiration (μmol co_2 m^{-2} s^{-1})
71-slickens	4.23	1.91	1400	1.3	(0.32–1.60)
66-slickens	4.50	2.06	3300	1.7	(0.36–1.96)
35-part slickens	5.09	2.04	2800	2.9	(1.72–2.74)
53-part slickens	5.20	2.02	2700	2.7	(1.66–2.82)
60-part slickens	5.30	1.89	1200	2.2	(2.21–4.75)
56-grassland	6.25	2.29	7100	8.8	(2.41–5.82)
57-grassland	7.32	2.30	6300	4.5	(2.87–6.65)

study areas downstream of the primary sites were surveyed also to include a wider range of contamination concentrations in the data set. The downstream locations were similar in terms of variety of plant cover, but did not include slickens.

2.2. Study design

Study sites were selected using a stratified random sampling approach. Sixty soil cores taken for geochemical mapping were divided into four equal-intervals by heavy metal concentration. Sites were then randomly selected from the intervals using a random number table in order to ensure representation of a wide range of contaminant concentrations and natural variability. Respiration sampling sites were established at each selected core site and maintained throughout the study. Six measurements were taken at each sampling time in each plot. Measurements were taken around a 1 m $\times$ 2 m rectangle; the long axis oriented east–west and centered on the original core location (measurement of soil respiration is described in Section 2.5). At the secondary study areas, respiration was measured once without a priori knowledge of metal concentrations. The plots were sampled along a grid established by global positioning system, with measurements from each plot (39 data points) included in the analysis. At each plot soil respiration measurements were made at each of three points of a 30 cm equilateral triangle centered on the location of a soil core used for geochemical analysis.

Soil samples for analysis of soil acidity, organic matter, and heavy metals were collected for use in two separate studies so there were slight differences in the collection and homogenization protocols between the primary and secondary study areas, but all soils were sampled to the same depth and were analyzed by the same methods (geochemical analyses are described in Section 2.3). From each primary plot, four blocks of soil (40 cm $\times$ 40 cm $\times$ 10 cm deep) were excavated with a stainless steel shovel from the perimeter of the sampling rectangle used for the respiration measurement. The soil blocks were bulked, homogenized, air-dried, and sieved (4 mm) and three replicates removed for laboratory analysis. The mean of the three replicates was reported, as variance between these laboratory replicates was very small. At secondary study areas a 5 cm diameter soil corer (AMS, Inc., sampling kit) was used to collect a 10 cm deep core in the center of each triangle of respiration measurements. The soil core was processed as described for the primary sites, but laboratory replicates were not analyzed.

2.3. Geochemical analyses

'Total acid soluble metals' were extracted from soil samples using a method based on US EPA method 3050B. Five grams of dried, powdered, soil were extracted with 12.5 ml each of concentrated, trace-metal-grade, HNO_3 and HCl, diluted to 50 ml, refluxed for 1 h at 95 °C, shaken,

and allowed to cool and settle overnight. This method releases metals bound to soil surfaces, iron oxides and organic matter in the soil and is considered a near total digest for trace elements but not for major elements bound in silicate minerals. Metal content of acid extracts was quantified on an ICP-OES (IRIS model, Thermoelemental, Franklin, MA) by US EPA method 200.7. Methods are discussed in detail in Feris et al. (2003). Soil organic matter was analyzed by the loss on ignition method at 350 °C (Nelson and Sommers, 1982). Measurements were made on homogenized mixtures of four, 10 cm deep cores sampled from each site. pH (H_2O) was measured by standard methods (Forster, 1995).

2.4. Metals contamination index (MCI)

The ores mined in Butte, Montana contain complex mixtures of elements in a sulfidic crystal matrix. An empirical contamination index was used to assess the degree of mine waste contamination in each sample (Feris et al., 2003). The index is derived by taking the sum of the logs of As, Cd, Cu, Pb, and Zn divided by the log of the respective background values for each species using the following formula: $MCI = \Sigma((\log(Me_n)/\log(background\,Me_n)/number\,of\,metals\,included\,in\,index\,(5))$, where n represents As, Cd, Cu, Pb, and Zn. Pre-mining concentrations of the principal contaminants were calculated from profiles in soil pits to be 10 mg As kg^{-1}, less than 1 mg Cd kg^{-1}, 16 mg Cu kg^{-1}, 17 mg Pb kg^{-1}, and 49 mg Zn kg^{-1}.

2.5. Soil respiration

Soil respiration (CO_2 efflux) was quantified in situ with a portable Li-6400 (Licor Instruments, Lincoln, Nebraska, Illeris et al., 2003) infrared gas analyzer fitted with a soil chamber (Licor 6400-09). At each test plot, an 80 cm diameter soil collar was installed (3–4 cm deep) in an area that had been cleared of surface vegetation (grass was cut to the surface with scissors and then removed before measurement). The instrument circulates the air in the chamber through a soda lime CO_2 scrubber effectively lowering the chamber CO_2 concentration to a described concentration below ambient CO_2. CO_2 flux is computed based on a running average of change in CO_2 concentration with time as CO_2 refills the chamber to a described concentration above ambient concentration. This process is repeated through three cycles and the intermediate flux data are fit with a regression, which is then used to calculate soil respiration (μmol CO_2 m^{-2} s^{-1}) at ambient CO_2. The average of the six measurements taken at each site was used to report soil respiration. All sites were measured repeatedly over 2 years in 2001 and 2002.

2.6. Statistics

QR was performed using Blossom software (available at www.fort.usgs/gov/products/software/blossom.asp).

Repeated measurements at sites were included individually in the analysis. Regression quantiles from 0.1 to 0.9 at 0.1 unit intervals were selected for the analysis. Of principal interest was the highest quantile ($\tau = 0.9$) because the slope and intercept of this quantile describes a function near the upper edge of the respiration data distribution. The quantile $\tau = 0.5$ describes the rate of change of the median of the response variable similarly to least squares regression. The other quantiles provide information about the variance of the data set; differences in slopes of the quantile lines indicate unequal variance. Cade and Noon (2003) provide an introduction to the use and theory of QR.

3. Results

3.1. Contamination gradient

Respiration measurements were made over a range of metal concentrations that spanned at least one order of magnitude with respect to each toxic species. Individual metal species were each highly linearly correlated with the MCI (Table 2). Metal concentrations were high in the slickens sites (Cu concentration 204 and 87 times above background for sites 66 and 71, respectively), but metal concentrations in several circumneutral pH grassland sites (sites 56 and 57) were much higher (copper concentration was 444 and 394 times above background for these sites, respectively). Organic matter content was also more than twice as high in the grassland sites compared to the slickens sites. Geochemical variables for sites with the lowest pH values and the highest MCI values are displayed in Table 1 to demonstrate that soil acidity poorly predicts metal concentration.

3.2. Quantile regression analysis

Quantile regression results of respiration values against the MCI and pH are displayed in Tables 3 and 4. QR of MCI vs. respiration indicated the presence of a ceiling in the respiration data relating to both the MCI and pH. Regarding the MCI for $\tau = 0.9$, respiration values drop from a calculated maximum value of 10.0–5.4 μmol

Table 2
Range (mg kg^{-1}) of principal toxic contaminants and Pearson's product moment correlations of each toxic metal species with the MCI ($n=69$)

Metal	Range (mg kg^{-1})	R-MCI
As	(1.4×10^1–8.8×10^2)	0.94
Cd	(bdl[a]–1.6×10^1)	0.90
Cu	(1.1×10^2–7.1×10^3)	0.98
Pb	(3.4×10^1–1.1×10^3)	0.96
Zn	(1.7×10^2–4.1×10^3)	0.86

[a] bdl, below detection limit

Table 3
Results of regressions of [$\tau = (0.1–0.9)$] for respiration data against the contamination index

Quantile (τ)	Slope	Intercept	P
0.9	−3.80	14.16	**0.025**
0.8	−1.94	9.37	0.105
0.7	−1.00	6.75	0.055
0.6	−1.28	6.68	0.089
0.5	−1.28	6.08	**0.037**
0.4	−1.03	5.20	**0.038**
0.3	−1.20	5.12	0.245
0.2	−1.31	4.83	0.487
0.1	−0.35	2.42	0.396

Shown are the slope and y-intercept for each regression line followed by the P for the asymptotic X-square approximation. Significant P values are in bold ($\alpha = 0.05$).

$CO_2 \ m^{-2} \ s^{-1}$, or 4.6 μmol $CO_2 \ m^{-2} \ s^{-1}$ over the MCI range ($1.09 < MCI < 2.30$) (Fig. 1). The slope of the line described by $\tau = 0.9$ was three times greater than for $\tau = 0.5$ (Table 3). This indicates that the maximum function is more responsive to metals contamination than median function. The increasing slopes of the quantile lines indicate that variance is unequal with respect to the MCI.

With respect to the $\tau = 0.9$ quantile line for the pH range ($4.23 < pH < 8.25$), respiration values drop from the calculated maximum of 8.6 μmol $CO_2 \ m^{-2} \ s^{-1}$ to a minimum of 2.4 μmol $CO_2 \ m^{-2} \ s^{-1}$ or 6.2 μmol $CO_2 \ m^{-2} \ s^{-1}$ over the pH range (Fig. 2). As with the previous regression of MCI vs. respiration, the slopes of the lines described by the upper quantiles were greater than for the lower quantiles, again indicating unequal variance (Table 4).

3.3. Explanatory power of MCI vs. pH

The $\tau = 0.9$ quantile line for pH provides an explanatory relationship over a wider response variable range (6.2 respiration units) than does the $\tau = 0.9$ quantile line for MCI (4.6 respiration units). Fig. 3 shows the relationship between MCI and pH. Low pH sites (pH < 6.5) were found only where metals concentrations were elevated,

Table 4
Results of regressions of [$\tau = (0.1–0.9)$] for respiration data against soil pH

Quantile (τ)	Slope	Intercept	P
0.9	1.54	−4.11	**0.012**
0.8	1.38	−3.94	**0.002**
0.7	1.12	−2.86	**<0.001**
0.6	0.97	−2.33	**<0.001**
0.5	0.84	−2.03	**<0.001**
0.4	0.86	−2.50	**<0.001**
0.3	0.71	−1.85	**<0.001**
0.2	0.60	−1.52	**<0.001**
0.1	0.58	−2.01	**<0.001**

Shown are the slope and y-intercept for each regression line followed by the P for the asymptotic X-square approximation of the quantile rankscore test. Significant P values are in bold ($\alpha = 0.05$).
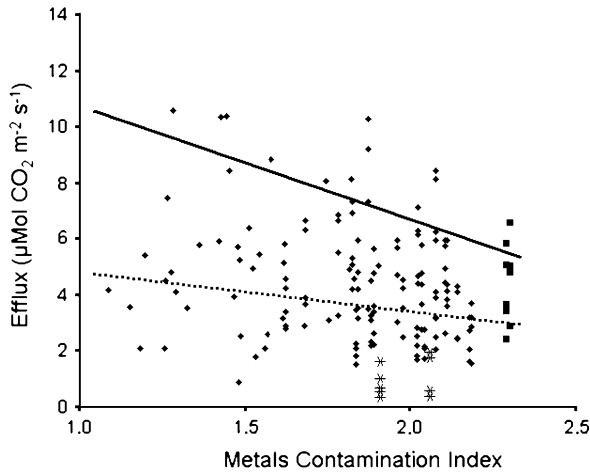
Fig. 1. Regression quantile analysis of respiration data against the contamination index ($n = 187$). The solid line represents the $\tau = 0.9$ quantile. The dashed line represents the $\tau = 0.5$ (or median) quantile. Respiration values acquired from slickens sites are represented by asterisks (*). Values acquired from the two most highly metal contaminated sites are represented by filled squares (■).

however elevated metals concentrations did not necessarily indicate low pH. The average respiration value in sites with low pH (below 6.5) was 2.58 μmol CO_2 m^{-2} s^{-1} ($n = 57$; stdev 1.35). The average respiration value for sites having a pH above 6.5 was 4.64 μmol CO_2 m^{-2} s^{-1} ($n = 130$; SD 2.04). At the slickens sites where the lowest respiration and pH values were found (respiration range 0.32–1.96 μmol CO_2 m^{-2} s^{-1}, pH 4.2 and 4.5) MCI values were not especially high (1.91 and 2.06) and high respiration values were found in sites with higher MCI values than those found in the slickens (Table 2). This pattern suggests that soil acidity rather than metals concentration exerts a greater control on soil respiration.
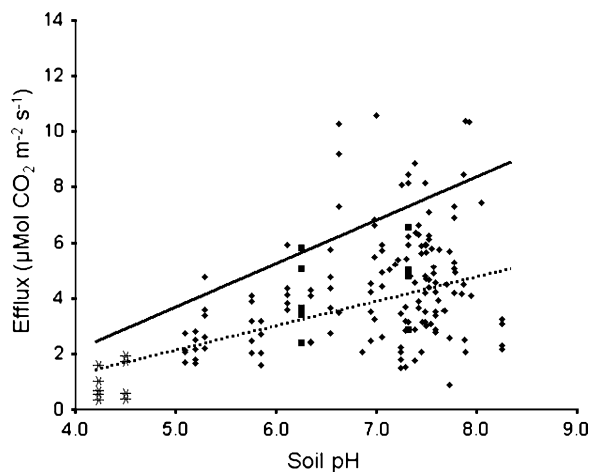

Fig. 2. Regression quantile analysis of respiration data against soil pH ($n = 187$). Solid lines represent the $\tau = 0.9$ quantile. Dashed lines represent the $\tau = 0.5$ (or median) quantile. Respiration values acquired from slickens sites are represented by asterisks (*). Values acquired from highly contaminated grassland sites are represented by filled squares (■).
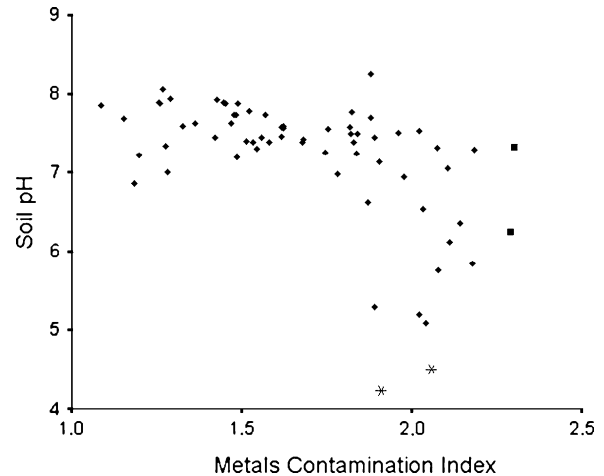

Fig. 3. Scattergram of soil pH against MCI. MCI and pH are correlated (Spearman's rho = -0.563, $p < 0.001$); as a result of their being low pH sites only where metal concentrations are elevated. However, no direct causal relationship is indicated, as there are also high pH sites where metals are elevated. The two slickens sites are represented by asterisks (*) and the two sites most highly contaminated with metals are represented by filled squares (■).

4. Discussion

4.1. The utility of quantile regression

We used QR to show that soil respiration was limited with respect to heavy metals and pH along a contamination gradient and that both increased metals and increased acidity constrained variation in soil respiration values. Quantile regression was a constructive alternative to least squares regression (LSR) because responses could not be ascribed to a single predictor variable and there was unequal variance in the response variable with respect to the independent variable, thus compromising the assumptions of standard LSR (Kaiser et al., 1994). Multiple linear regression was not an appropriate alternative to QR, because of multi-collinearity in the set of predictor variables (e.g. individual metal concentrations). Furthermore, multiple linear regression could not readily account for interactions among predictor variables.

QR may prove to be a useful approach in detecting and describing trends in soil processes along gradients. Many soil processes are studied along gradients, examples include; liter decomposition rates (Belyea, 1996), nutrient availabilities (Zhu and Carreiro, 2004), and microbial community response to toxins or the physical environment (Aceves, et al., 1999; Bååth and Anderson, 2003; Feris et al., 2003; Lee and Jose, 2003; Sardinha et al., 2003). It is common practice to analyze wedge-shaped data distributions by LSR even when the assumptions of LSR are violated (Thomson et al., 1996), and even though this estimate of the mean function ignores bias introduced by unmeasured factors (Cade et al., 1999).
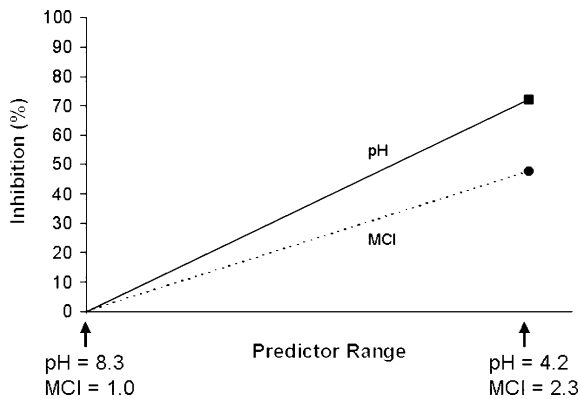
Fig. 4. Depression of soil respiration over the ranges of the two predictor variables MCI (dashed line) and pH (solid line). Maximum respiration values decline by 48% over the MCI range (filled circle) and by 72% over the pH range (filled square).

4.2. Estimating inhibition of soil function

Applying QR to a highly variable data set such as that described above allowed a simple estimation of the inhibition of soil function with respect to metals contamination and pH. The maximum quantile line for the MCI represents the estimated repression of the maximum soil function due to the metals contamination. In Fig. 4, a soil functional inhibition estimate is calculated based on the regression lines of the 0.9 quantile of the MCI range ($1.0 < MCI < 2.3$). The y value at $MCI = 1$ is taken to indicate an unimpaired soil (0% inhibition) and the remaining y values are expressed in terms of the percentage of maximum soil function that would be expected to be lost at a given MCI value (dashed line). The solid line represents the same estimate calculated for pH over the pH range ($8.3 > pH > 4.2$). Maximum respiration values decline by 48% over the MCI range and by 72% over the pH range.

4.3. Application to remediation of soil function in low pH slickens

The estimates of limiting effects were used to provide insight as to the potential effect of a current remediation strategy on rehabilitating areas of slickens. The negative effects of acidity and metals on soil processes have been well characterized (Fritze, 1991; Bååth and Arnebrant, 1994; Vanhala, 1999). At low pH values (below 6.5) toxic metal ions would be expected to be in solution and bioavailable regardless of the contaminant concentration (Nimick and Moore, 1991). In high metals sites where pH is circumneutral and significant amounts of organic matter are present, the metals would be expected to be less bioavailable (Doelman and Haanstra, 1984; Kinniburgh et al., 1999). Reducing the bioavailability of metals

through the neutralization of slickens has thus been recommended as an economical treatment option for areas of slickens (Davis et al., 1999). A working estimate of functional inhibition makes it possible to predict the effects that remediation efforts based on pH neutralization would have on restoring soil function in the slickens.

At a given site it would be expected that alleviation of a factor limiting soil function would lead to an increase in function to a point where it becomes limited by some other factor. Here, where we have shown that respiration is limited with respect to both pH and MCI, we would expect that measures to remediate pH would relieve the pH limitation, but that MCI limitation would remain. At the slickens sites, where pH values were pH 4.2 and 4.5, MCI values were 1.91 and 2.06 (Table 2). Measures that would neutralize pH, potentially through organic matter additions or liming (Davis et al., 1999; Kiikkilae et al., 2001), may therefore be expected to relieve the limiting effect of pH on soil function, but would not relieve the limiting effect of the metals. According to the MCI inhibition line calculated for $\tau = 0.9$ this corresponds to 33 and 40% inhibition for the two sites, respectively, or that soil respiration would be restored to 60 and 66% of its potential maximum through pH treatment.

4.4. Conclusions

Quantification of heavy metals contaminant effects on soil ecosystem concentration processes necessitates the separation of natural spatiotemporal variation in process rates from variation that can be ascribed to the contaminants. A myriad of factors such as organic matter, structure, parent material, biota, and pH affect soil function. QR was valuable because it avoided the necessity of discriminating between multiple sources of variation. Instead, QR identifies limits on processes and changes in the variance of a response along a gradient, working with instead of against natural variability to elucidate trends. It is often unrealistic or too time consuming and expensive to attempt to measure all of the relevant predictor variables. A simpler approach is to explore factors that limit the maximum soil function, recognizing that not all of the factors contributing to soil function will be measured.

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