Putting Presence or Absence of Constituents in Biosolids in Perspective -

The vanishing zero,
Parts is Parts,
and looking at the problem from a new direction

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The Vanishing Zero

- Often refers to the ability of analytical instrumentation to get to very----- very low levels.
- "detection limits" keeps getting farther and farther away, both in distance and **understanding**.
- The good and the bad of the widening gap between -----
  - instrument detection limits (sub-ppb) and
  - toxicological relevant regimens (ppm).
- This leads to advocating extreme measures to counter indeterminable or even negligible probability of risk.
  - In other words, "If you can detect it you should regulate it."

But we must remember.....

Paracelsus, sometimes called the father of Toxicology wrote:[1]

"All things are poison and nothing is without poison, only the dose permits something not to be poisonous."

Or, more commonly
"The dose makes the poison."

[1] p. 435, *Verkehrsmedizin-Fahreignung, Fahrsicherheit, Unfallrekonstruktion*, B. Madea, F. Mußhoff, and G. Berghaus, Köln: Deutscher Ärzte-Verlag, 2007, http://[illegible]

Some 'Parts' Math

100% = 1,000,000 mg/Kg (ppm)
10% = 100,000 mg/Kg (ppm)
1% = 10,000 mg/Kg (ppm)
1,000 mg/Kg or 1g/Kg = 1000ppm
1 mg/Kg =1 ppm
1 µg/Kg =0.001 ppm = 1 ppb
1 ng/Kg = 0.000001 ppm = 1 ppt

Concentrations of chemicals in soil are typically measured in units of the mass of chemical (milligrams, mg or micrograms, ug) per mass of soil (kilogram, kg). This is written as mg/kg or ug/kg. Sometimes concentrations in soil are reported as parts per million (ppm) or parts per billion (ppb).
For soil, 1 ppm = 1 mg/kg of contaminant in soil, and 1 ppb = 1 ug/kg. A measurement of 6 mg/kg is the same as 6 ppm or 6,000 ppb, which is equal to 6,000 ug/kg.

Agricultural

2/3 of Biosolids are made up of.....

- Carbon
- Oxygen
- Silicon
- Hydrogen
- Nitrogen
- Sulfur

Data are medians from the TNSSS 2007

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50%+

Data are medians from the TNSSS 2007

Comparison of Biosolids to Soil constituents

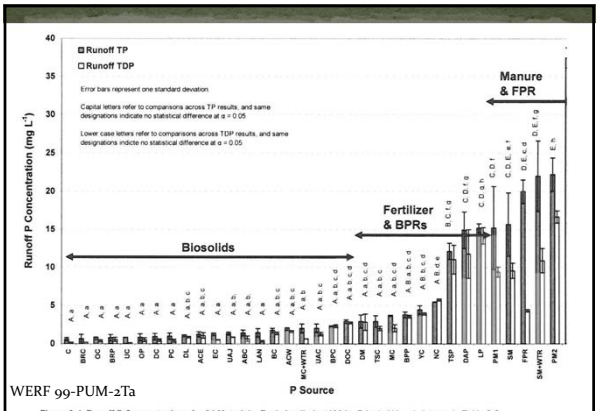
Element	Biosolids Mean %[2]	Biosolids Median %[2]	Typical Soils %[1]
C	31.2	31.4	1.6
O	19.6	20.4	49.0
Si	6.5	5.1	31.0
Ca	4.1	2.8	0.9
H	3.8	4.1	--
N	3.9	4.0	0.2
Fe	2.8	1.6	1.8
P	2.2	1.9	0.03
S	1.3	1.2	0.12
Al	1.3	1.1	4.7

[1] Schacklette, H.T. and J.G. Boeragen. 1984. Element Concentrations in soil and other surficial materials of the conterminous United States. USGS Professional Paper 1270.
[2] TNSSS 2006

Comparison of Manures to Biosolids to Soil

Element	Typical Manure Values[3] %	Biosolids Median[2] %	Typical Soils %[1]
N	3.8-5.3	4.0	0.2
P	0.8-1.9	1.9	0.03
Fe	0.1-0.4	1.6	1.8
S	0.4-0.9	1.2	0.12
Ca	1.3-8.1	2.8	0.9
Mg	0.6-0.9	0.45	0.44
Na	0.4-0.7	0.1	0.59

1 Schacklette, H.T. and J.G. Boeragen. 1984. Element Concentrations in soil and other surficial materials of the conterminous United States. USGS Professional Paper 1270.
[2]2006 TNSSS
[3] ASABE D384.2 March 2005 presented as a range, varies with specie and growth stage



WERF 99-PUM-2Ta

Figure 3-4. Runoff P Concentrations for 34 Materials, Each Applied at 100 kg P ha⁻¹. Abbreviations as in Table 3-2.

Compare 1988 and 2006 Biosolids Data

	CA 2008mg/Kg median[3]	National 1988 mg/Kg median[7]	National 2006 mg/Kg median[2]	Median Soils Conc. mg/Kg[3] CA	503 Table 3 mg/Kg[4]
As	6.6	5	5	2.7	41
Cd	1.9	4	2	0.275	39
Cr	--	44	32	69	N.R.
Cu	360	451	463	21.6	1500
Pb	21	78	48	47.9	300
Hg	1.2	2	0.8	0.19	17
Mo	11	5	11	0.85	(75)[6]
Ni	21	19	23	27	420
Se	7.5	3	6	0.015	100
Zn	790	746	784	153	2800

Notes: [2]2008 Annual Reports summarized in US EPA Region 9,[3] US EPA 2007 median values, [5]Soil results for California are median values in Kearney Foundation Special Report " Background Concentrations of Trace and Major Elements in CA Soils 1996, [4]US EPA 1993; [6]Table 1 Requirement; N.R. Not Required [7] NSSS 1988 median values

Compare Fertilizer to Manure to Biosolids Data

	CA 2008 mg/Kg median[1]	Typical Means for Various FarmFertilizers /Chemicals[2]	Manures Typical Values[7]	Median Soils Conc. mg/Kg[3] CA	503 Table 3 mg/Kg[4]
As	6.6	0.3-1662	3.7-13	2.7	41
Cd	1.9	0.75-398	.25-2.5	0.275	39
Cr	--	1.4-338	--	69	N.R.
Cu	360	1.0-1101	36-465	21.6	1500
Pb	21	4.6-10,013	7.6-46	47.9	300
Hg	1.2	0.07-3.6	NA	0.19	17
Mo	11	--	5-19	0.85	(75)[6]
Ni	21	1.4-890	16-29	27	420
Se	7.5	--	--	0.015	100
Zn	790	1.6-353	150-656	153	2800

Notes: [1]2008 Annual Reports summarized in US EPA Region 9, [2] 1999 EPA draft Rpt varies with manufacuture see rpt for detail [3]Soil results for California are median values in Kearney Foundation Special Report " Background Concentrations of Trace and Major Elements in CA Soils 1996, [4]US EPA 1993; [5]Table 1 Requirement; N.R. Not Required [7] various see WERF 99PUM-1

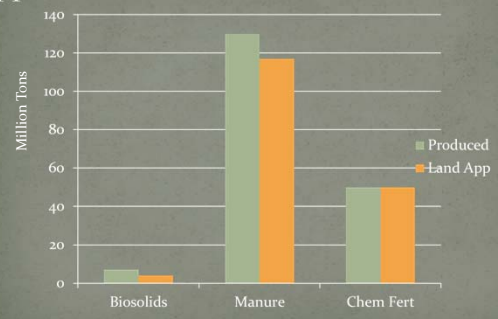
Table 4-2. Metal Concentrations in Fertilizer Products (mg/kg)

Product	As	Cd	Cr	Cu	Pb	Hg	Ni	Vn	Zinc
Phosphate (P_2O_5)	11.3[1] (61)[2] 0.5-20.5[3]	65 (57) 0.15-250	173.3 (27) 63-896	56.6 (58) 0.2 -.1,170	12.2 (49) 1-200	0.10 (5) 0.003-0.2	27.5 (34) 0.5-151	216 (8) 48.7-721	240.2 (29) 31.3-1,550
NPK for phosphorus (P)	12.8 (84) 0.05-155	30.6 (85) 0.03-47	83.9 (60) 4.3-616	31.4 (88) 0.44-700	216.5 (85) 0.1-5,425	0.07 (14) 0.003-0.2	28.5 (69) 0.5-195	165.7 (14) 25-396	233.6 (67) 1-2,193
NPK for nitrogen (N)	5.3 (49) 0.04-13.2	5.0 (46) 0.03-47	50.6 (41) 0.05-201	41.3 (47) 0.14-544	31.8 (49) 0.2-422	0.2 (7) 0.11-0.4	11.8 (43) 0.1-85.7	64.8 (42) 0.05-163	204.5 (38) 0.2-4,442
Potash (K_2O)	0.3 (17) 0.05-1.5	NA	0.5 (14) 0.05-2.75	1.0 (43) 0.05-5	NA	0.1 (16) 0.003-0.2	1.4- (41) 0.05-4.4	1.2 (16) 0.05-9	1.6- (39) 0.19-8.75
Sulfur (nutrient)	5.0 (9) 0.1-19	36.6 (4) 0.03-145	37.9 (6) 0.05-214	24.3 (9) 0.04-109	5.4 (6) 0.2-15	0.1 (3) 0.01-0.40	48.9 (4) 0.1-195	99.1 (4) 0.046-396	384.8 (4) 0.21-1,480
Sulfur (pH)	7.8 (3) 0.1-19	NA	NA	40.4 (3) 2-109	6.4 (2) 4-8.7	NA	NA	NA	NA
Lime ($CaCO_3$)	14.6 (10) 1-48	2.5 (10) 0.1-8.1	21.2 (7) 1.25-73	42.0 (9) 2.3-158	44.5 (10) 0.7-150	0.1 (8) 0.01-0.41	7.9 (8) 1.4-23	14.0 (8) 1-49	353.0 (7) 7.7-1770
Gypsum	4.5 (4) 3-8.5	1.7 (2) 0.8-2.5	1.4 (1)	23.7 (4) 7.2-42	4.6 (4) 1.5-11	0.011 (1)	3.0 (1)	33.9 (4) 1.4-50	53.8 (1)

EPA Report "Estimating Risk from Contaminants Contained in Agricultural Fertilizers" Draft Report OSW August 1999

Sand Dune Stabilization

Representation of Tons of materials applied to land in the US



2007 NEBRA rpt; WERF 99PUM-1

Current uses if looked at on a National Basis

% of Cropland Acres[4]

	Produced	1 T/A	2 T/A	5 T/A	10T/A
Biosolids[3]	7.5 E6 dmt	1.8%	0.9%	0.3%	0.2%
Manure if at [1]	75 E6 est dmt	18%	9%	3%	2%
Manure if at [2]	335 E6 est w?mt	81%	40.5%	13.5%	9%

[1] Adapted from 2003 USDA rpt 824 and 2009 USDA rpt to congress
[2] 2005 USDA ARS Annual Rpt Nat program 206 (referring to EPA)
[3] 2005 NEBRA Biosolids Survey
[4] Cropland Ac - 406,424,909 Acres - 2007 USDA

Rangeland Improvement

Organics in Perspective

Brobst, R.B. 2011 Biosolids: Putting Regulators and Researchers in Touch with YOU… thePractitioner. Whitter/Dublin CA. Jan 18/19, 2011 Brobst.bob@epa.gov

Pharmaceuticals Results from sampling of 74 POTWs in USA (all results are µg/kg dry solids)

	Number Detects[1]	Minimum[2]	Mean[3]	Maximum[4]	SD[3]	SE of Mean[3]
4-Epianhydrotetracycline (EATC)	37/74	126	259.6	2,160	264.1	34.2
4-Epitetracycline (ETC)	71/74	47.2	959.3	4,380	950.9	111.3
Anhydrotetracycline (ATC)	46/74	94.3	244.9	1,960	281.9	33.15
Azithromycin	71/74	10.2	675.2	5,205	1,054	123.4
Carbadox	36/74	27.2	315.4	3,110	341.9	39.99
Carbamazepine	71/74	8.74	149.9	3,082	307.7	45.39
Cimetidine	66/73	2.50	229.8	8,330	1,028	122
Ciprofloxacin	74/74	74.5	8,180	40,800	8,248	-
Clarithromycin	41/74	8.68	37.54	617	75.52	8.89
Codeine	18/74	10.7	23.65	328	41.49	4.97
Cotinine	33/74	13.4	46.45	1,610	110.3	9.1
Dehydronifedipine	17/74	3.48	4.46	21.65	2.97	0.356
Diltiazem	63/74	1.81	37.83	225	54.96	6.442
Diphenhydramine	74/74	36.7	820.8	5,730	848.7	-
Doxycycline	63/74	50.2	709.5	5,090	815.6	94.34
Enrofloxacin	11/74	12.55	16.05	66	10.19	1.28
Erythromycin-total	63/74	2.53	40.81	180	32.06	3.76
Fluoxetine	70/72	20.1	236.5	3,130	393.9	46.75
Gemfibrozil	66/74	12.1	215.3	2,650	425.9	49.89
Ibuprofen	48/74	99.5	570.6	11,900	1,561	183.5
Ketoprofen	71/74	22	911.3	9,210	1,098	133.6
Minocycline	29/65	351	595.6	8,650	1,031	130.2
Naproxen	38/74	20.9	82.24	1,020	139.3	16.41
Norfloxacin	25/74	99.3	170.1	995.5	174.5	20.9
Ofloxacin	73/74	234	6,303	58,100	8,257	968.3
Oxytetracycline (OTC)	28/74	21.05	46.17	467	58.86	6.79
Roxithromycin	43/74	18.9	49.52	2,950	264.6	31.56
Sulfamethoxazole	29/73	3.91	19.54	651	76.91	9.16
Tetracycline (TC)	72/74	38.3	1,053	5,270	1,114	130.5
Thiabendazole	52/74	8.42	33.8	238	46.83	5.9

Brobst, R.B. 2010 Presented at Biosolids: Putting Regulators and Researchers in Touch with YOU the Practitioner. Whitter/Dublin CA. July 18/19, 2011 Brobst.bob@epa.gov

Hormones and Sterols Results from sampling of 74 POTWs in USA(all results are µg/kg dry solids)

	Number Detects[1]	Minimum[2]	Mean[3]	Maximum[4]	SD[3]	SE of Mean[3]
Androstenedione	30/69	108	285.2	1,520	314.4	38.76
Androsterone	47/69	17.65	117.7	1,107	157.3	19.17
β Stigmastanol	72/74	3440	143,928	1,330,000	207,816	24,381
β Estradiol 3-benzoate	17/70	30.2	132.2	1,850	326.8	40.27
β Sitosterol	65/74	24,400	3,024,435	1,640,000	282,854	33,137
Campesterol	73/74	2,840	88,611	524,000	93,351	10,980
Cholestanol	73/74	3,860	459,202	4,590,000	631,126	74,086
Cholesterol	71/74	18,700	726,710	5,300,000	780,980	91,520
Coprostanol	73/74	7,720	2,787,676	43,700,000	5,358,128	627,896
Desmosterol	52/74	2,730	14,616	94,400	16,170	1,902
Epicoprostanol	72/74	868	739,301	6,030,000	1,107,295	130,241
Equilin	13/69	23	28.49	100.3	14.99	1.927
Ergosterol	48/74	4,530	19,439	91,900	18,565	2,182
Estriol	16/70	7.56	25.59	232	43.41	5.41
Estrone	52/69	27.2	109.6	965	163.3	19.86
Progesterone	17/73	142	287.5	1,290	319.2	38.22
Stigmasterol	68/74	11,000	118,977	568,500	101,753	11,916
Testosterone	17/69	27.45	102.1	2,040	266.7	33.24

1 Number of reportable results per total sample results. Note that some of the sample results were missing due to breakage, analytical error, etc.
2 Reportable Minimum from Detects
3 Mean, SD and SE of Mean Estimated with NDs using Kaplan-Meier Method with Nonparametric Statistics (includes maximum outlier) utilizing EPA's ProUCL

Concerns over Organics

- the fate of contaminants is compound, biosolids and management specific
- Do we prioritize by
  - Concentration
  - Persistence
  - Toxicity
  - Alphabetically
- Known risks are likely small
- Breakdown in Treatment and in environment
  - Retention/Release/Partitioning
  - Degradation
  - Volatilization
  - Photolysis
  - Plant uptake and metabolism
  - Leaching and runoff

IDSA Meeting 2010
339. Antimicrobial Prescription Data Reveal Wide Geographic Variability in Antimicrobial Use in the United States, 2009

Antibiotic use in US was 0.85 prescriptions in 2009

The South U.S. prescription rate was significantly higher than the rate for the West (t-test, $p<.0001$).

Alaska had the lowest rates with 0.52 prescriptions per capita, followed by Oregon (0.57), Colorado (0.60), **California (0.61)** and Washington (0.61).

Lauri A. Hicks, DO, CDC
ISDA - Infectious Diseases Society of America

A Snapshot of Antibiotic Use

Europe

10,900 tons combined Use (1998)

- 7000 tons-human use
- 3900 tons-animal use

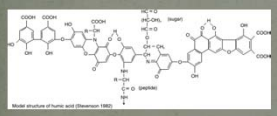
United States

12,000 tons combined Use (1997)

4800 tons-human use

7200 tons-animal use

organics

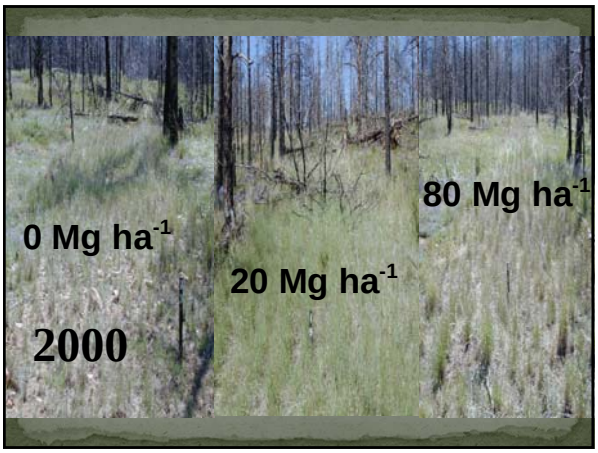


- Hormones and Sterols
  - 0.8% of the Biosolids
    - Top 2
      - β Sitosterol
      - Coprostanol

      71% of 0.8%
- Pharms and Antimicrobials
  - 0.072% of biosolids
    - Top 2
      - Triclosan
      - Triclocarban

      67% of 0.072%

Data use were TNSSS calculated means for compound with adequate number of hits



Old World Meets New

Other work with the TNSSS

TNSSS Preliminary PLFA/FAME Hierarchal Cluster Analysis

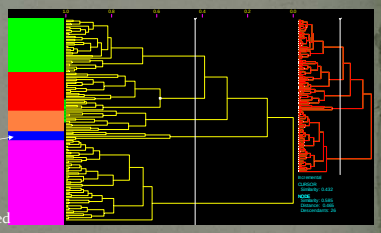
Class B
Anaerobic Biosolids

Class A
Aerobic & Composted

Class B Ponds & Anaerobic

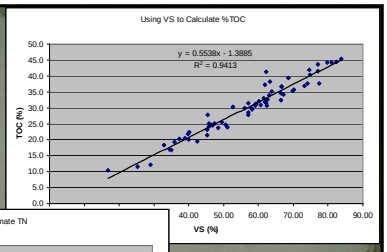
Chem +Misc.

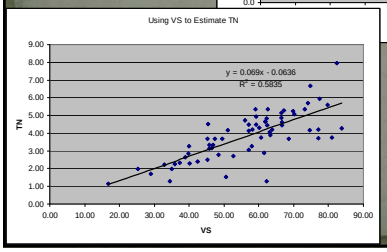
Non Applied Biosolids
Landfilled and Incinerated



ORD/LRPCD
Ronald F. Herrmann
6/1/10

Can we use the data as a predictive tool?





δ13C and δ15N

δ13C Min -36.1 Max -15.8 Mean -23.4 ‰

δ15N Min -2.0 Max 16.8 Mean 7.0 ‰

C:N Min 1.7 Max 33.1 Mean 9.9 ‰

- Later I hope to divide this out by region/treatment.

Comparison of Chemical Quality

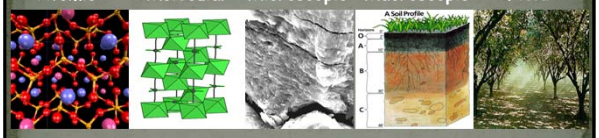
	Cu mg/Kg	Zn mg/Kg	Cd mg/Kg	Pb mg/Kg	Mo mg/Kg
1	214	327	2.8	66	6.7
2	1005	617	1.8	54	36
3	250	2134	1.6	n.d.	15.5
4	81	319	6.3	107	10.4

Comparison of Chemical Quality

	Cu mg/Kg	Zn mg/Kg	Cd mg/Kg	Pb mg/Kg	Mo mg/Kg
NYC	214	327	2.8	66	6.7
Small Town 1	1005	617	1.8	54	36
Hog	250	2134	1.6	n.d.	15.5
Small Town 2	81	319	6.3	107	10.4
Table 3	1500	2800	41	330	75

Levels of Detail in Research

Atomic | **Molecular** | **Microscopic** | **Macroscopic** | **Field**



- XRF
- XPS
- XAS

Requires synchrotron radiation.

- XRD
- TGA
- FTIR
- DRS

- Enhanced Visual Analysis:
  1. SEM
  2. TEM
  3. AFM

- Field Plots
- Equilibrium Studies
- Kinetic Studies
- Extractions

- Visual/ Intuitive Insight
- Field Plots

Adaptation of Bertsch and Hunter, 1996.