Predictions of pH change due to anaerobic digestion

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Overview

This file uses a speciation model from https://github.com/sashahafner/NH3-RTM (v1.0, https://github.com/sashahafner/NH3-RTM/releases/tag/v1.0) to predict effects of differences in animal slurry chemical composition on pH.

Prep

Load all functions.

```
source('NH3_mods.R')
```

Use eqSpec to calculate equilibrium speciation.

1. Raw pig slurry

Define composition.

```
totp1 <- c(H. = 0.0, NH3 = 0.208, H2CO3 = 0.112, K. = 0.0, Na. = 0.0, Cl. = 0.0, HAc = 0.21)
```

Calculate pH.

```
eqp1 <- eqSpec(tot = totp1, temp.c = 18, of = 'all')
-eqp1$l.a[1]
```

```
##       H.
## 5.554241
```

pH is 5.6, much lower than obs. Adjust with KOH.

```
eqp2 <- eqSpec(tot = totp1, temp.c = 18, pH = 6.87, adjpH = 'KOH', of = 'all')
totp2 <- eqp2$tot
totp2
```

```
##          H.         NH3       H2CO3          K.         Na.         Cl.
## -0.09265512  0.20800000  0.11200000  0.09265512  0.00000000  0.00000000
##         HAc
##  0.21000000
```

That's a lot of KOH.

Check CO2 partial pressure for fun.

```
eqp2$p.CO2
```

```
## [1] 0.5331638
```

Try reducing VFA instead.

```
eqp3 <- eqSpec(tot = totp1, temp.c = 18, pH = 6.87, adjpH = 'HAc', of = 'all')
totp3 <- eqp3$tot
totp3
```

```
##       H.      NH3    H2CO3       K.      Na.      Cl.      HAc
## 0.000000 0.208000 0.112000 0.000000 0.000000 0.000000 0.117785
```

That's plausible.

2. Raw cattle slurry

Define composition.

```
totc1 <- c(H. = 0.0, NH3 = 0.149, H2CO3 = 0.129, K. = 0.0, Na. = 0.0, Cl. = 0.0, HAc = 0.193)
```

Calculate pH.

```
eqc1 <- eqSpec(tot = totc1, temp.c = 18, of = 'all')
-eqc1$l.a[1]
```

```
##       H.
## 5.055505
```

pH is 5.1, even lower than obs was for pig. Adjust with KOH.

```
eqc2 <- eqSpec(tot = totc1, temp.c = 18, pH = 6.82, adjpH = 'KOH', of = 'all')
totc2 <- eqc2$tot
totc2
```

```
##         H.        NH3      H2CO3         K.        Na.        Cl.        HAc
## -0.1459859  0.1490000  0.1290000  0.1459859  0.0000000  0.0000000  0.1930000
```

That's a ton of KOH. Try reducing VFA instead.

```
eqc3 <- eqSpec(tot = totc1, temp.c = 18, pH = 6.82, adjpH = 'HAc', of = 'all')
totc3 <- eqc3$tot
totc3
```

```
##         H.        NH3      H2CO3         K.        Na.        Cl.        HAc
## 0.00000000 0.14900000 0.12900000 0.00000000 0.00000000 0.00000000 0.04812209
```

That's plausible.

3. Digestate

Define composition. 1/10th as much TIC.

```
totd1 <- c(H. = 0.0, NH3 = 0.297, H2CO3 = 0.191, K. = 0.0, Na. = 0.0, Cl. = 0.0, HAc = 0.019)
```

Calculate pH.

```
eqd1 <- eqSpec(tot = totd1, temp.c = 18, of = 'all')
-eqd1$l.a[1]
```

```
##       H.
## 9.103265
```

pH 9.1. Clearly these differences in composition are *more than* enough to explain the differences in pH.

4. Removing VFA from raw slurry

What effect does removing VFA have? First pig.

```
totp4 <- totp3
totp4['HAc'] <- 0
totp4
```

```
##    H.   NH3 H2CO3    K.   Na.   Cl.   HAc
## 0.000 0.208 0.112 0.000 0.000 0.000 0.000
```

```
eqr1 <- eqSpec(tot = totp4, temp.c = 18, of = 'all')
-eqr1$l.a[1]
```

```
##       H.
## 9.379774
```

Plenty.

Then cattle.

```
totc4 <- totc3
totc4['HAc'] <- 0
totc4
```

```
##    H.   NH3 H2CO3    K.   Na.   Cl.   HAc
## 0.000 0.149 0.129 0.000 0.000 0.000 0.000
```

```
eqr2 <- eqSpec(tot = totc4, temp.c = 18, of = 'all')
-eqr2$l.a[1]
```

```
##       H.
## 8.672005
```

Plenty of effect here too.

Conclusions

1. We cannot completely explain observed pH values of raw slurry or digestate, but this isn't too worrying because we don't have complete information on composition.
2. Observed differences in VFA and TAN in raw vs. digested slurry are more than enough to explain the observed pH difference.
3. Simply removing raw slurry VFA is enough to explain the observed pH differences.