Metals removal mechanisms and methods and current status

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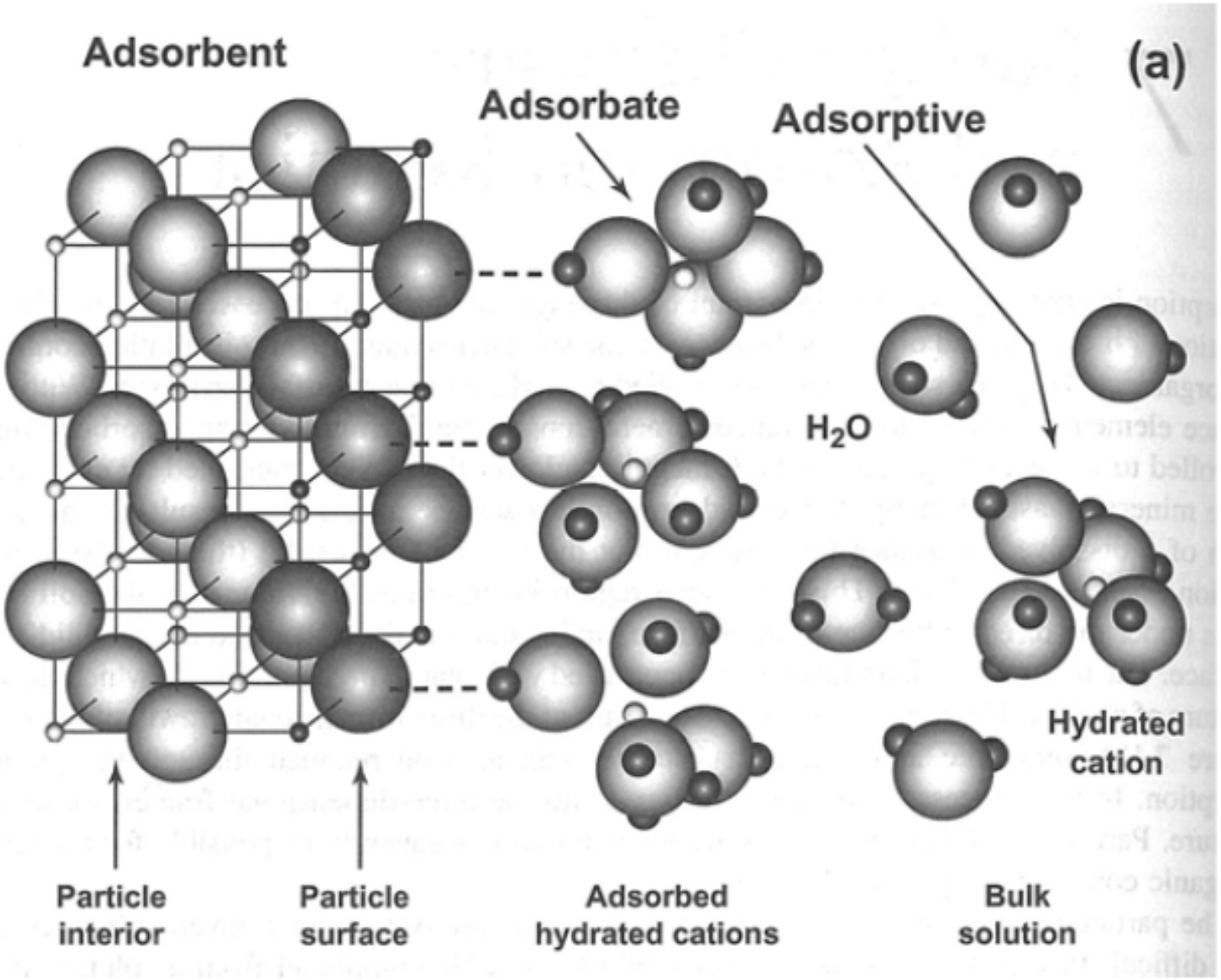
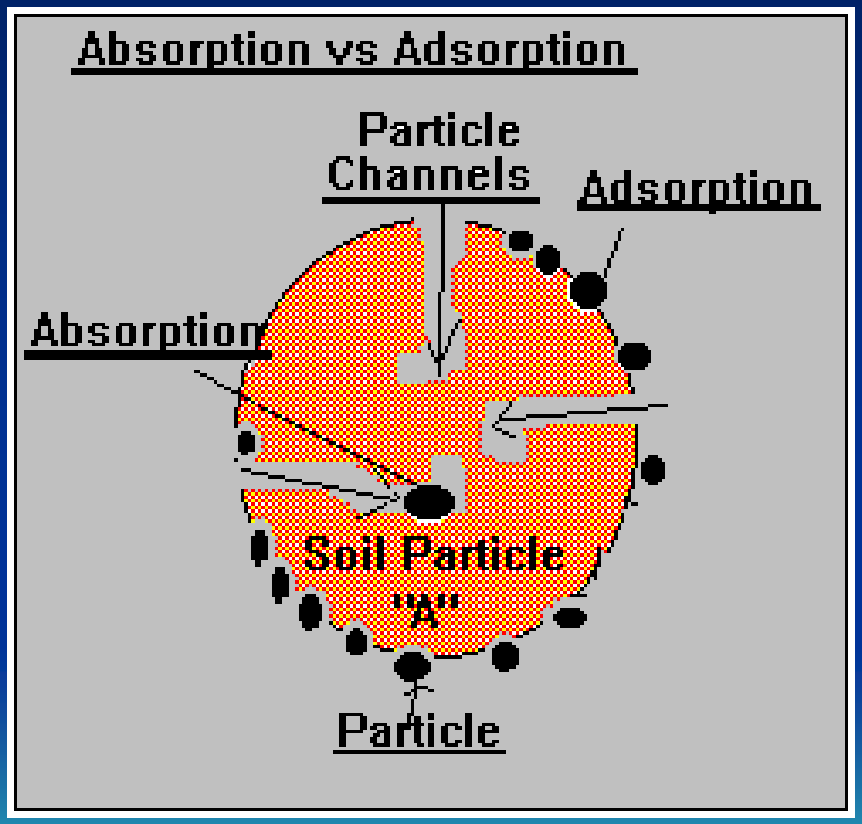
Today

- Basics of metal removal (probably TMI)
- Historical and current Regional Information
- Current Methods
- The Future

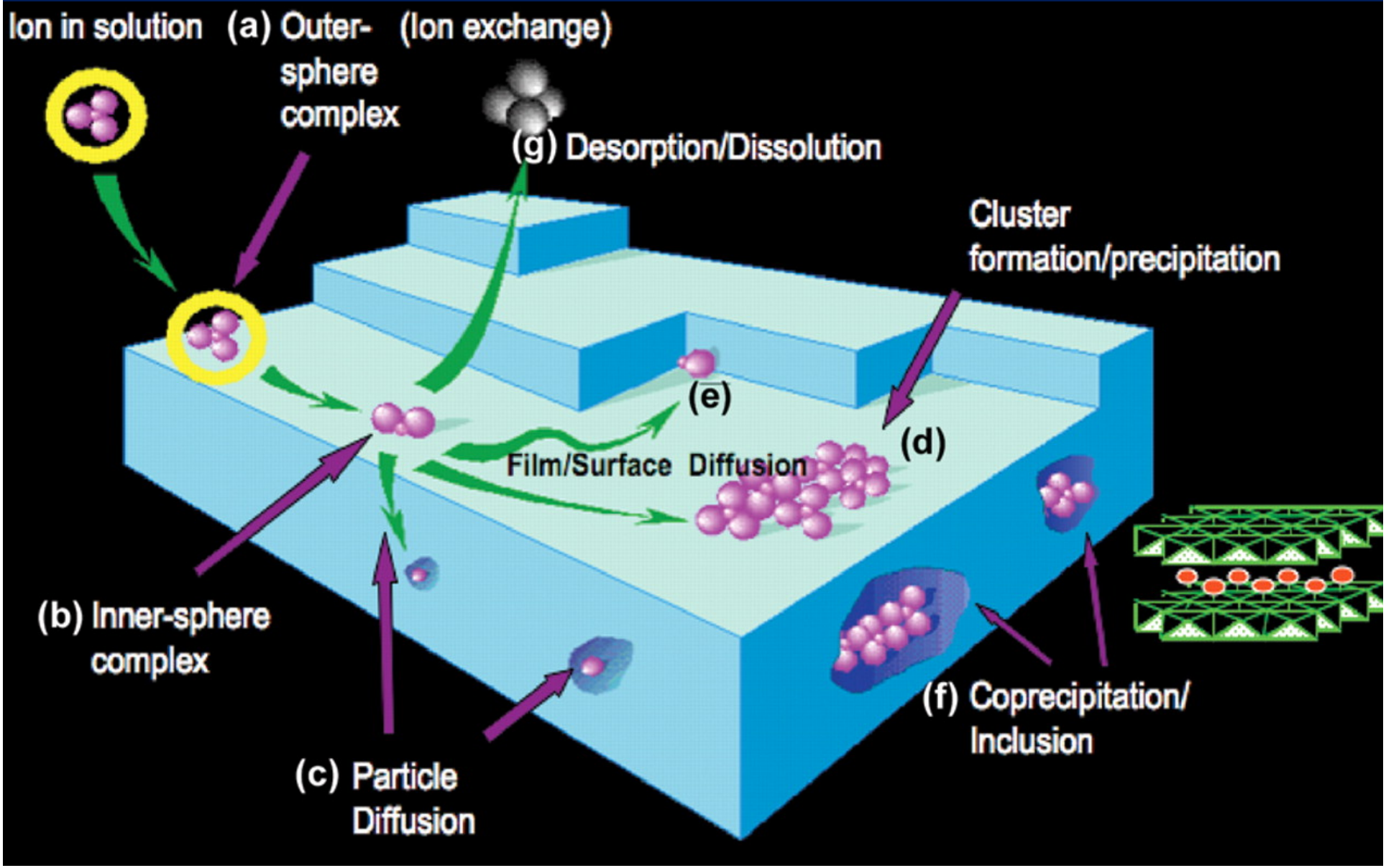
Definitions



Absorption vs Adsorption



Various removal mechanisms



Impact of Environmental Factors on Sorption Complex

Environmental factors such as:

- pH
- Surface loading
- Ionic strength
- Type of sorbent
- Time

All impact the type of sorption complex or product!

Impact of Environmental Factors on Sorption Complex

EXAMPLE:

TABLE 5.2. *Effect of I and pH on the Type of Pb Adsorption Complexes on Montmorillonite*[a]

I (M)	pH	Removal from solution (%)	Adsorbed Pb(II) (mmol kg^{-1})	Primary adsorption complex[b]
0.1	6.77	86.7	171	Inner-sphere
0.1	6.31	71.2	140	Mixed
0.006	6.76	99.0	201	Mixed
0.006	6.40	98.5	200	Outer-sphere
0.006	5.83	98.0	199	Outer-sphere
0.006	4.48	96.8	197	Outer-sphere

In general: Higher pH and Ionic Strength favor inner-sphere complexation

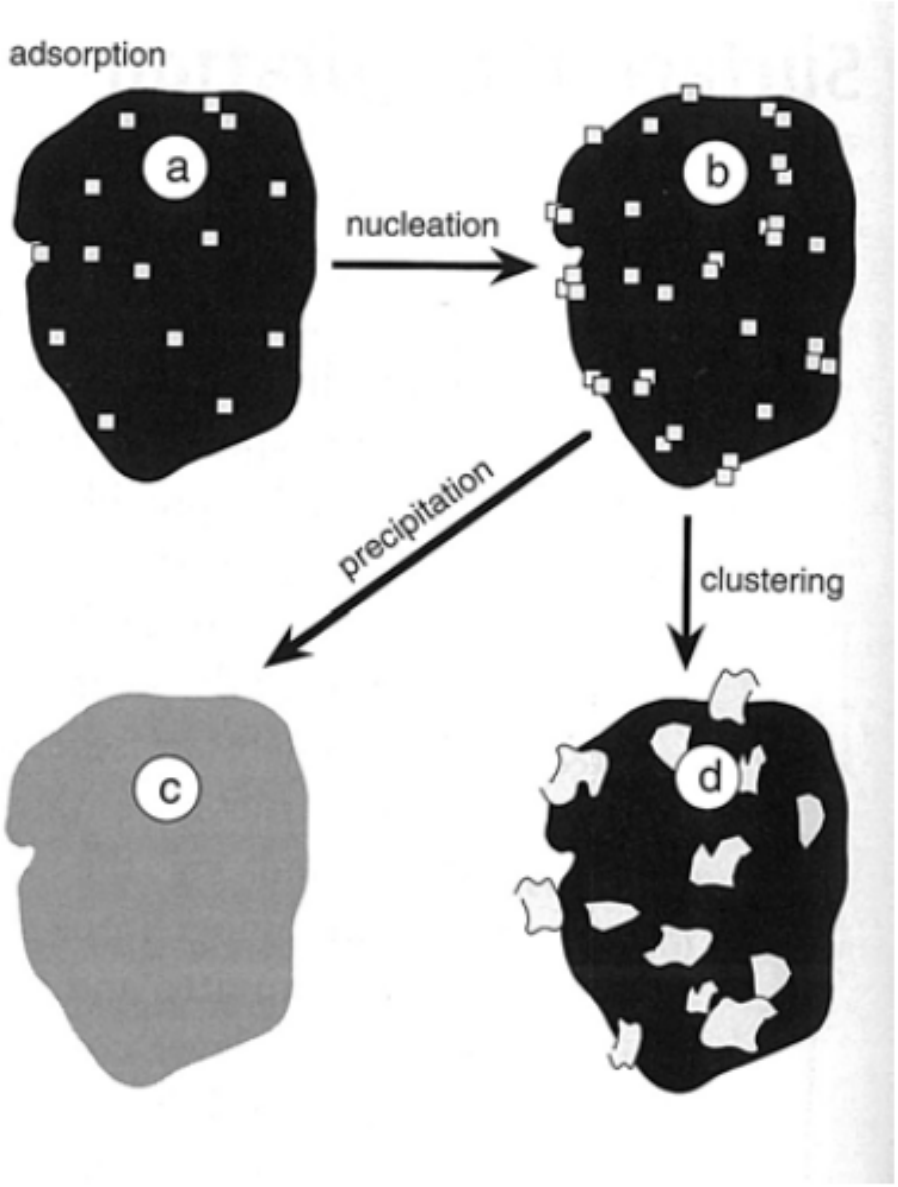
Surface Precipitation: Steps

A) At low surface coverage isolated site binding is the dominant sorption mechanism

B) With increased surface loading, metal hydroxide nucleation begins

C) Further increases in surface loadings results in surface precipitation

D) Or surface clusters (aggregates)

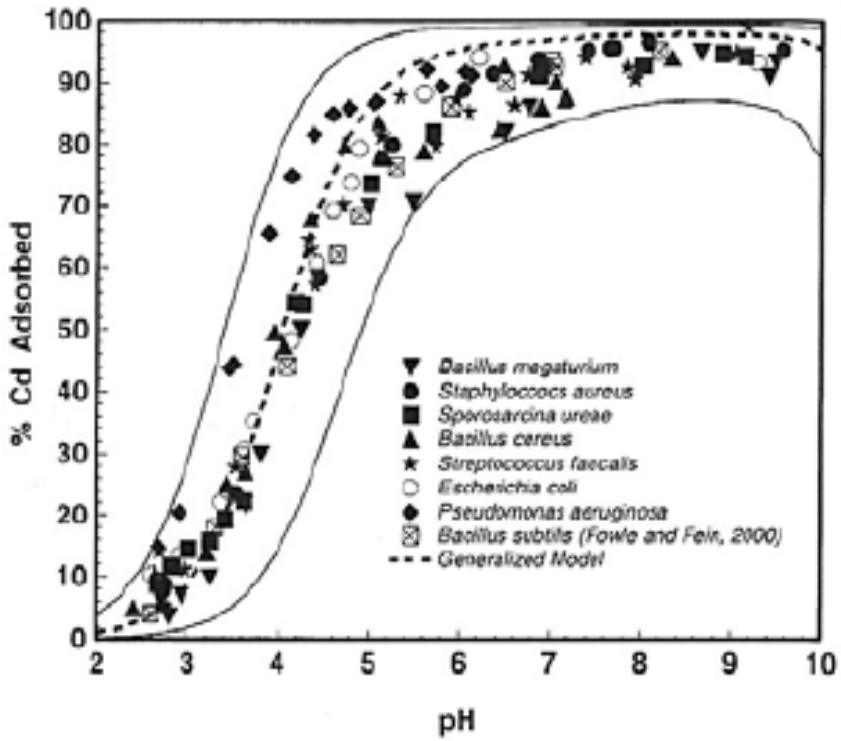


Sorption of Metal Cations

- Divalent transition and heavy metal cations are more strongly bound than the alkaline earth cations due to Inner-sphere complexation.

- Recently, studies of metals on bacterial surfaces have appeared.

- The figure shows data For Cd sorption on various Gram positive and gram ne-Gative bacterial species.



Historical changes in relative occurrence in biosolids

- 40 City Study (late 1970s)
  - Zn>>Pb>Cu>CrT>Ni>>Cd>Mo>Se>As>Hg
- 1988
  - Zn>>Cu>CrT>Pb>Ni>>Cd>Mo>As>Se>Hg
- 2006
  - Zn>Cu>>CrT>Pb>Ni>>Mo>Se>As>Cd>Hg

2006 Biosolids Data

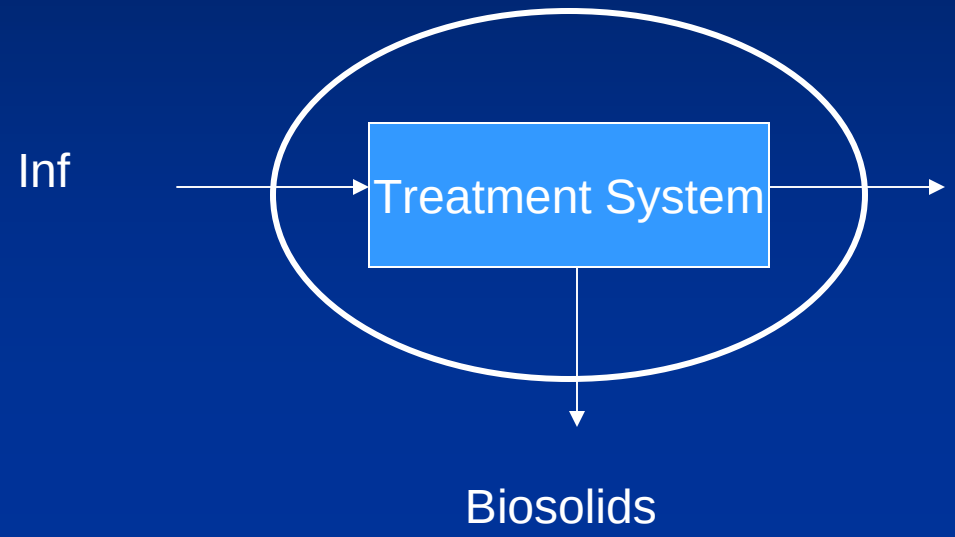
	CO 2006 mg/Kg[1]	R8 2006 mg/Kg[1]	National 2006 mg/Kg[2]	Typical Soils Conc. mg/Kg	503 Table 3 mg/Kg[5]
As	4	8	7	5.5[3]	41
Cd	2.5	3	3	0.27[4]	39
Cr	25	30	83	40[4]	N.R.
Cu	550	525	569	16.3[4]	1500
Pb	34	45	80	11.8[4]	300
Hg	0.8	2.3	1.3	0.05[3]	17
Mo	11	12	17	1-2	(75)[6]
Ni	18	24	53	15[4]	420
Se	8	10	7	0.29[3]	100
Zn	599	645	1029	54.3[4]	2800

Notes: [1]2006 Annual Reports summarized in US EPA Region 8 BDMS,[2] US EPA 2007, [3] As, Hg, Se are median values from Shacklette and Boerngen 1984; [4] Cd, Pb, Zn, Cu and Ni are background Great Plains means from Holmgren et al 1993; [5] US EPA 1993: [6]Table 1 Requirement; N.R. Not Required

Published Removal Efficiencies & Regional Examples

	Range (%)	Median (%)	Region 8 Example 1	Region 8 Example 2	Region 8 Example 3
As	11-78	45	21		
Cd	25-99	67			
Cr	25-97	82			
Cu	2-99	86	77	89	
Pb	1-92	61		81	
Hg	1-95	60		98	
Mo	-	-			
Ni	2-99	42			
Se	25-89	50		32	
Zn	23-99	79	80	51	

Basic Mass Balance



If not zero
Then error

$$Met_{\text{inf}} - Met_{Eff} - Met_{biosolids} = 0$$

Not everyone is this simple but I am sure we can make this work

Removal Importance
Review Your MAHL

- Health and Safety
- To understand your process
- To meet NPDES Effluent Limitations
- Prevention of Process Inhibition
- Prevention of Anaerobic Dig.* Inhibition
- Protection of Sludge Quality

Exceeding of MAHLs in the last 5 years for many metals

- As
- Cd
- Cr-Tot
- Cr VI
- Cu
- Pb
- Hg
- Mo
- Ni
- Se
- Ag
- Zn

Issues may be related to not able to balance the mass balance

- Number of samples used in analysis
- Statistics use to handle data
  - Detection limit issues
    - Too many MDL
    - Too high MDL used
- Analytical errors
- Flow measurement errors
- Biosolids production measurement errors
- Rounding errors

Where can we go from here

- Sustainability
  - Maintaining existing quality or improving
    - Biosolids
    - Effluent
- Understanding what is actually happening
- Ability to back check
  - Monitor and understand concerns
    - MAHL, safety factors etc

Where can we go from here

- Need to understand which analytical methods and frequency are required for appropriate/usable results
- Need to look at metal removals (as well as other parameters) on a mass balance basis
  - This may be more difficult with organics

Thank You

Questions??????????????????
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