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Estimating the Lime Equivalence of Biochar for Quality Assessment

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Research Problems

Biochar application for soil health benefits

- ✓ ↑ soil organic carbon
- ✓ ↑ soil water retention
- ✓ ↑ soil nutrient retention
- ✓ ↑ soil porosity
- ✓ ↑ water infiltration
- ✓ ↑ microbial abund. & activity
- ✓ ↓ soil acidity
- ✓ …

Research Problems

Lime equivalence of biochar

?

The capacity of biochar to reduce soil acidity is determined by its lime equivalence

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$$

IBI biochar qualify indicators:

- pH, lime equivalence,
- EC, mineral ash content,
- OC content, H/OC molar ratio,
- Total & available nutrients
- SSA, particle size distribution,
- Presence of contaminants,
- …

Research Problems

Biochar Lime Equivalence

The lime equivalence of a material is a comprehensive expression of its alkalinity (CO_3^{2-}, HCO_3^- & OH^-) and acidity (H^+, Al^{3+} & Fe^{3+})

$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$

$HCO_3^- + H_2O \rightarrow H_2CO_3 + OH^-$

$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$

$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$

Biochar alkalinity indicators

pH

Ca, Mg, Na & K contents

Mineral ash content

Research Problems

Acidity (soil, biochar & others)

Active acidity

Water soluble H^+, Al^{3+}, Fe^{3+} & org acids

Indicated by pH_{water}

Potential acidity

Exchangeable acidity

Exchangeable H^+, Al^{3+} & Fe^{3+}

Estimated by pH_{KCl}

$$\text{Micelle}\begin{matrix}Al^{3+}\\H^+\end{matrix} + 4\,KCl \longrightarrow \text{Micelle}\begin{matrix}K^+\\K^+\\K^+\\K^+\end{matrix} + Al^{3+} + H^+ + Cl^-$$

Residual acidity

Insoluble acidic components

Neutralizable by titration

$$\text{Micelle}\begin{matrix}Al\\H\end{matrix} + 2\,Ca(OH)_2 \longrightarrow \text{Micelle}\begin{matrix}Ca^{2+}\\Ca^{2+}\end{matrix} + Al(OH)_3 + H_2O$$

Research Problems

Reported biochar pH_{water} values: 5.4–11.9

Is higher pH biochar also greater in lime equivalence?

Will land-applied high pH (e.g., >10.0) biochar reduce effectively soil acidity?

Can we estimate the acid neutralization capacity and the lime equivalence of biochar from its

pH?

EC (salinity, soluble base cation contents)?

Mineral ash content?

Objectives

- To quantify the lime equivalent of various biochar products
- To associate the lime equivalent of biochar with pH, mineral ash content, and other quality parameters
- To identify the influencing factors and evaluate pH for estimating biochar lime equivalence

Experiments

1) Test biochars

Ground to <0.85 mm

Rogue biochar, wood-derived, commercial, OR

TerraH biochar from hardwood, commercial, MO

TerraS biochar from softwood, commercial, MO

Bob biochar, wood-derived, commercial, PA

Coco biochar, coconut shell-derived, farm, OR

RH400 biochar, rice husk 400°C slow pyrolysis, custom-made, lab

CSM300, 350, 400, 450, 500, 550 & 600; cottonseed meal-derived, custom-made, lab

PL300, 350, 400, 450, 500, 550 & 600; poultry litter-derived, custom-made, lab

Experiments

2) Biochar characterization

Ground to <0.85 mm

Mineral ash content

750°C ignition loss, muffle furnace

pH

1:10 solid/water ratio, 2-h mixing, pH meter

Electrical conductivity (EC)

1:10 solid/water ratio, 2-h mixing, EC meter

Water soluble Na^+, K^+, Ca^{2+} & Mg^{2+}

1:10 solid/water 24-h extraction, IC

Experiments

3) Biochar lime equivalent measurement

Ground to <0.85 mm

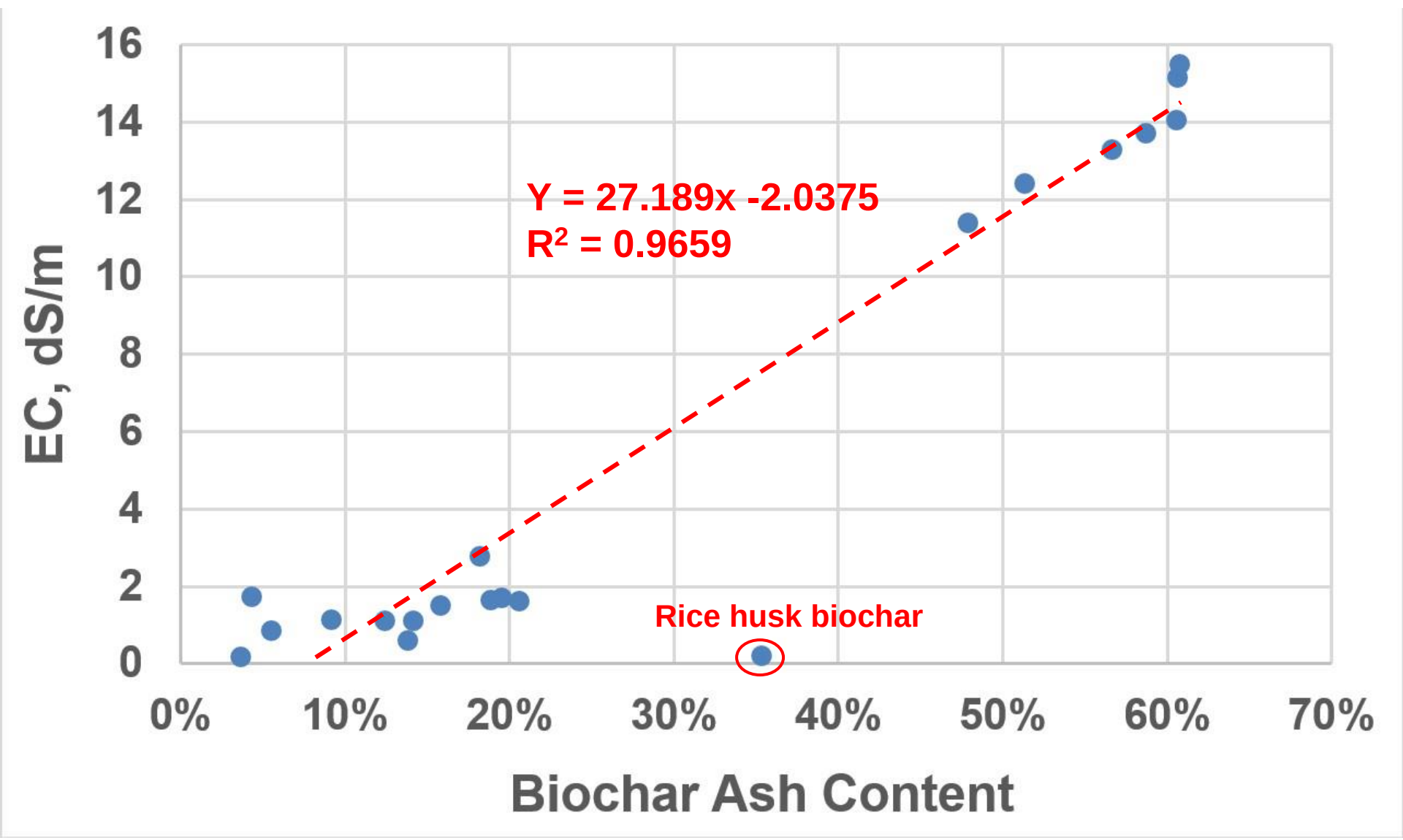
- Weigh 5.0 g biochar to a 250-mL conic flask
- Include an empty flask as procedure blank
- Add 25.00 mL of 1.0 M HCl to each flask
- Heat flasks to nearly boiling
- Add 100 mL deionized water to flask
- Heat flasks to boiling for 1 min
- Cool flasks to room temperature
- Centrifuge the slurry at 4000 rpm for 15 min
- Obtain 50.00 mL of 0.45-μm supernatant filtrate
- Auto titrate filtrate w/ 1.0 M NaOH to pH >7.0

$$CaCO_3\ equivalent, g\ kg^{-1} = \frac{(V_{NaOH,blank} - V_{NaOH,sample}) * C_{NaOH} \times 125}{dry\ mass\ of\ sample\ (g)}$$

Results

Biochar	Ash, %	pH	EC, dS m^{-1}	ΣBC, meq kg^{-1}	LE, g kg^{-1}
Rogue	4.31	10.25	1.72	184.75	-35.04
TerraH	13.79	9.47	0.615	85.41	118.06
TerraS	3.66	7.23	0.178	31.17	-68.34
Bob	9.15	9.44	1.14	137.82	14.88
Coco	5.52	6.03	0.870	94.33	-84.73
RH	35.30	8.08	0.221	-	-95.14
CSM300	12.43	9.06	1.10	106.44	23.52
CSM350	14.14	9.63	1.12	116.16	69.62
CSM400	15.79	10.11	1.50	140.15	64.75
CSM450	18.21	10.35	2.77	166.14	188.34
CSM500	18.86	10.31	1.64	157.45	78.19
CSM550	19.52	10.27	1.70	157.41	-23.09
CSM600	20.55	10.31	1.62	145.84	44.22
PL300	47.87	9.50	11.4	1294.41	88.49
PL400	56.62	10.32	13.3	1310.72	29.94

Experiments



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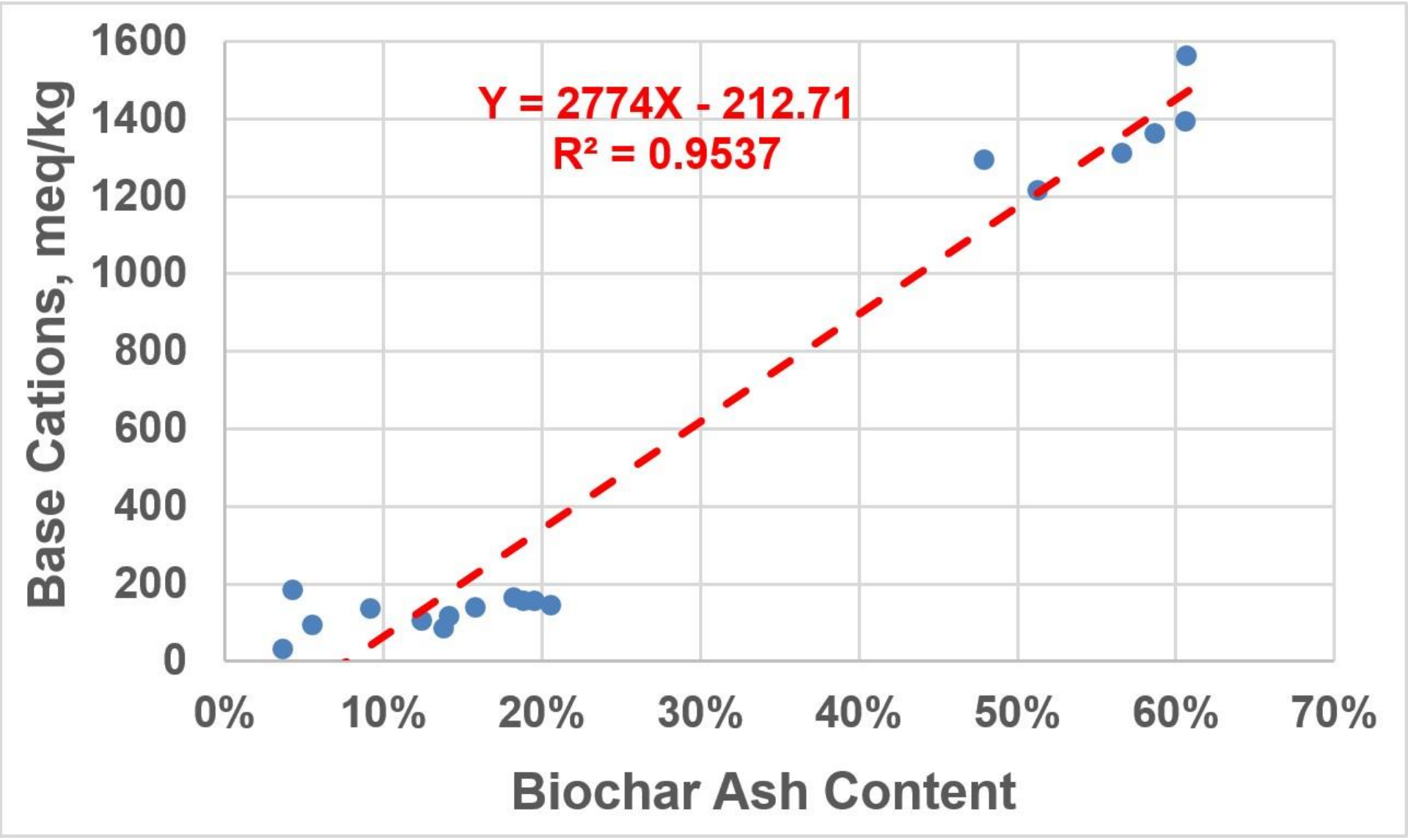

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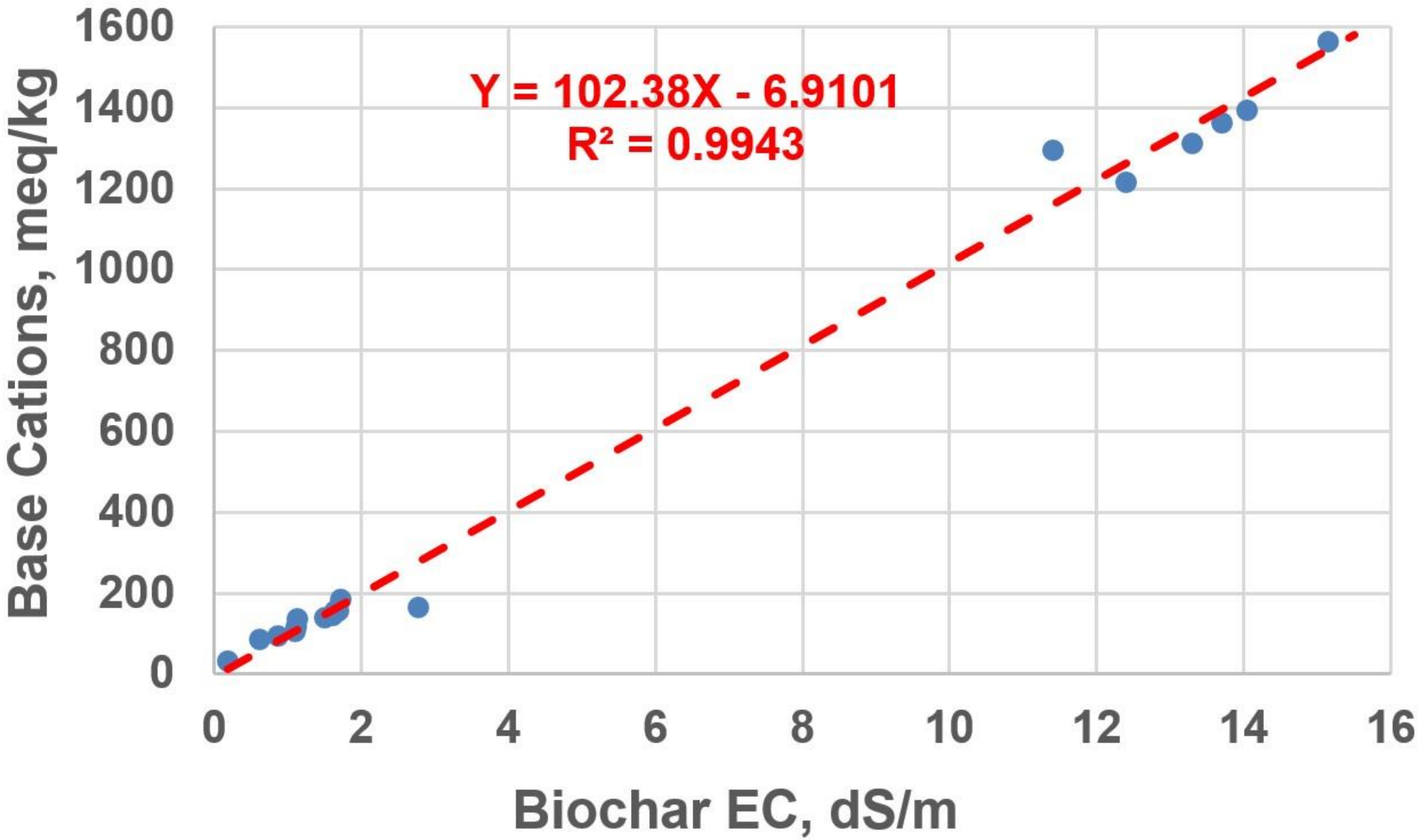

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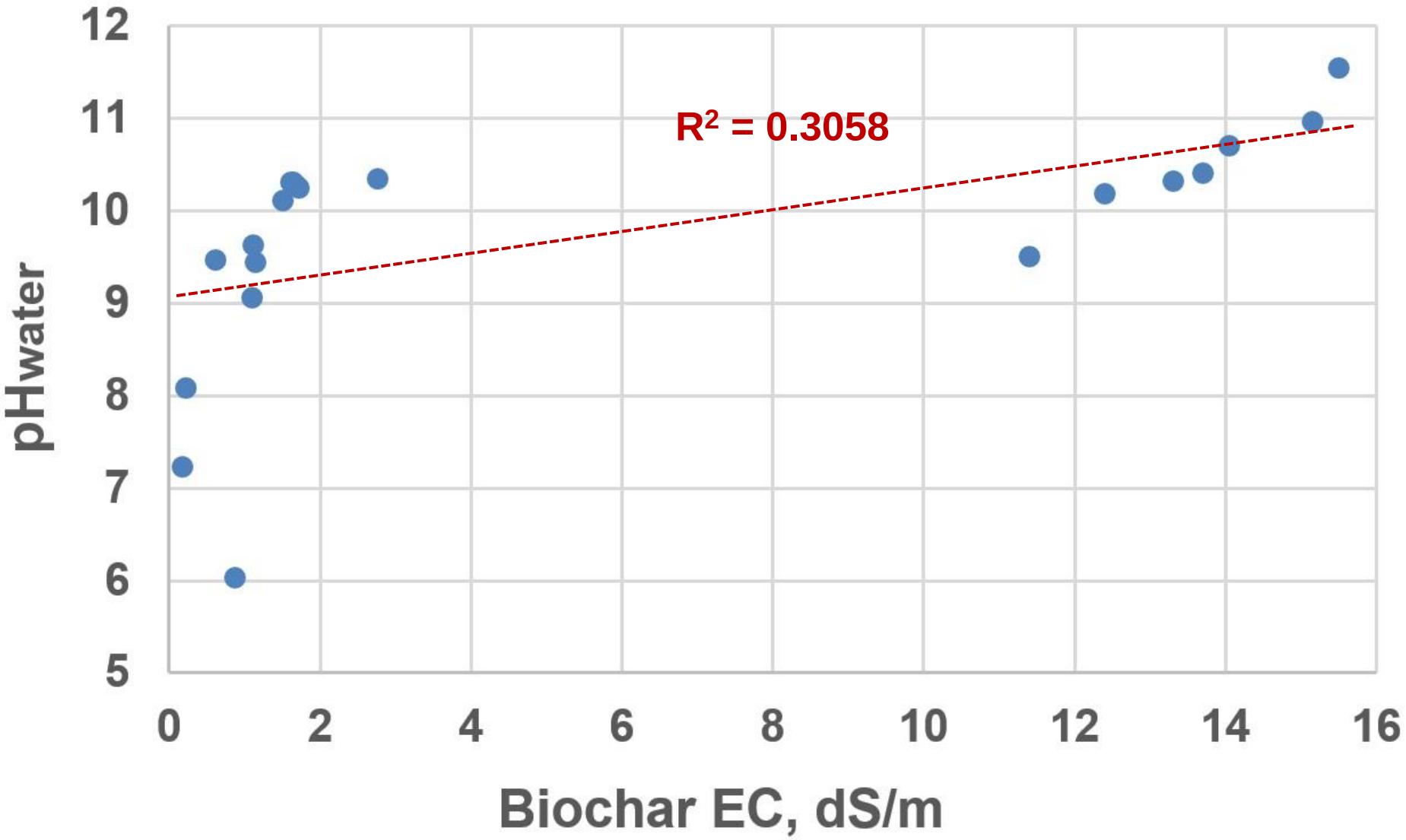

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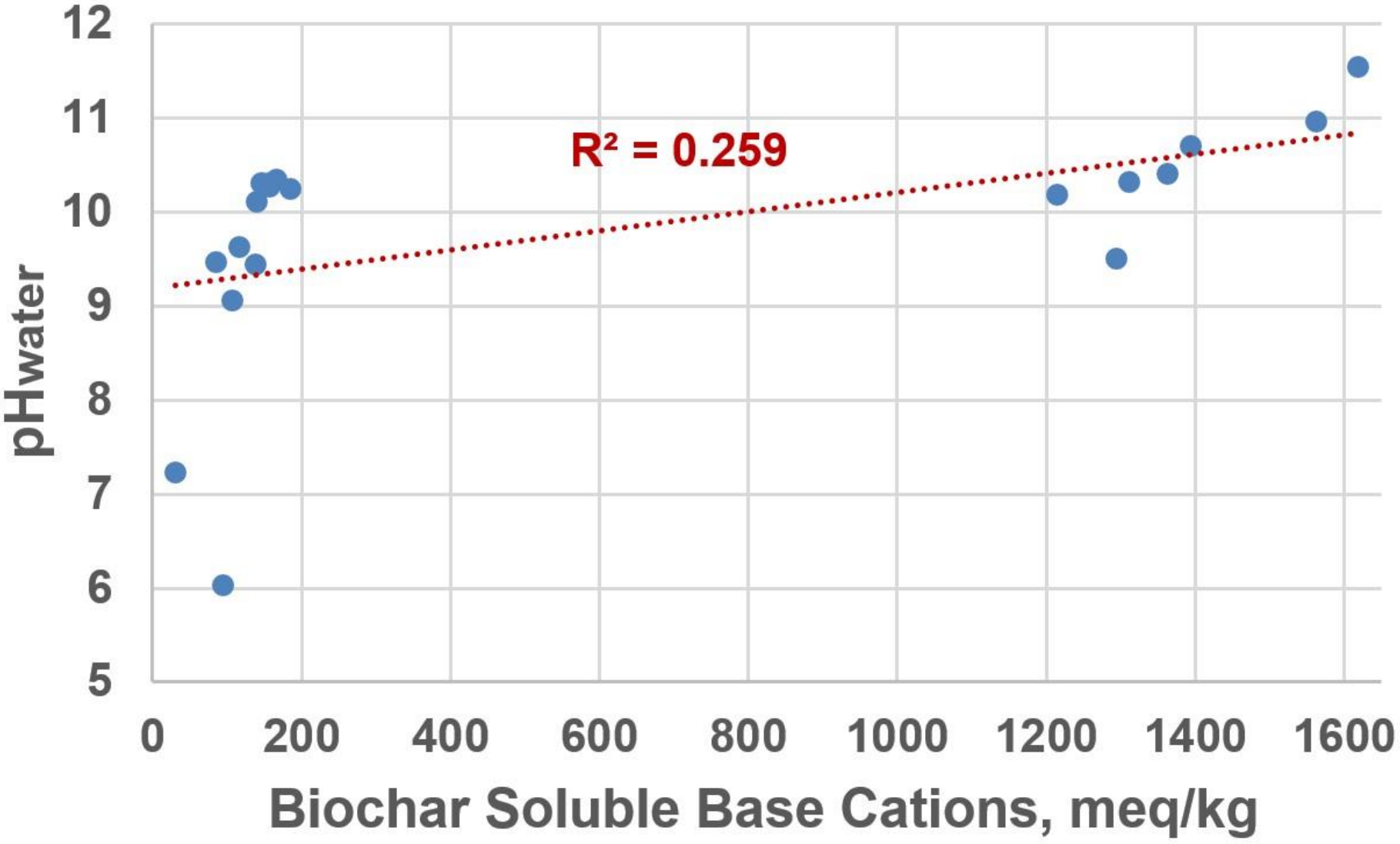

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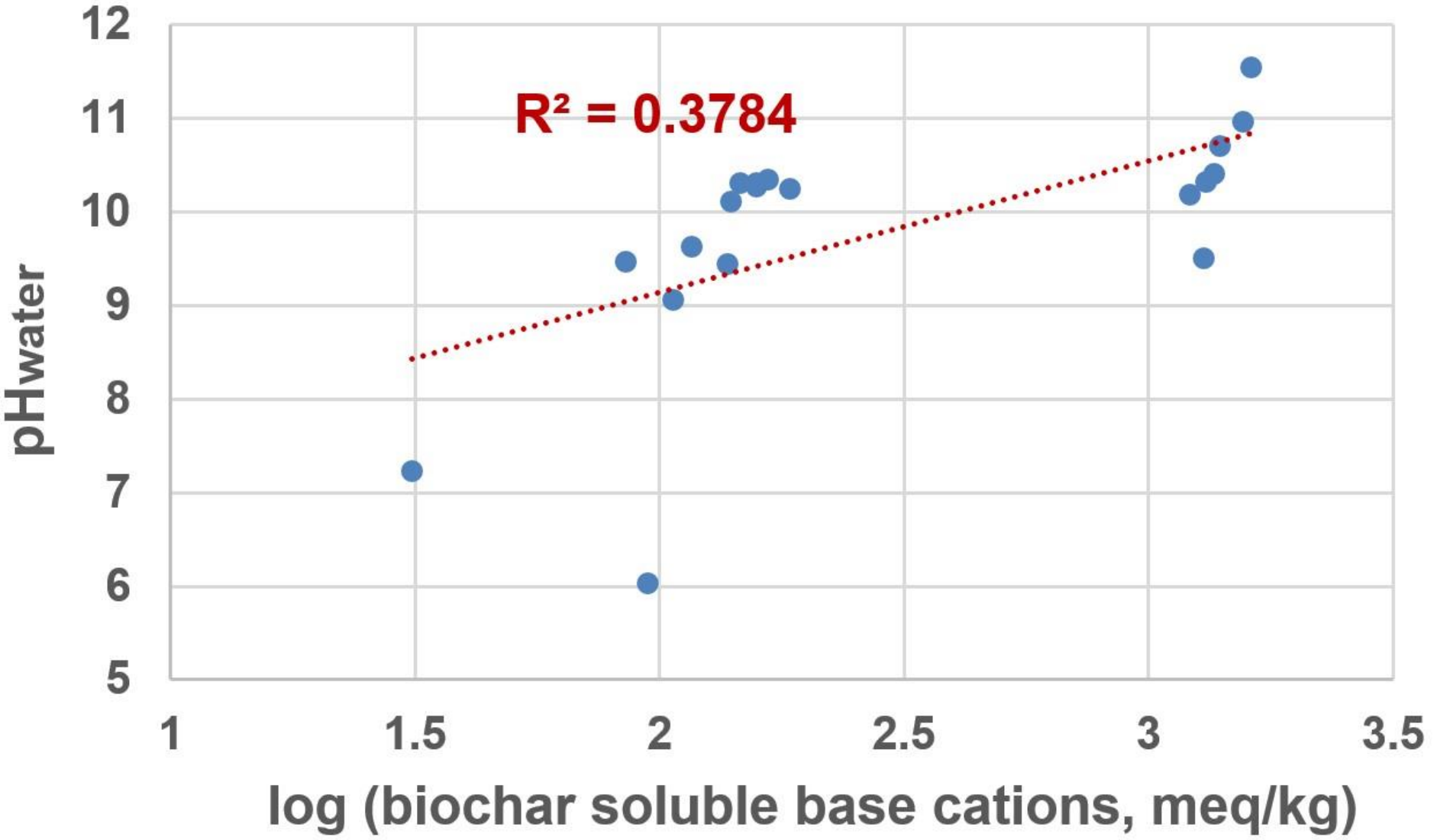

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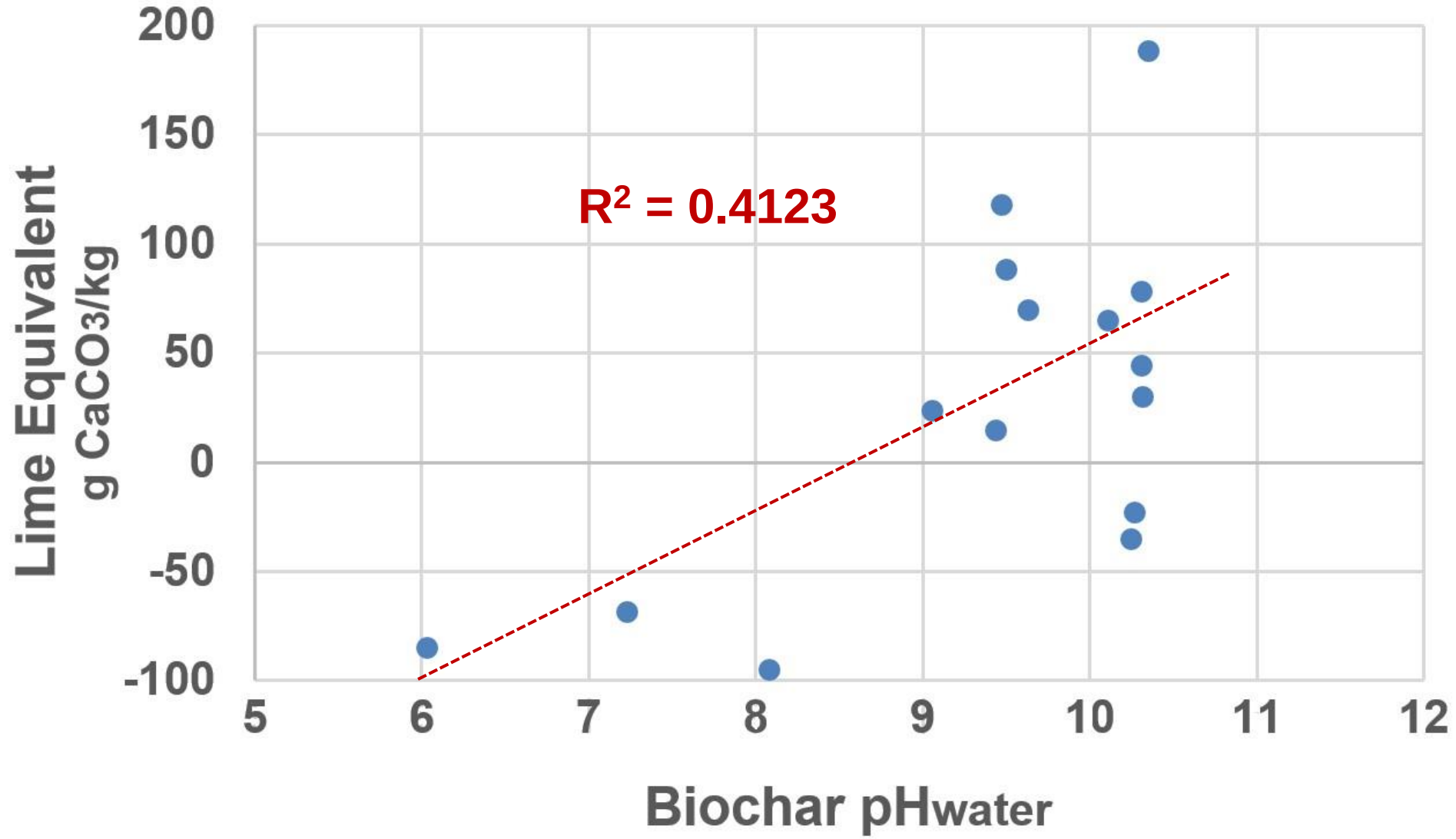

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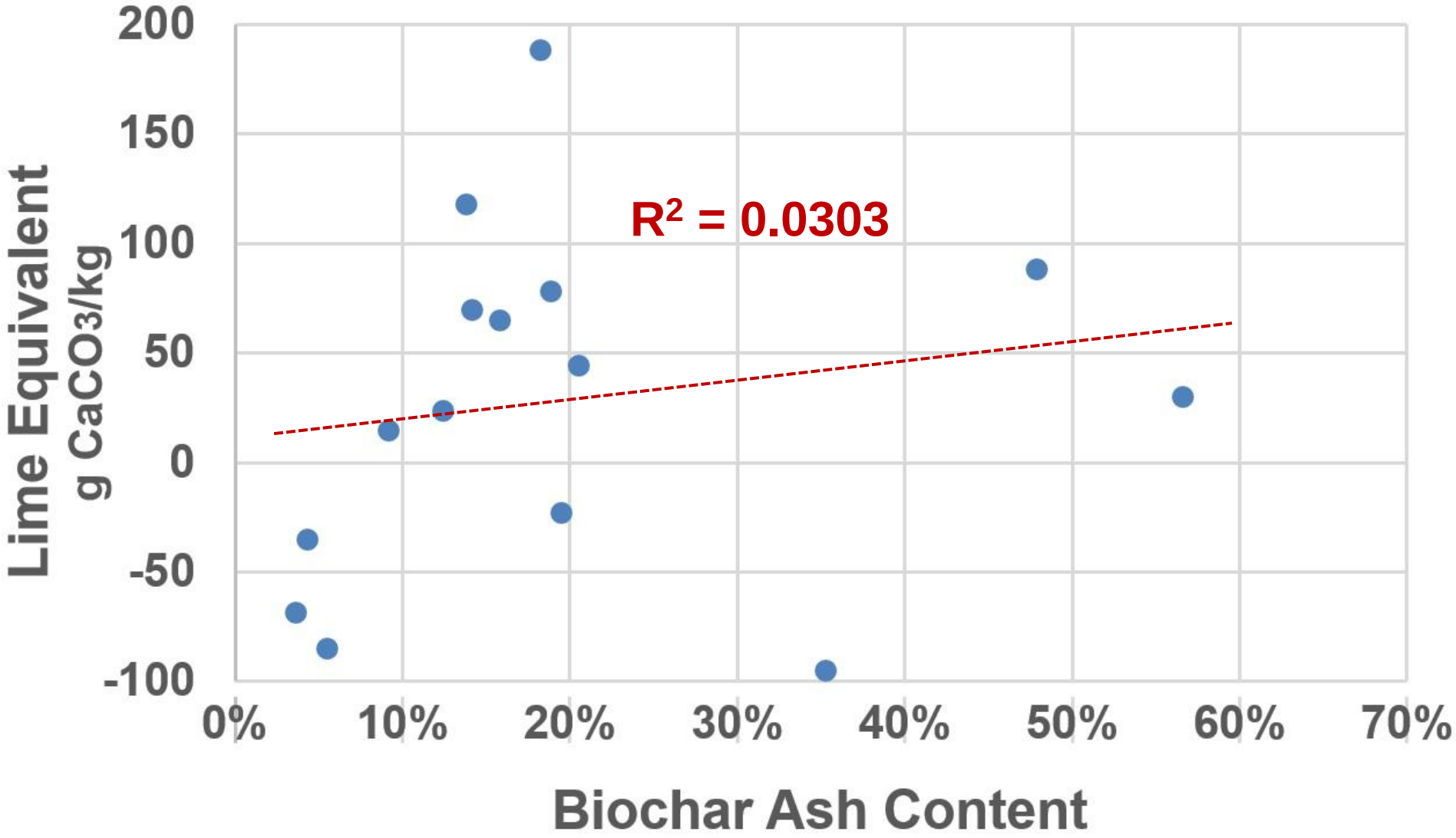

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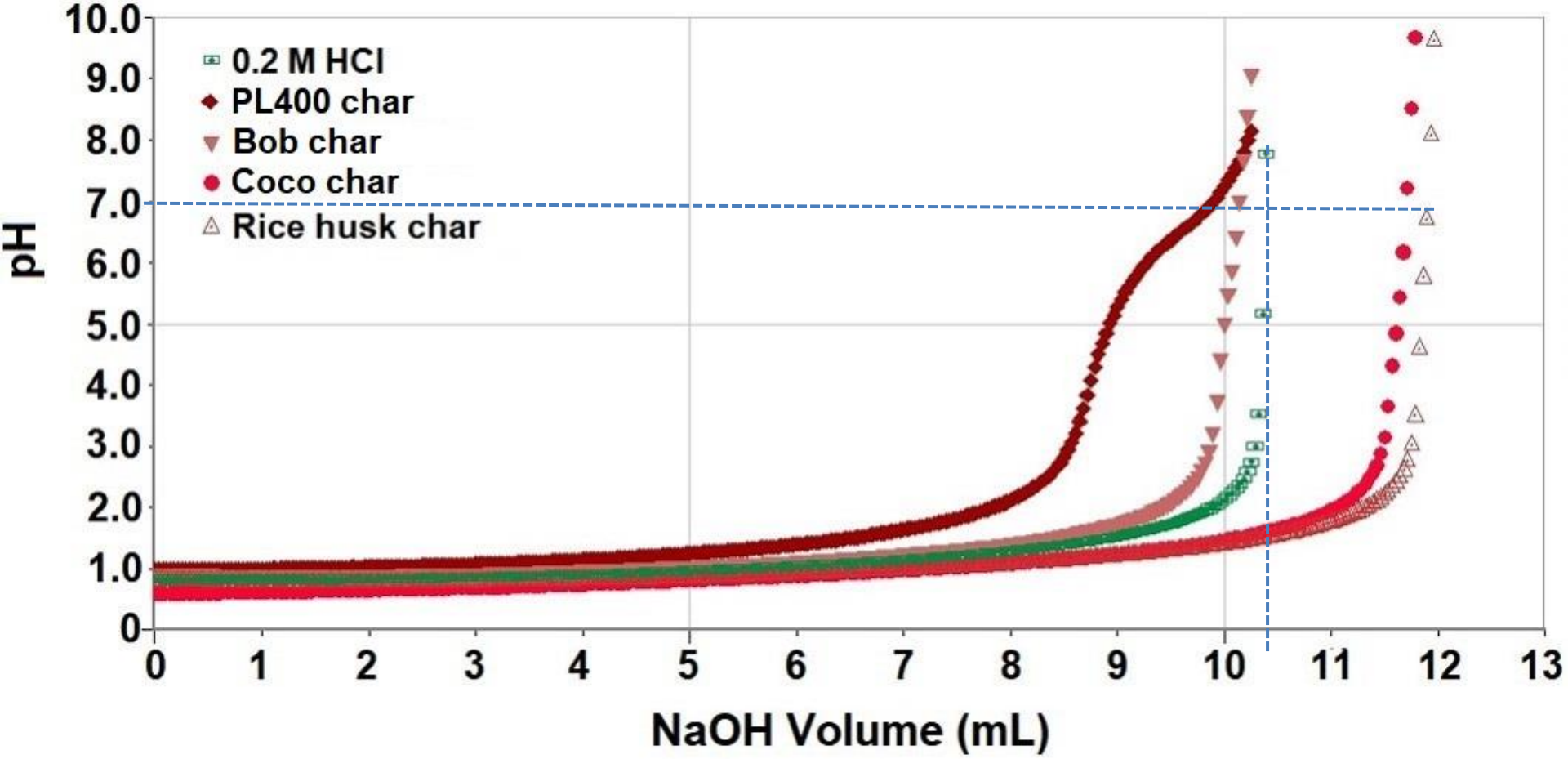

Conclusions

- **Differently sourced biochars varied significantly in lime equivalent ranging from -100 to 200 g $CaCO_3$ kg^{-1}**
- **The lime equivalence of biochar was not closely related to its mineral ash content or pH; high ash content and high pH products may have a negative lime equivalent**
- **Depending on the feedstock and production conditions, biochar may contain substantial potential acidity presumably from pyrolytic organic acids**
- **Biochar amendment may help temporarily elevate soil pH; the long-term effect for reducing soil acidity could not be secured.**