Redox potential as a soil health indicator – how does it compare to existing methods?

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Abstract

Soil health is the capability of soil to provide ecosystem services. These can be quantified through multiple separate indicators (N-mineralization, water infiltration, aggregate stability, etc.) or by a single proxy that integrates many soil processes. Two commonly used integrative measurements are the soil 24h-respiration test (CO2burst) and the visual evaluation of soil structure (VESS). Both are fast, but capture only a part of whole phenomenon of soil health. Soil redox potential is a promising soil and plant health indicator. The redox potential is controlled by soil chemical oxidation-reduction reactions and therefore integrates several processes. However, this method has been tested only on a few soils. In this study, we evaluated redox by comparing it with other established soil health indicators on 35 fields in Finland. Based on the results, redox correlated well with soil biological activity, structure, and texture. Soils with good structure had an oxidized redox status. A low redox state was connected to high biological activity. The carbon farming practices resulted in lower oxidation. A combination of redox and pH could be used to classify soils. The analysis supports the use of redox as a soil health indicator, but further research is needed in identifying the processes and properties the redox is an indicator for.

Introduction

The capability of soil to provide ecosystem services through four soil functions: carbon cycle, nutrient cycle, pest regulation and soil structure maintenance (Kibblewhite et al., 2008) is defined as "soil health." It is closely related to soil quality and productivity, but is more integrative and focused on soil biology (Lal, 2016). Soil biology is a challenging phenomenon to map through indicators (Wade et al., 2022), especially compared to well-established methods for chemical (Gibbons et al., 2014) and physical (Hartge and Horn, 2009) soil quantification.

Biological soil health can be quantified through different approaches. Functional indicators focus on ecosystem processes (e.g. carbon metabolism: basal respiration, CO_2-burst test, aerobic and anaerobic incubations). Compositional indicators measure key species groups (e.g. microbial diversity and biomass, nematode and earthworm counts) (Weil and Brady, 2016). One of the most commonly used functional indicators is the 24 h CO_2 respiration rewetting soil test for biological activity (Franzluebbers et al., 1996). In this method, a soil sample is dried and rewetted, which results in a flush of CO_2 ("CO_2burst"). It responds to management and correlates with important soil processes such as nitrogen mineralization, making it a popular tool for managing soil health (Haney et al., 2018). Initially described in 1950's (Birch, 1958), but research is still ongoing on the mechanisms of the burst (Barnard et al., 2020, p. 2; Hicks et al., 2022). Physical, chemical and biological soil processes control the flush of CO_2 (Barnard et al., 2020), therefore it is an integrative indicator for many soil properties.

Soil redox potential status is another integrative indicator of soil properties and processes. The redox potential of soil is the product of oxidation-reduction reactions. It measures the general availability of electrons, or the relative difference between oxidation (loss of electrons) and reduction (gain of electrons) (Zhang and Furman, 2021). In soils, one of the main reactions is the oxidation of organic matter ($(CH_2O)_n$), which supplies electrons, allowing the reduction of other compounds and producing CO_2 and water, for example:

$$4Fe(OH)_3 + 12H^+ + 4e^- \rightarrow 4Fe^{2+} + 12H_2O\text{(reduction)}$$
$$CH_2O + H_2O \rightarrow CO_2 + 4H^+ + 4e^-\text{(oxidation)}$$
$$4Fe(OH)_3 + CH_2O + 8H^+ \rightarrow 4Fe^{2+} + CO_2 + 11H_2O$$

(eq 1.)

In fully aerobic soils, oxygen serves as the electron acceptor, resulting in the production of CO_2 and H_2O. The redox potential is controlled by the rates of reduction and oxidation processes in soil and is connected to soil respiration, for example in rewetted agricultural soils, where redox is a strongly correlated predictor of CO_2 flux (Bartolucci et al., 2021). Based on this, redox could be a promising indicator for soil carbon cycle (labile carbon pools) and structure (oxygen availability), two key components of soil health (Kibblewhite et al., 2008).

Redox can also serve as an indicator for nutrient availability and pest regulation (Husson, 2013). Redox can be thought of as a parallel to pH, which measures proton availability, as redox (Eh) measures electron availability. And as pH, redox can influence nutrient availability considerably. Redox is managed to avoid toxic As and Cd buildup in rice paddies (Evans et al., 2021) and to improve Mn supply (Husson, 2013; Zhang and Furman, 2021). A key challenge for using redox as an indicator is however, that is changes rapidly with soil water and oxygen conditions (Zhang and Furman, 2021). Husson et al. proposed to use redox potential as a soil test from dried soil samples. (Husson et al., 2016). In the test, dried soil would be rewetted and the redox would be measured for 2 min. In theory, the test is similar to the CO_2 burst test, but taking only 2 min instead of 24 h. It therefore has great potential for a high-throughput indicator for soil health, but it should be tested in different soils and under different management to see how it correlates with established soil tests and how it reacts to management.

To evaluate redox as a soil biological health indicator, we compared it to existing measures of soil health (CO_2burst, visual evaluation of soil structure VESS and soil organic matter). We used 18 sites from an ongoing carbon sequestration experiment (Carbon Action, 2019-; (Mattila et al., 2022)), where each site had a carbon farming trial plot and a control plot. We measured CO_2burst and redox from dried and rewetted samples and compared the results with each other and other analyses of soil properties. The results were used to classify soils and to evaluate the change in soil health from three years of carbon farming. This allowed the evaluation of the redox potential as an indicator of soil health.

Materials and methods

The materials for the study were soils sampled from the Carbon Action experiment (Mattila et al., 2022) intensive observation set (Mattila, 2020), where 20 farms test carbon sequestration (cover crops, compost, grazing practices, intercrop leys and subsoiling). The experiment started in 2019 and the samples were collected in July 2021. Each farm had a split field, where one side had carbon farming practices implemented and the other was held as a continued-normal-practice control. The samples were collected from 3 GPS located points on each field from a 10 m radius from the center of the point with a 16 mm soil corer from a depth of 0-17 cm. Each field had 30 cores collected, which were pooled, dried at room temperature (fan assisted) and gently sieved through a 5 mm sieve. As the soil sieving and milling can influence the results, all soil sample processing was done following established guidelines (Franzluebbers and Haney, 2018). (Due to an unfortunate laboratory accident, 5 samples were lost during processing, resulting in an overall sample amount of n=35.) The sampled soils covered a large range of soil texture and organic matter: the median clay content was 35% (4-63%) and the OM 6.8 % (2.6-15.5%). The farming systems covered annual cropping, grass in rotation and perennial pastures.

For CO_2 burst analysis, the dry samples were rewetted to approximately 50 % pore space (i.e. 30 ml of soil and 9 ml of water; Woodsend lab manual). The sample was placed in a 475 ml container and sealed with a CO_2 measurement cap fitted with a datalogger (Woodsend IRTH). The CO_2 concentration was measured for 24 h and the increase in CO_2 level over time was converted to mg CO_2-C/kg^{3}soil by multiplying with container air space, dividing by sample mass and converting to mass units using the ideal gas law.

For the redox analysis, soils were also rewetted to 50% pore space (Husson et al., 2016). The Redox was measured with an Extech RE300 Exstik Platinum oxidation-reduction-potential sensor (platinum electrode, silver/chloride reference electrode). The flat end ORP sensor was pressed to the moist soil sample and allowed to stabilize 1-3 minutes, until the ORP reading changed only slowly. Three repeated measurements were made of the same sample and the average value was used. The sample pH was measured with a Horiba LAqua Twin pH meter, using 1:1 ratio of distilled water:soil. The ORP reading was converted to Eh (mV) by adding the reference electrode voltage (200 mV) and pH corrected to a relative hydrogen score by the equation $rH_2 = Eh/30 + 2$ pH. For interpretation, the readings were compared to suggested norms for "healthy" soils (Husson, 2013).

For additional interpretation, the soil samples were classified according to organic matter content, soil clay content, soil structure (VESS (Ball and Munkholm, 2015)) and type of crop (perennial, annual). These were collected and published as ongoing monitoring in the Carbon Action experiment (Mattila and Girz, 2021).

The statistical analysis was done in R programming language (R Core team, 2022). Correlations between measured variables were calculated with Pearson's correlation. Significance between the differences in two groups was tested with Mann-Whitney U-test (Wilcoxon). The effect size of carbon farming practices was tested by fitting a linear model to the data, using each farm as a blocking factor.

Results and discussion

Redox potential can be used to classify soils and monitor management effects

The redox potential Eh of soils ranged from reduced to slightly oxidized +340 to +560 mV and from acidic pH 5.8 to slightly alkaline pH 7.6 (Figure 1). Most of the sampled soils were in a region of the Eh/pH space, which is considered favorable for plant growth (Husson, 2013). Compared with the favorable region, one soil was too reduced and 10 samples were too oxidized. The reduced sample was a seasonally waterlogged silty clay loam soil, the oxidized alkaline sample was a low organic matter sandy loam soil. The acidic and oxidized soils were a more complex set of soils with either a very high OM level (>12%) or a very high clay level (>60%). The two soils in the "optimum" range were silty clays with an OM 6% and a history of grass cultivation and horse manure application. Compared to the four soils evaluated in Husson et al. (2016), the soils in this study were more reduced (530 vs. 470 mV), which could be expected on the basis of differences in climate (warm vs. cool temperate) and organic matter level (2% vs. 8%).

The addition of carbon compounds to the soil through carbon farming decreased Eh (Figure 1 and Figure 2). This supports the findings of Husson et al. (2016) where conservation agriculture (residue retention and minimum tillage) reduced Eh by 10-25 mV. In this study, the reduction was on average -20 mV ($p < 0.05$; 95% range -94-+26 mV). The largest reductions (-90 mV) were on sites that had compost soil amendments applied. This would suggest that soil redox potential reacts to the addition of readily decomposable organic matter. Overall, the redox potential test on dried and rewetted soils could differentiate soils based on their

OM and clay status, but it also reacted on short-term changes to soil management. Poor soil condition (waterlogging, OM or tillage) was reflected by the placement in the Eh/pH chart. This reactivity to soil conditions and management makes redox a promising indicator of soil health.

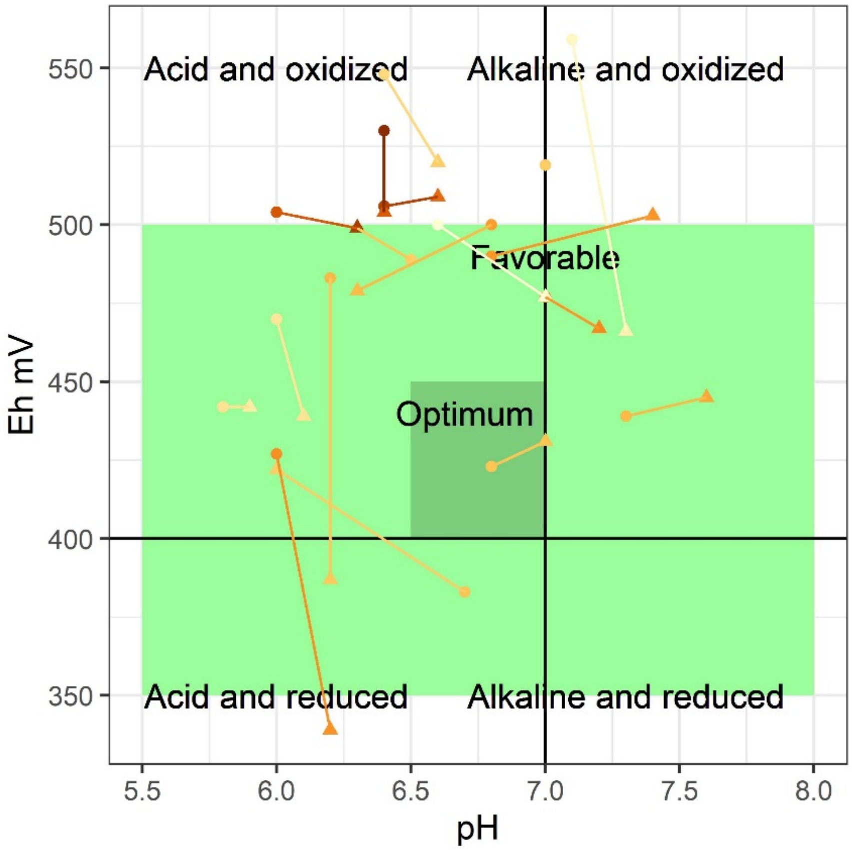

Figure 1. Tested soils in a pH/Eh Pourbaix plot. Triangles= carbon farming plots, rounds = control plots. Color = OM content. Favorable and optimum regions from (Husson et al., 2016).

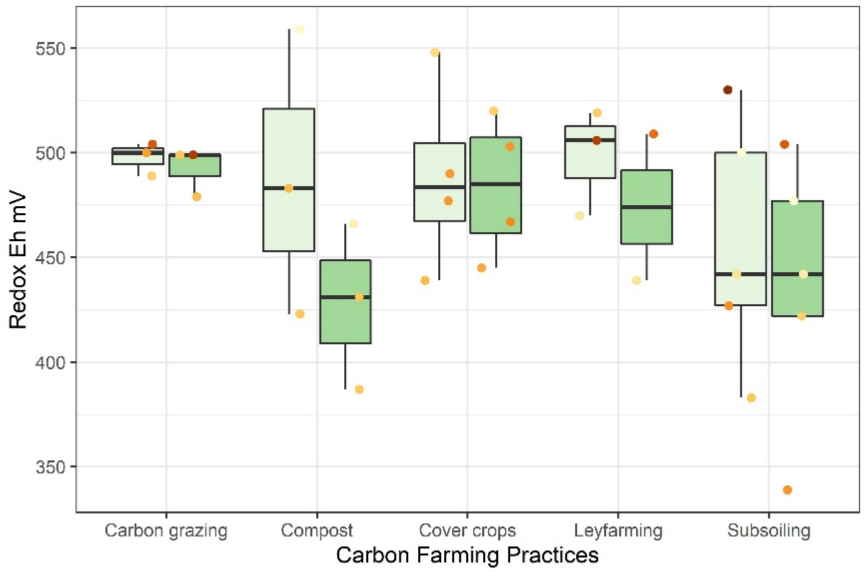

Figure 2. The effect of carbon farming practices on soil redox potential. (Light shade= control plot; dark shade = carbon farming plot. Samples taken in July 2021, on the third year of the experiment.)

Redox complements, but does not replace other measures of soil health

The Eh correlated significantly with CO_2burst ($p<0.001$) and explained 36% of variability (R^2=0.36). In contrast, the correlations of pH ($p=0.06$) and clay ($p=0.80$) with CO_2burst were nonsignificant. Organic matter (OM) by itself was not-significant ($p > 0.10$; $R^2 = 0.08$), but when included in a linear regression with Eh, it was significant ($p < 0.001$) and together the two variables explained 50% of the variability in CO_2burst. This supports earlier findings, that the CO_2burst is more related to the availability and quality of organic matter than the quantity (Haney et al., 2012). Redox potential explains the variation in biological activity better than organic matter or texture. It may be, that this is due to the rewetting experiment conditions, where labile carbon compounds are oxidized (eq. 1), and that the redox is not directly related to the biological activity, but to the physicochemical factors controlling CO_2 flush from rewetting (Barnard et al., 2020). In any case, when combined with soil OM, the redox potential can explain the majority of the biological activity related to the carbon cycle, making it a promising soil health indicator or a rapid proxy for respiration tests.

However, the redox should not be used to predict CO_2burst. Even when including the pH correction to Eh (i.e. hydrogen potential rH_2), redox explained only 35% of the variability (R^2=0.35) (Figure 3). Reduced conditions co-existed with high biological activity: of the five soils with high biological activity, four had reduced redox status ($rH_2 < 28$). The one exception was a very high OM level (14%) pasture site. Thus, reduced conditions were a requisite for high biological activity. However, as also three reduced soils had only moderate biological activity, reduced conditions do not guarantee a high biological activity. Likewise, the CO_2 burst was highly variable under oxidized conditions, suggesting that redox cannot replace CO_2 burst as a biological soil health test.

The trend of oxidized redox and low biological activity in the lab tests is in direct contrast with field observations, where high oxidation correlates with high respiration (Bartolucci et al., 2021). However, in field conditions, the redox was changing over time (with soil drying) and in our observations the redox changed between samples in an artificial drying-rewetting experiment. In the field experiments, oxygen limited respiration on a rewetted wetland. In the laboratory test, respiration was more likely limited by carbon compound availability or the amount of microbial biomass, similar to the CO_2burst (Barnard et al., 2020). In any case, field experiments on drained, low organic matter soils would be needed to estimate how well the lab test redox results correlate with in-field CO_2 burst events.

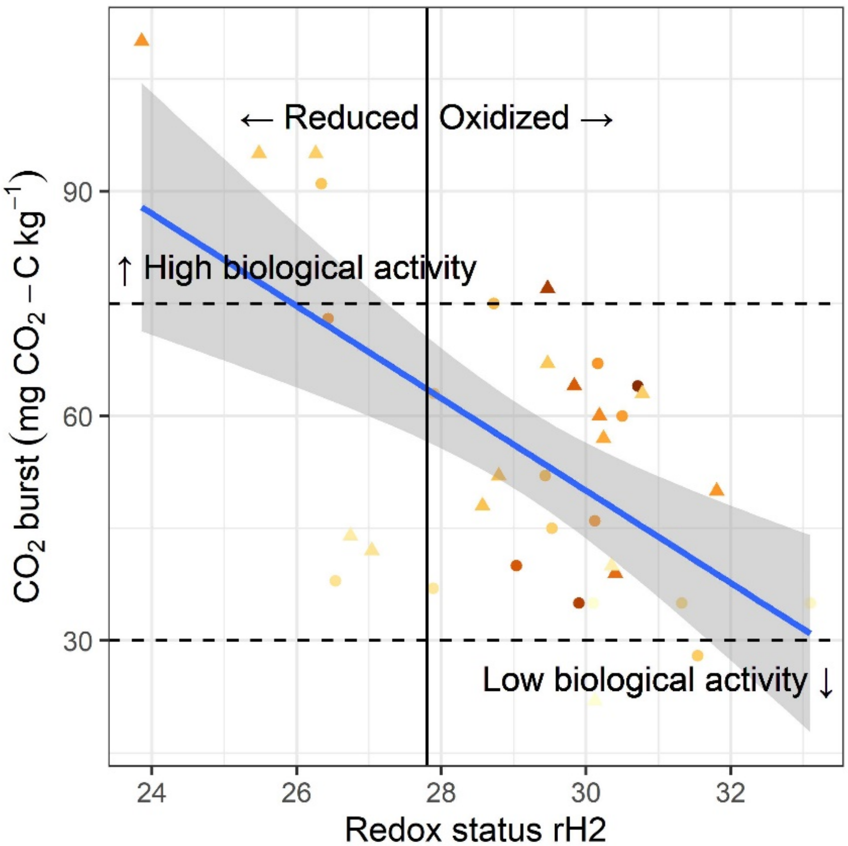

Figure 3. Soil biological activity vs. redox state (rH2). The colors represent OM concentration and the shape is the treatment vs. control group.

Redox potential tracked changes in soil management (Figure 2; Eh -20 mV p = 0.048*), but the difference between management practices in CO_2burst was not significant (increase of 8 mg-C/kg, p = 0.06). CO_2 burst is considered as an intermediate indicator, changing over a period of a few years (Weil and Brady, 2016). In this test, three years was not enough to result in a detectable difference in CO_2burst. It may be, that the CO_2 burst integrates more variables (Barnard et al., 2020) than the redox and that some variables have developed in opposite directions, confounding the effect of management. However, CO_2burst was found to correlate with texture but not with structure, while redox correlated with both texture and structure (Table 1), suggesting that redox can integrate soil properties that change very rapidly, such as structure (Weil and Brady, 2016).

Soil structure had a marked effect on the redox potential (Figure 4) (VESS vs. rH2, R^2=0.35, p=0.04). In soils with good structure (VESS < 2.75) the redox status was more oxidized (rH_2 30.5) compared to soils with poor structure (VESS >3.25; rH_2 28.6) (Figure 4). Even in poor structure soils, most soils were classified as oxidized, indicating that redox cannot be used as a replacement for the soil structure evaluation, but that good structure is often found together with oxidized soils. OM correlated with VESS (R^2=0.42): soils with high OM were often classified as having a good structure (Figure 4).

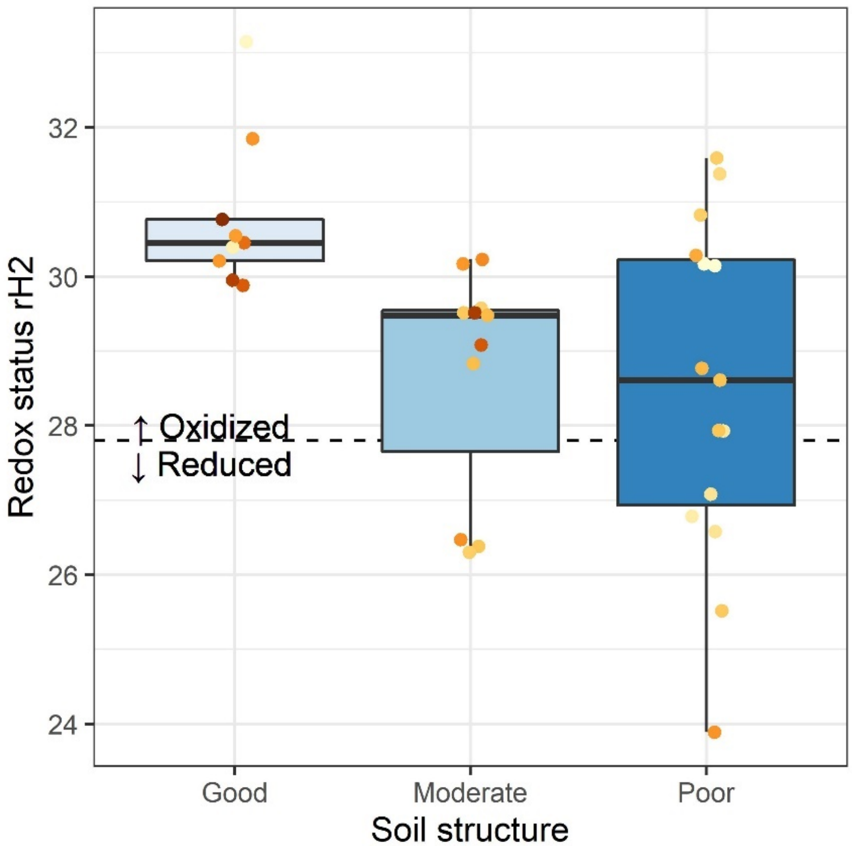

Figure 4. The redox status (rH2) of soils with a good structure (VESS) was more oxidized than for soils with a poor structure. The colors on the points describe the soil OM concentration.

Overall, redox can be an important additional measure for soil health quantification (Table 1). It correlates with soil structure (VESS) and biological activity (CO_2burst). As it does not correlate with OM, it is a measure of the active organic matter pool, possibly similar to water soluble organic carbon (Haney et al., 2012). However, especially the pH-corrected rH_2 score correlates with soil clay content, so the interpretation should be based on soil texture. Although redox correlates with other soil health indicators, it is not a replacement for those. For example, soils with a good structure have a high redox (Figure 4), but also some poor structure soils may also have similar values. Soils with high biological activity have low redox potentials (Figure 3), but a low redox potential can also be found in a soil with moderate biological activity.

As the redox potential changes more rapidly with management than CO_2burst (Figure 2), it is a promising indicator to track management-induced changes in soil health. In this application, it could also be used to classify soils based on their Eh and pH (Figure 1). These results supported the earlier findings on the use of soil redox potential to classify soils and to follow their change due to management (Husson, 2013; Husson et al., 2016). As the earlier studies were conducted in a warm temperate climate with lower OM and clay content, similar findings in high OM and clay environments support continuing investigations into the role of redox in quantifying soil health.

A major challenge in interpreting the redox results is the integrative nature of the redox potential. It is a combined effect of all ongoing soil oxidation and reduction reactions, which defines the redox potential. It may be hypothesized that the organic matter decomposition would drive the potential in a drying-rewetting test, but in this study, soil texture was found to correlate with redox potential, suggesting that other reactions than organic matter related were also driving the potential. Further studies on the interpretation of redox in different textures and farming systems would be needed to make it an applicable tool for managing soils.

Table 1. Correlation between soil redox status (Eh and pH corrected rH2) and commonly used soil health indicators (Structure VESS; CO2burst; Organic matter; and Clay content) (Weil and Brady, 2016).

				Rapid	-Change	-	Permanent
		Eh	**rH2**	**VESS**	**CO_2-burst**	**OM**	**Clay**
Redox	**Eh**	**1.00**	0.88				
Hydrogen score	**rH2**	0.88**	**1.00**				
Structure	**VESS**	-0.35*	-0.41*	**1.00**			
Biol.activity	**CO_2burst**	-0.60**	-0.59**	0.01	**1.00**		
Organic matter	**OM**	0.16	0.09	-0.42*	0.28	**1.00**	
Texture	**Clay**	-0.31	-0.34*	0.48**	0.47**	-0.11	**1.00**

Conclusions

Redox presents a rapid measurement of soil oxidative-reductive status. When applied to a simplified soil drying-rewetting test, it could be used to classify soils into oxidized and reduced. In addition, the redox status correlated with CO_2burst, indicating that it can quantify the amount of readily available substrates for microbial activity. When combined with organic matter concentration, it could explain most of the variability in measured CO_2burst results. It also correlated with soil structure and texture, making it a promising general indicator of soil conditions. Simultaneously, the correlation with soil texture and structure and the fact that it is an outcome of several reduction-oxidation reactions, makes interpretation of redox challenging. Currently, it can be used as an index for soil health, but more studies on the mechanisms of redox and it's change over time could reveal, what are the soil processes it is an indicator of.

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