Pollution Prevention: TRI Meets LCA

Using Life Cycle Assessment methods to assist in human and environmental health decision-making

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EPA Toxics Release Inventory (TRI)

- Emergency Planning and Community Right-to-Know Act (1986):
  - Section 313 – Creates the Toxics Release Inventory (TRI)
    - List of locations producing releases of certain hazardous chemicals
    - Quantities and management category
  - Incentivizes pollution prevention and reduction across numerous industries by:
    - Establishing a uniform reporting system by which peer companies may be compared
    - Generating highly local interest in hazardous chemical releases through public data availability

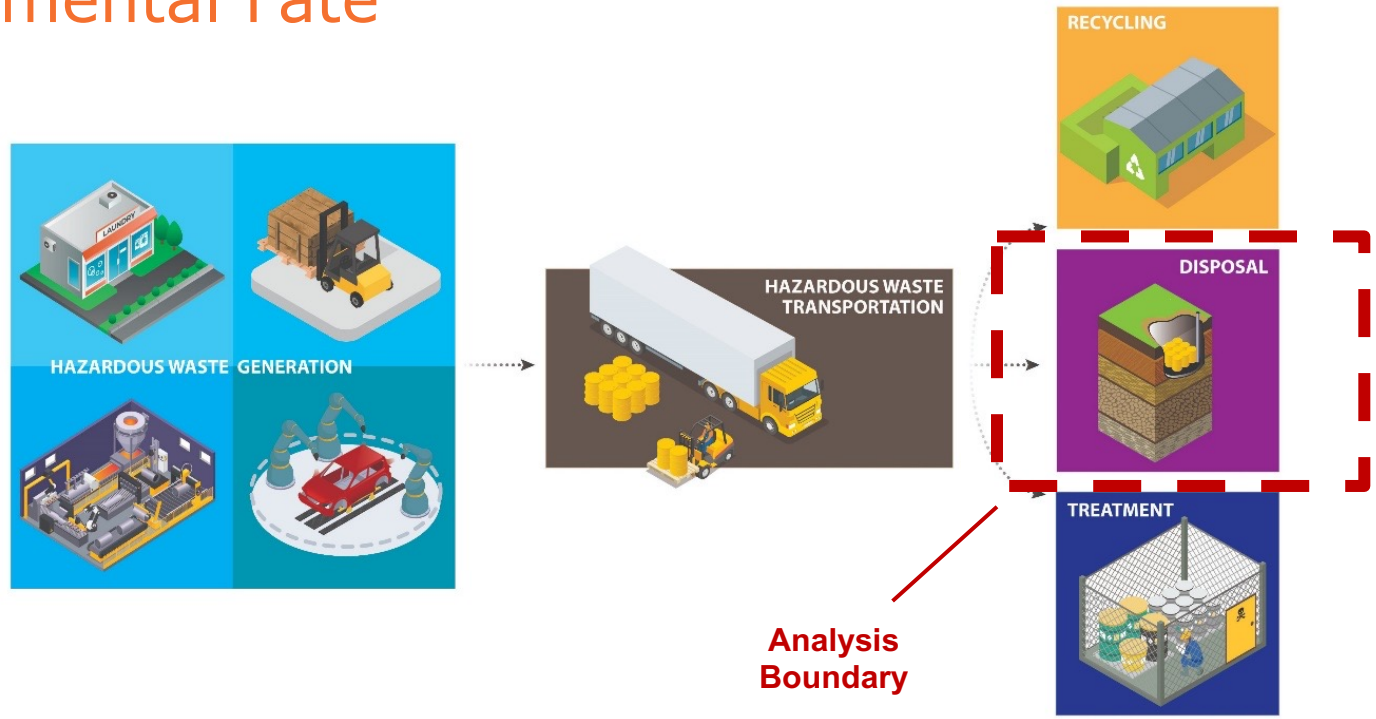
TRI National Analysis: Methods of Waste Management and Environmental Fate

Disposal (Direct Release):

- Air (Stack and Fugitive)
- Water

Other Disposal Methods:

- Landfill (RCRA "C" and others)
- Treatment & Release
- Underground Release
- Surface Impoundment



Source: EPA Hierarchy of

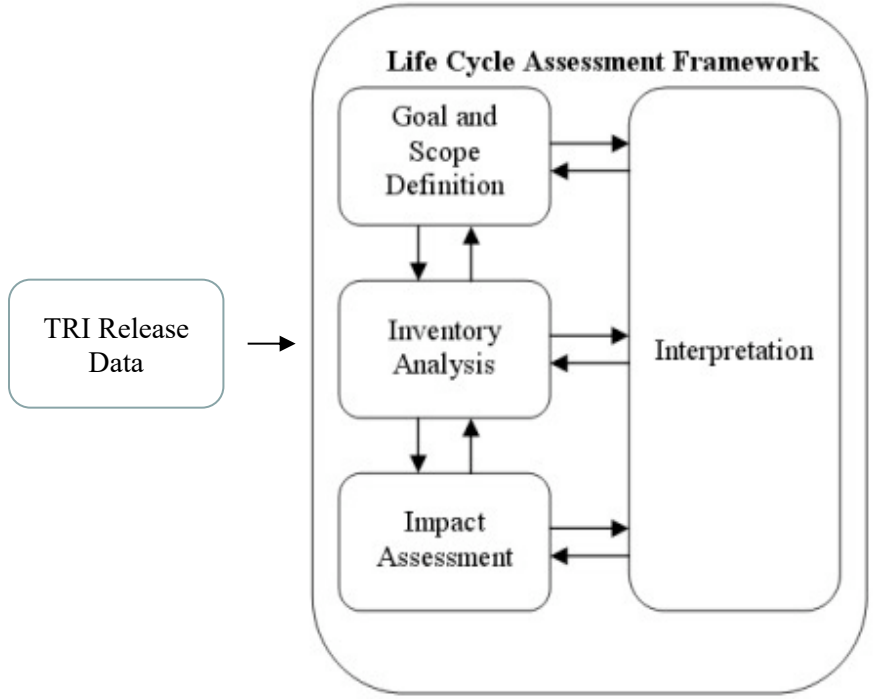
Life Cycle Assessment: TRI Data as an "Inventory"

Life Cycle Assessment (LCA) – Method for analyzing the potential impact of a product or service over its lifetime.

Borrowed from LCA:

- Inventory Analysis
- Impact Assessment

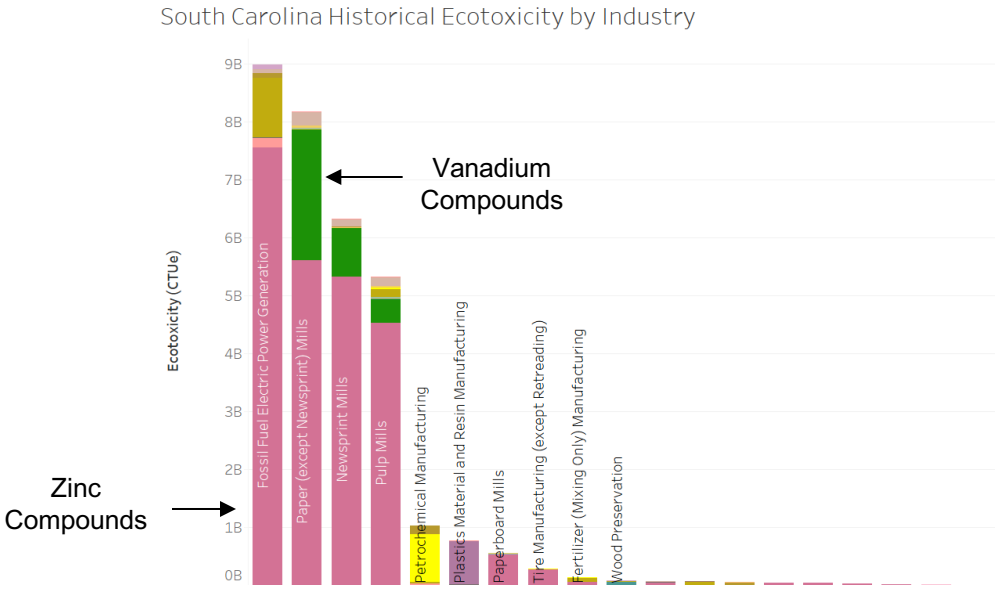
Using LCA tools, it is possible to assign impact values to chemical releases to air and water from manufacturing plants.

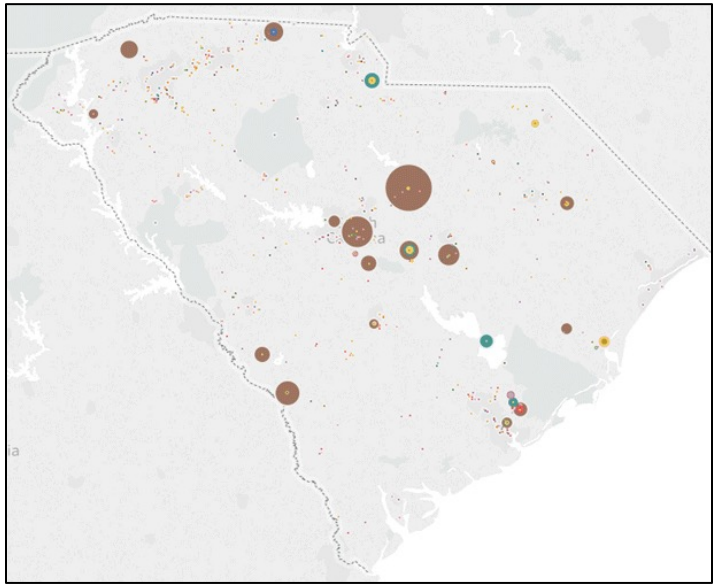


TRACI – Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts

Comparative Toxicity Unit (CTU_e) is proportional to the affected species in an aquatic ecosystem.

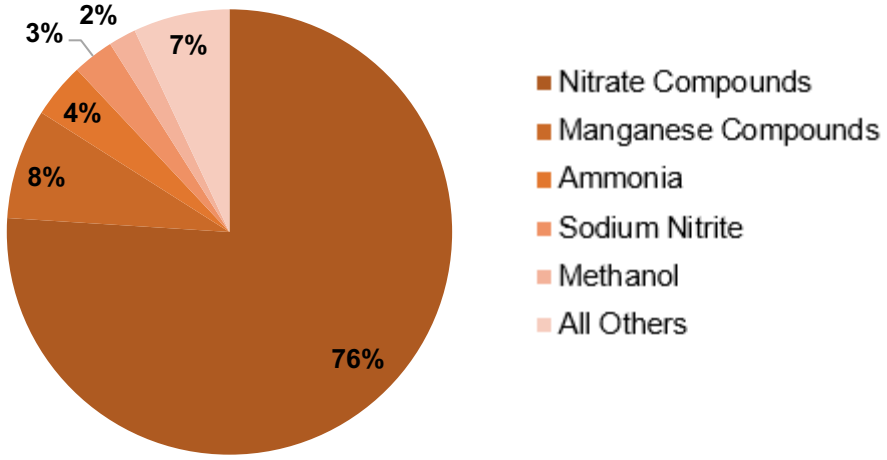
$$CTU_e = W(kg) * CF\left(\frac{CTU_e}{kg}\right)$$



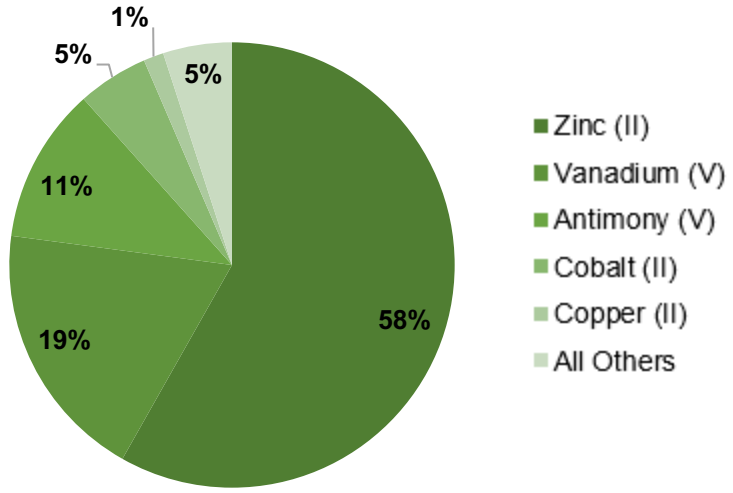


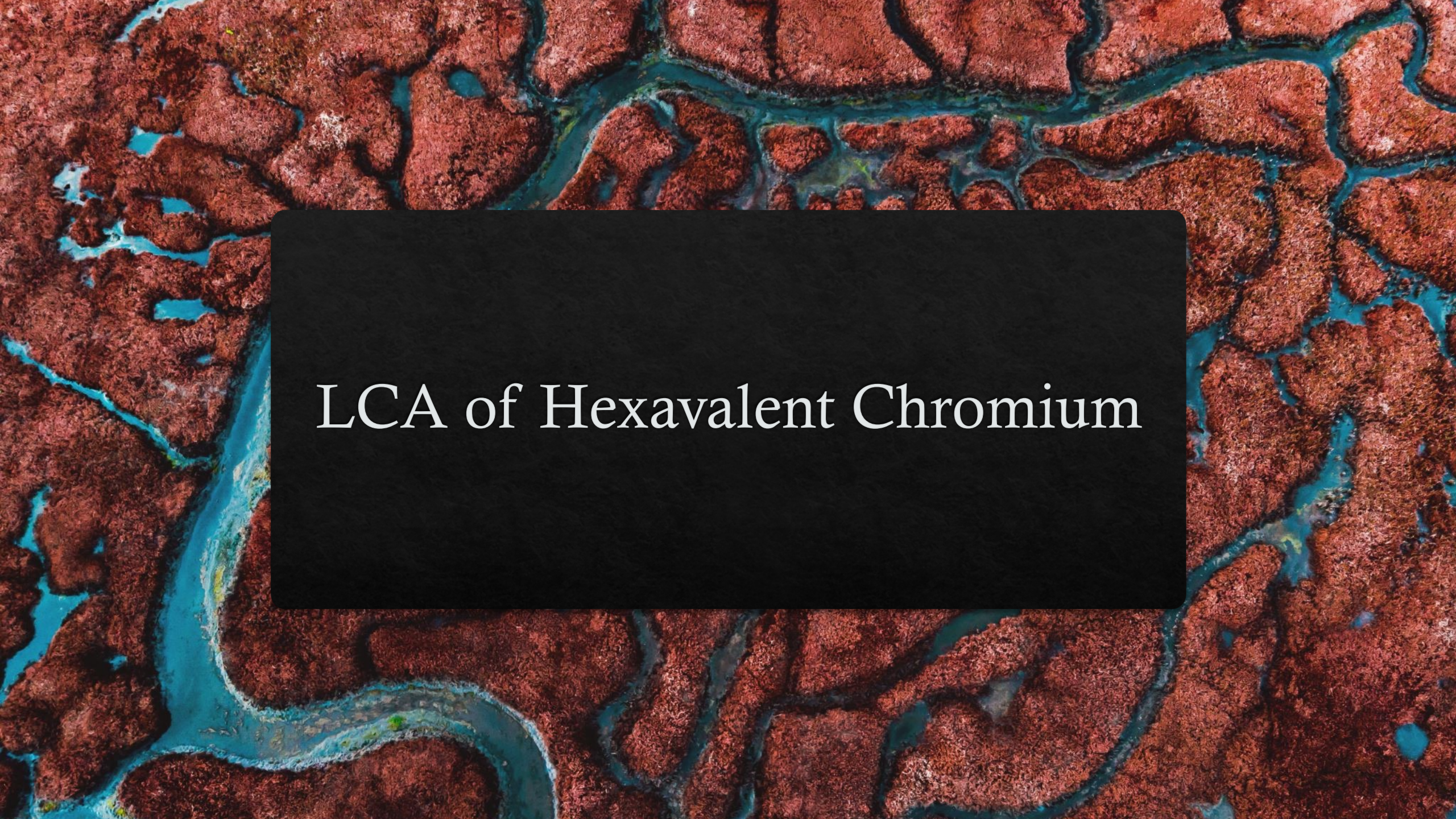
South Carolina Manufacturing Industry Chemical Releases to Water, 2016

Chemical Release Share by Mass



Chemical Release Share by Ecotoxicity




LCA of Hexavalent Chromium

Background: Why Hexavalent Chromium?

Extremely Toxic and Carcinogenic

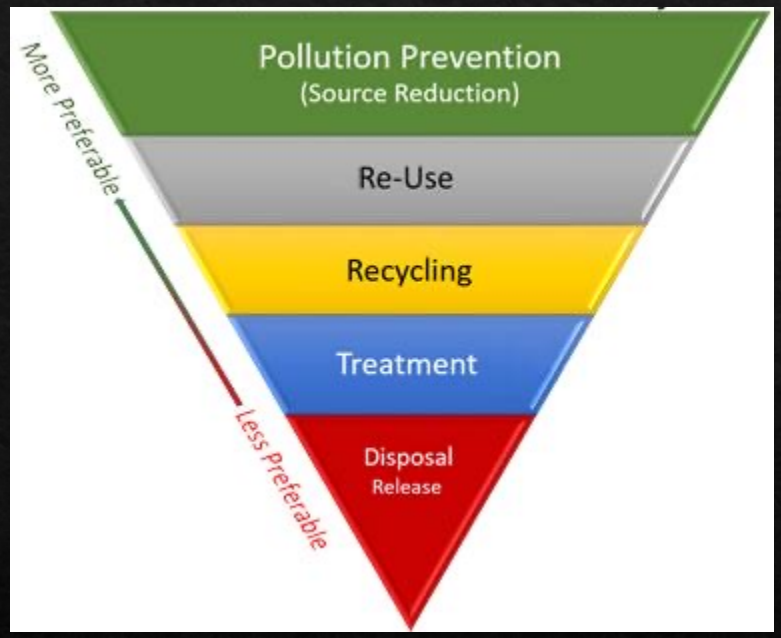
Anthropogenic Pollutant used for over 100 years

Goal

- Reduce Use and Emissions
  - Source Reduction
- Find sustainable alternative that is also economically beneficial
- Conduct LCA comparison

Environmental Protection Hierarchy

Pollution Prevention Act (1990)



Hexavalent Chromium - Cr(VI)

- Second most stable state of chromium
- Not commonly found in nature
- Soluble and mobile in the environment
- Typical forms of chromate (CrO_4^{-2}), chromic acid (H_2CrO_4), or dichromate ($Cr_2O_7^{-2}$)

Toxicity and Carcinogenicity

Direct links to GI damage, kidney failure, nasal septum perforation

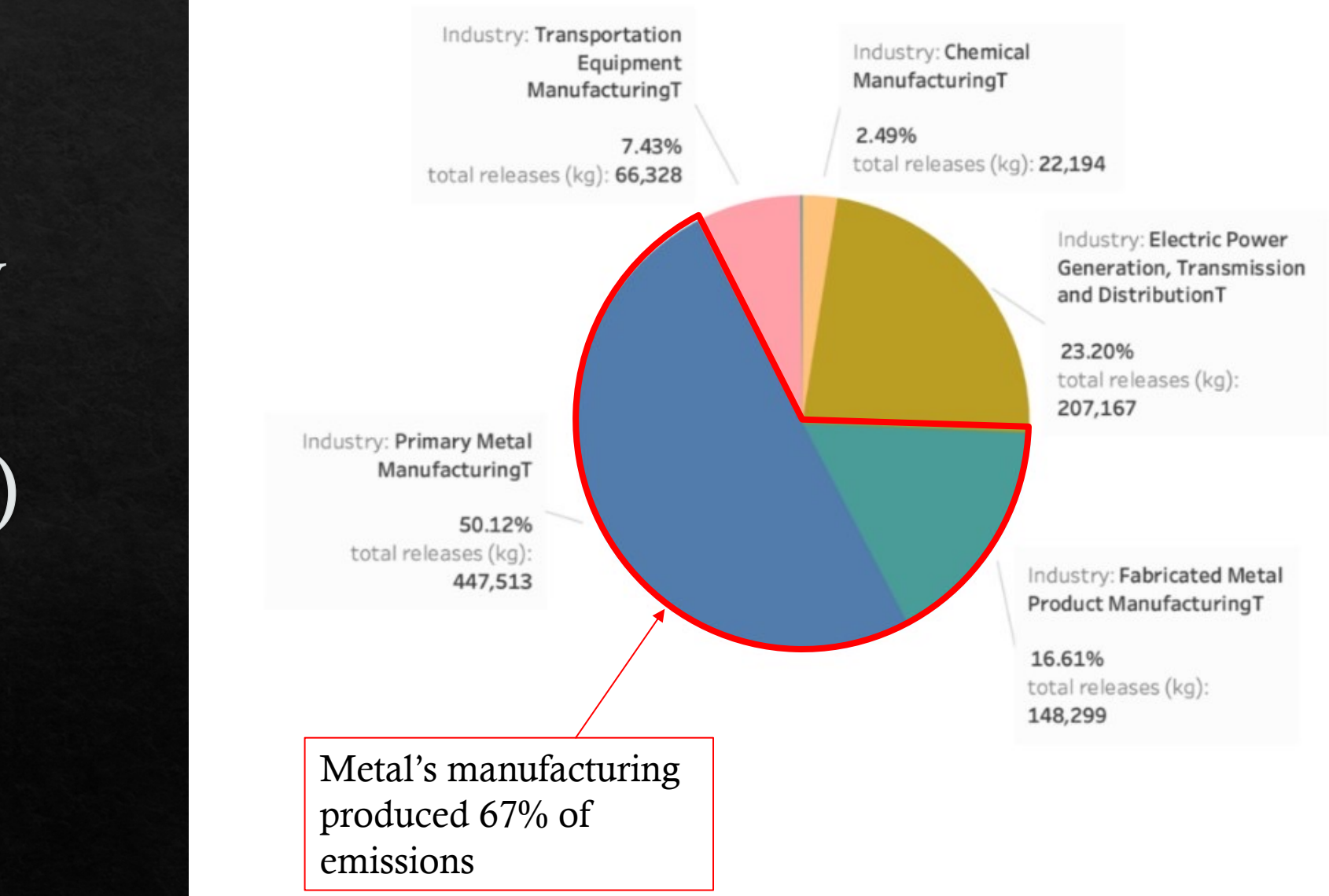
Skin ulcers, rashes blisters

Intestinal and lung cancers, DNA damage

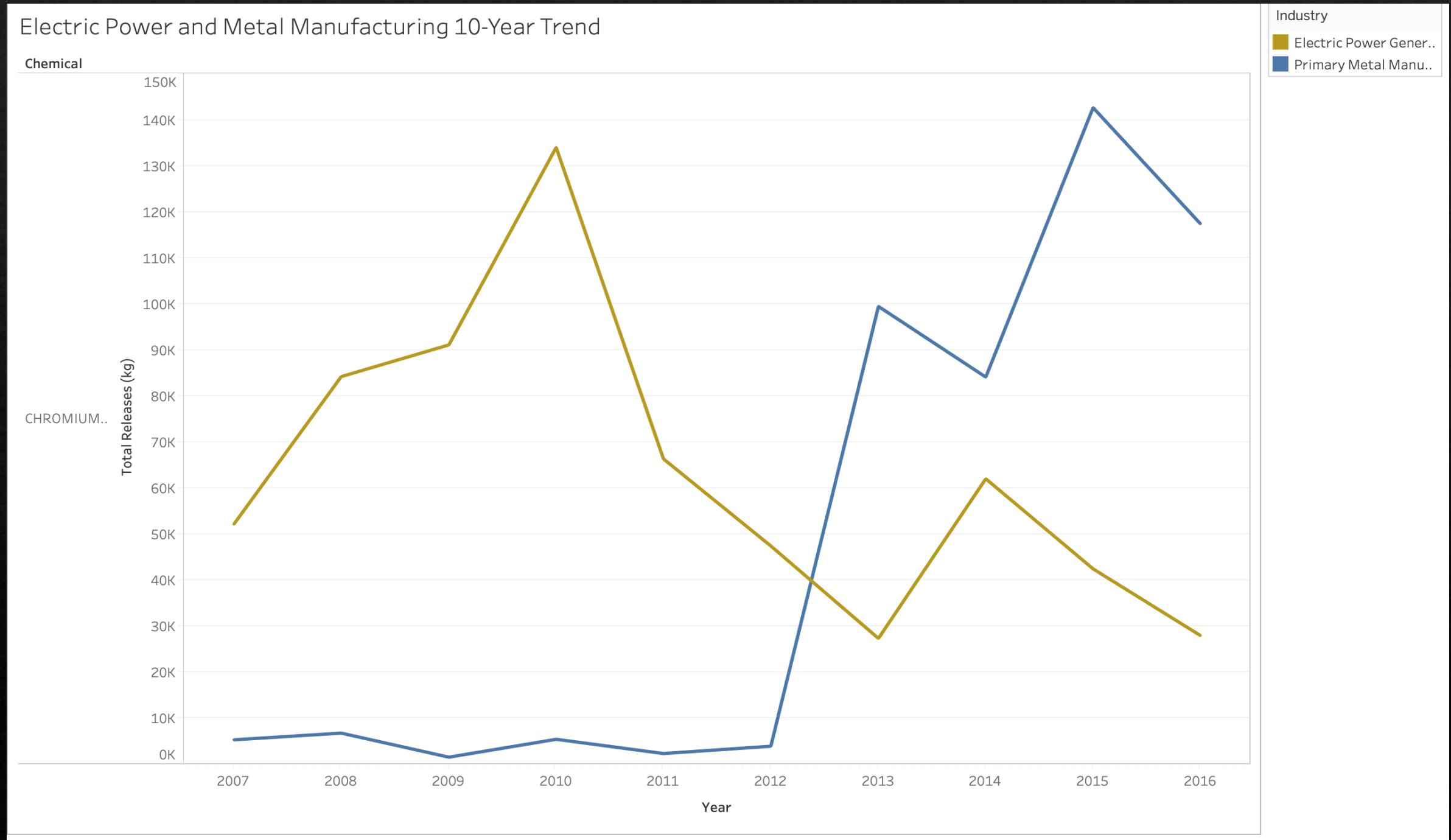
Government Restrictions

- Tightly regulated by EPA with Clean Air Act, Clean Water Act, and CRCLA
- In 2009, US Department of Defense (DoD) restricted the use of hexavalent chromium on military vehicles and weapons
- The EU's REACH – all industrial products that contain hexavalent chromium will be banned by 2024.

Chromium Total TRI Releases by Industry (2011-2016)



Metal's manufacturing produced 67% of emissions


Electric Power and Metal Manufacturing 10-Year Trend
Chemical
CHROMIUM..
Total Releases (kg)
150K
140K
130K
120K
110K
100K
90K
80K
70K
60K
50K
40K
30K
20K
10K
0K
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
Year
Industry
Electric Power Gener..
Primary Metal Manu..

Passivation

- Aluminum Anodizing and Chromium Conversion Coatings
- Cr(VI) creates oxide layer with metal to prevent corrosion
  - Improves conductivity and paint adhesion

Alternative

- Minimal toxicity
- Anti-corrosive performance
- Similar process costs
- Avoid trivalent chromium Cr(III)
  - Can oxidize to hexavalent in the environment
  - Causes impurities in oxide layer

Titanate (TiO_3)

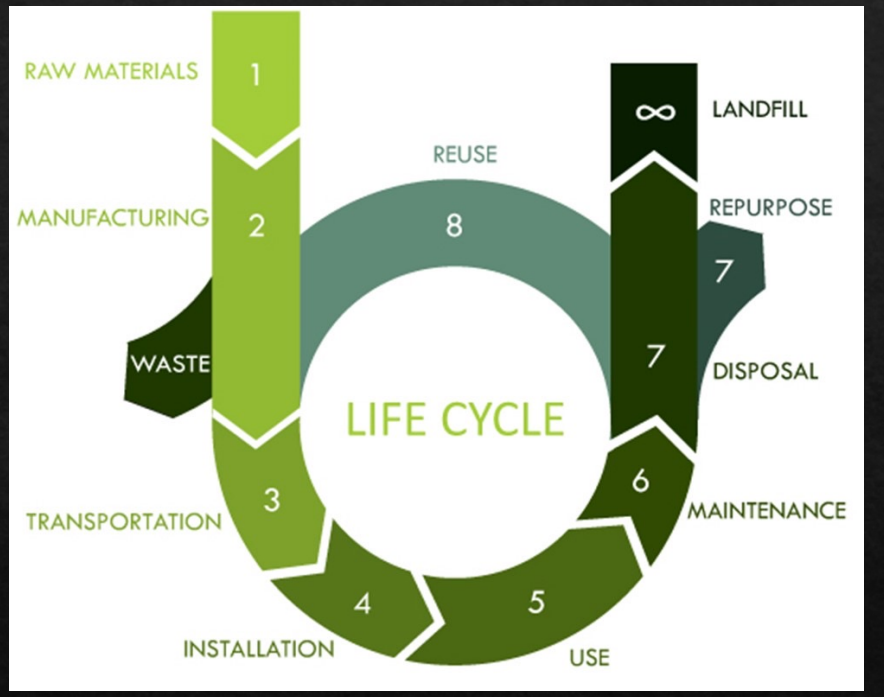
Minimally toxic or carcinogenic

Similar chemistry to chromium in aqueous media

Corrosion protection

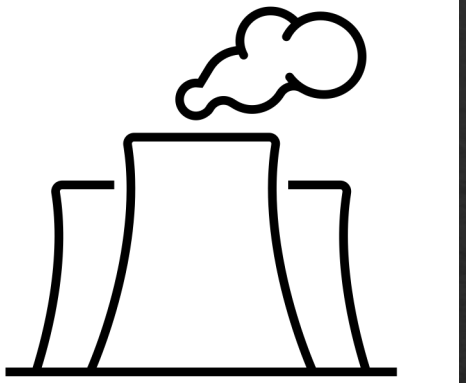
LCA Goal

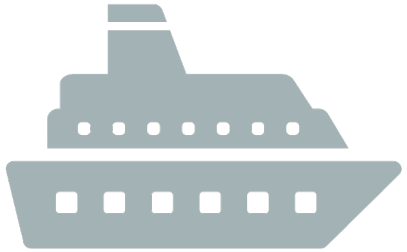
- A side-by-side "cradle to grave" analysis of hexavalent chromium and titanate to study overall energy and environmental impacts



Scope

- USA (South Carolina) focused
- No energy, capital, or water usage to make the manufacturing facilities/machines were calculated. Values were assumed to be equal.

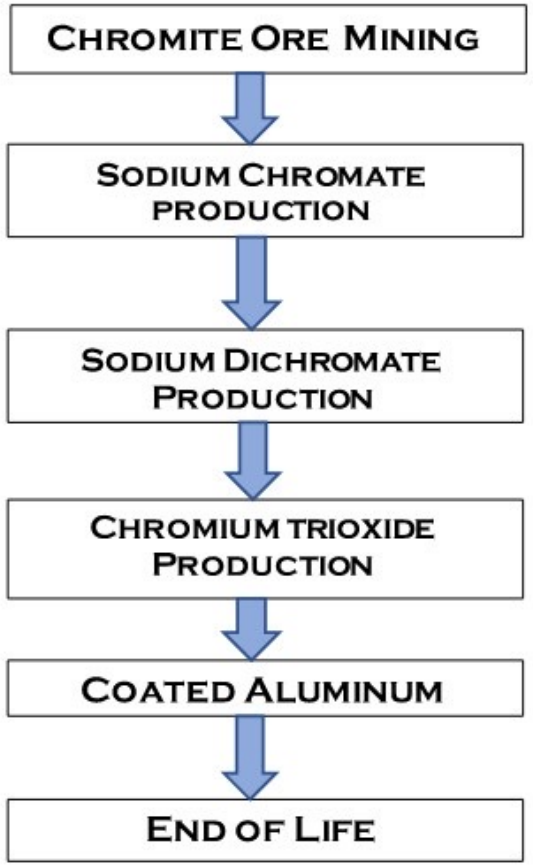


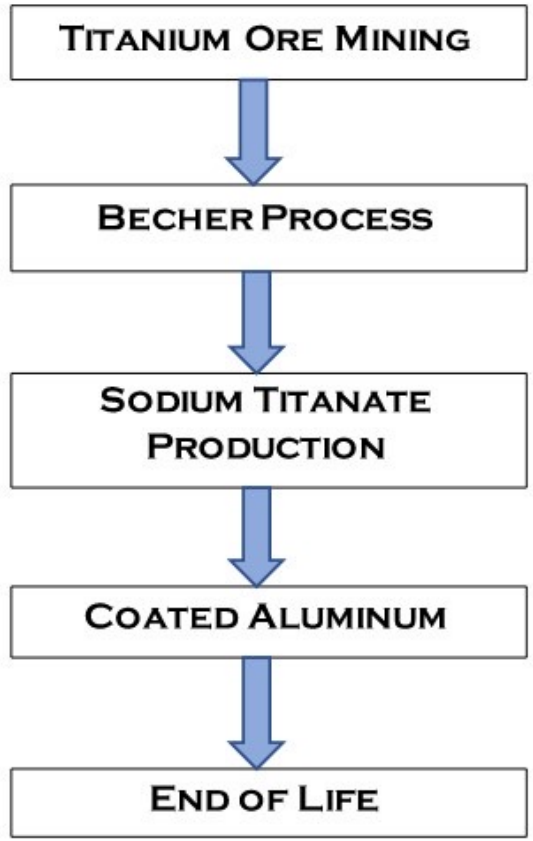


Assumptions

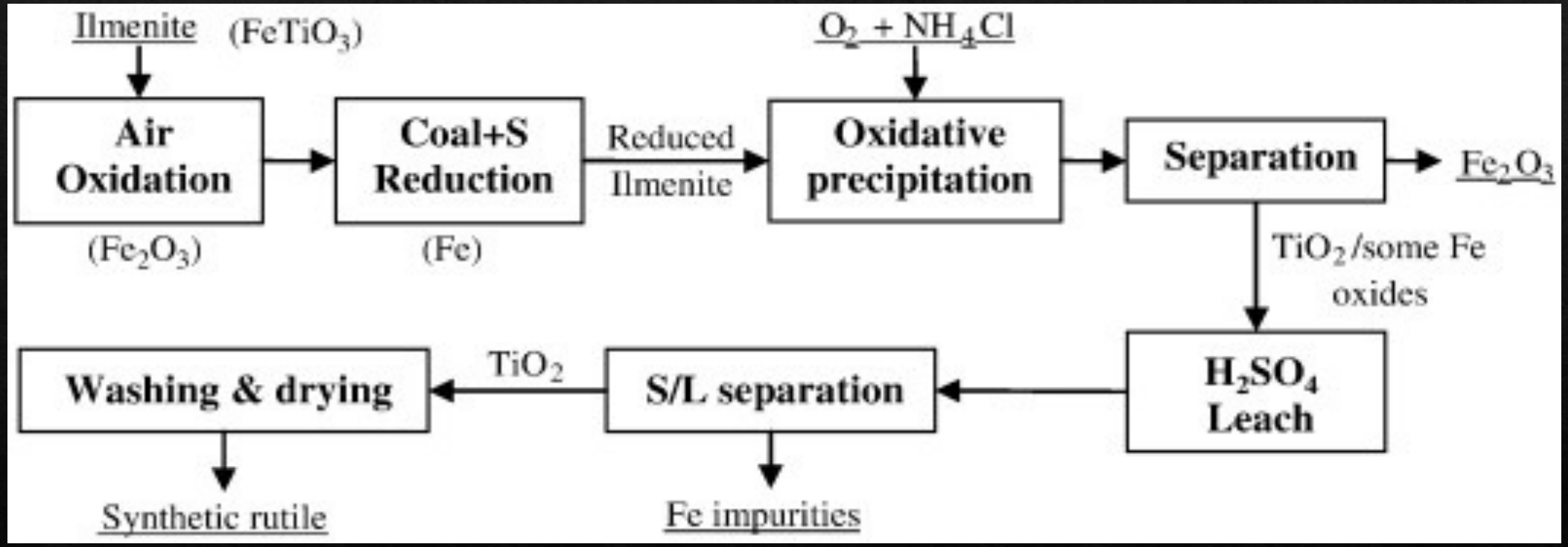
- Aluminum chosen as substrate for this LCA
  - Increasing ratio of aluminum to steel in industry (e.g., cars, aerospace)
- Energy/materials inputs and outputs
  - Electricity powered by gas
- Where are your materials sourced?
  - Chromium not mined in the US
  - Low grade titanium ore (ilmenite)

Process Flows





Becher Process



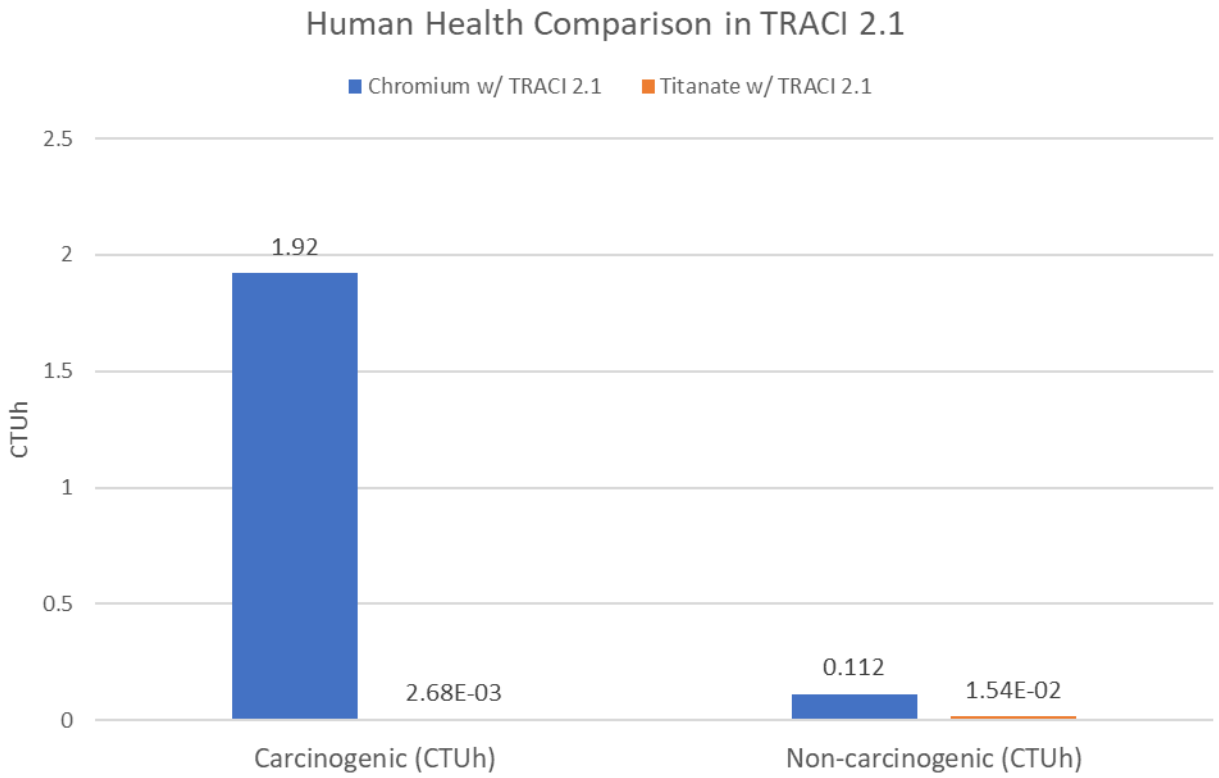
Impact Assessment

Focus on human health carcinogenic and non-carcinogenic and ecotoxicity

TRACI 2.1 impact analysis program

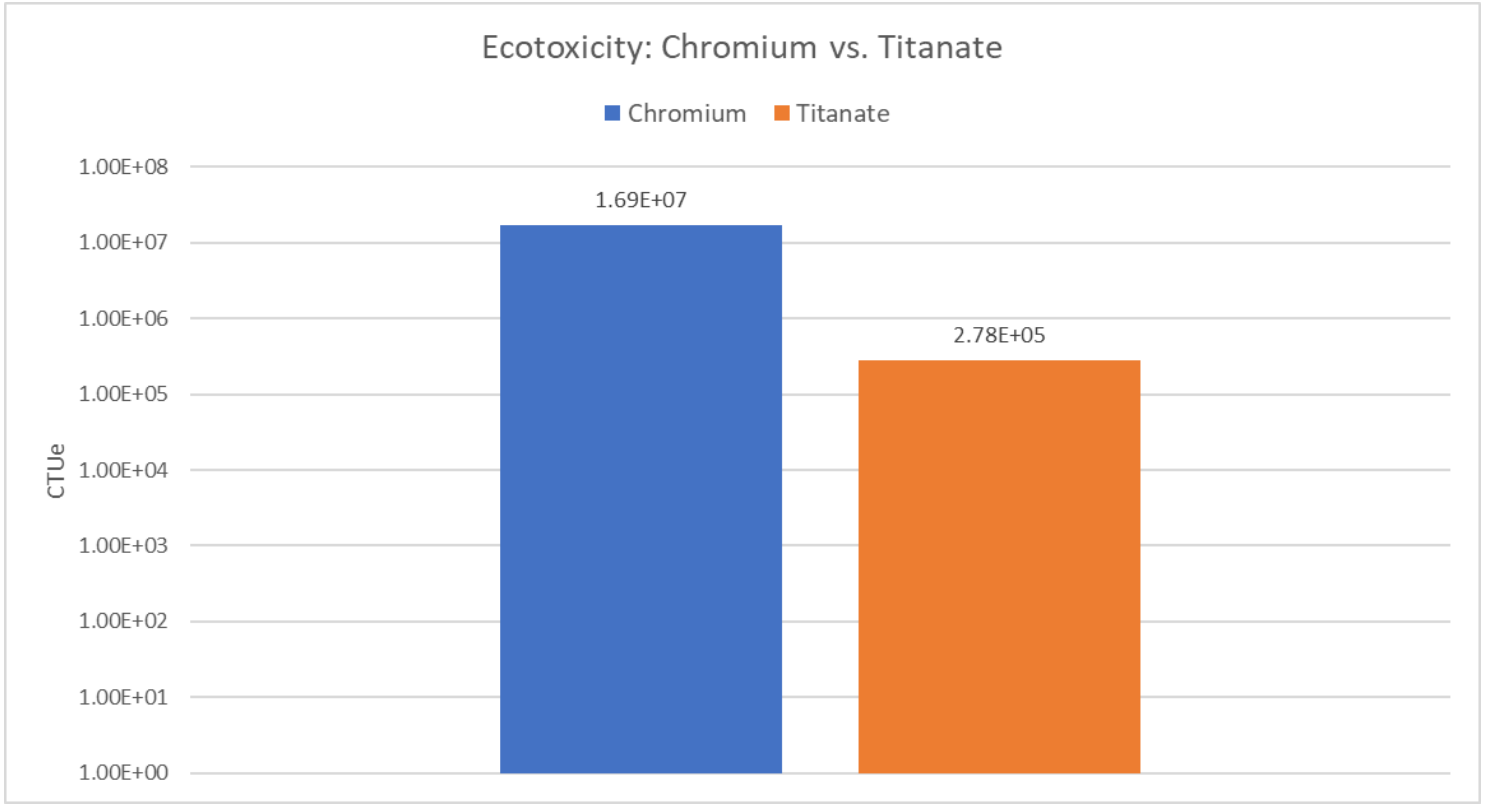
Human Health

CTUh = possible cases per kg contaminant



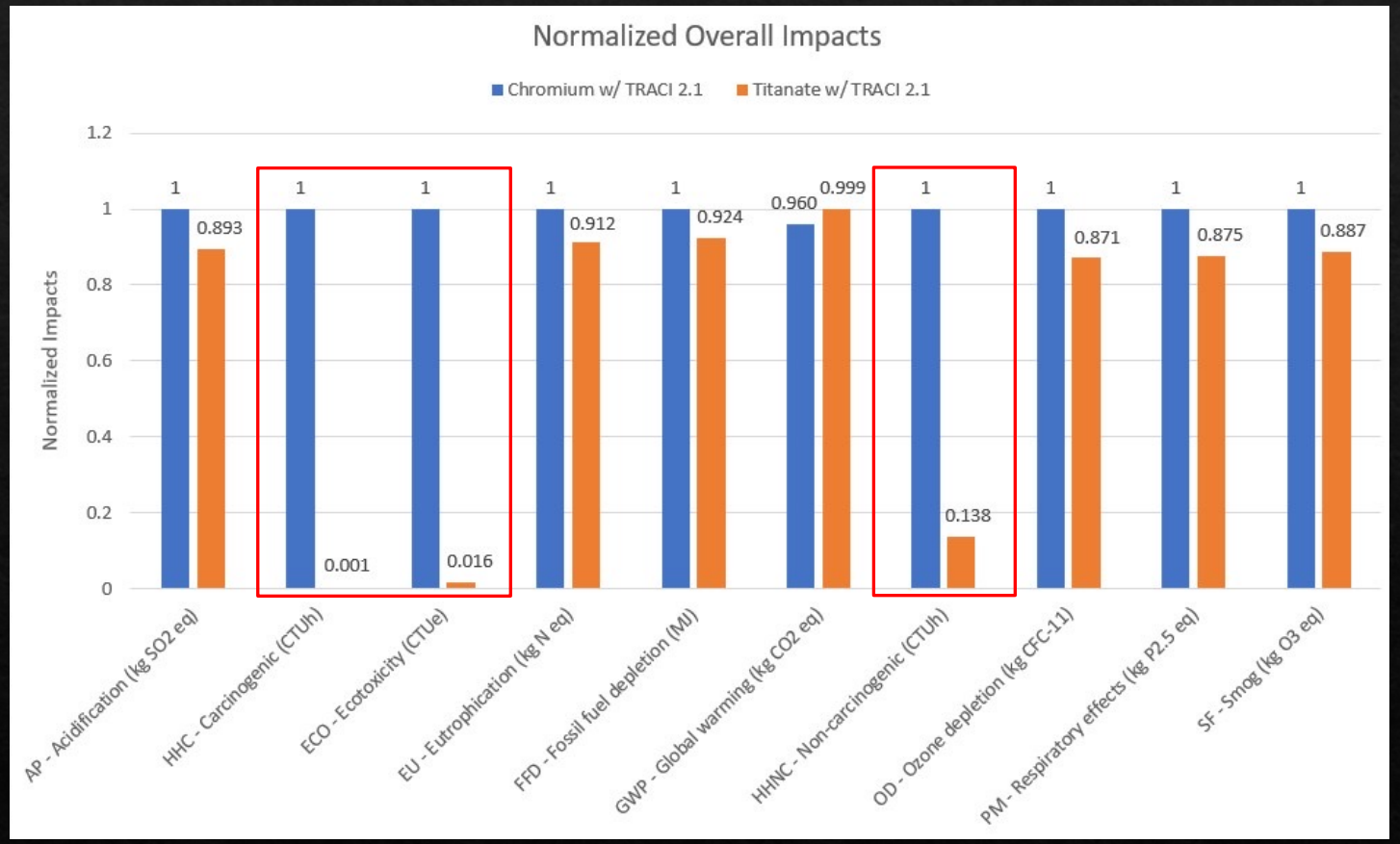
Ecotoxicity

CTUe = [fraction of potentially affected species (PAF) *m^3*day]/kg



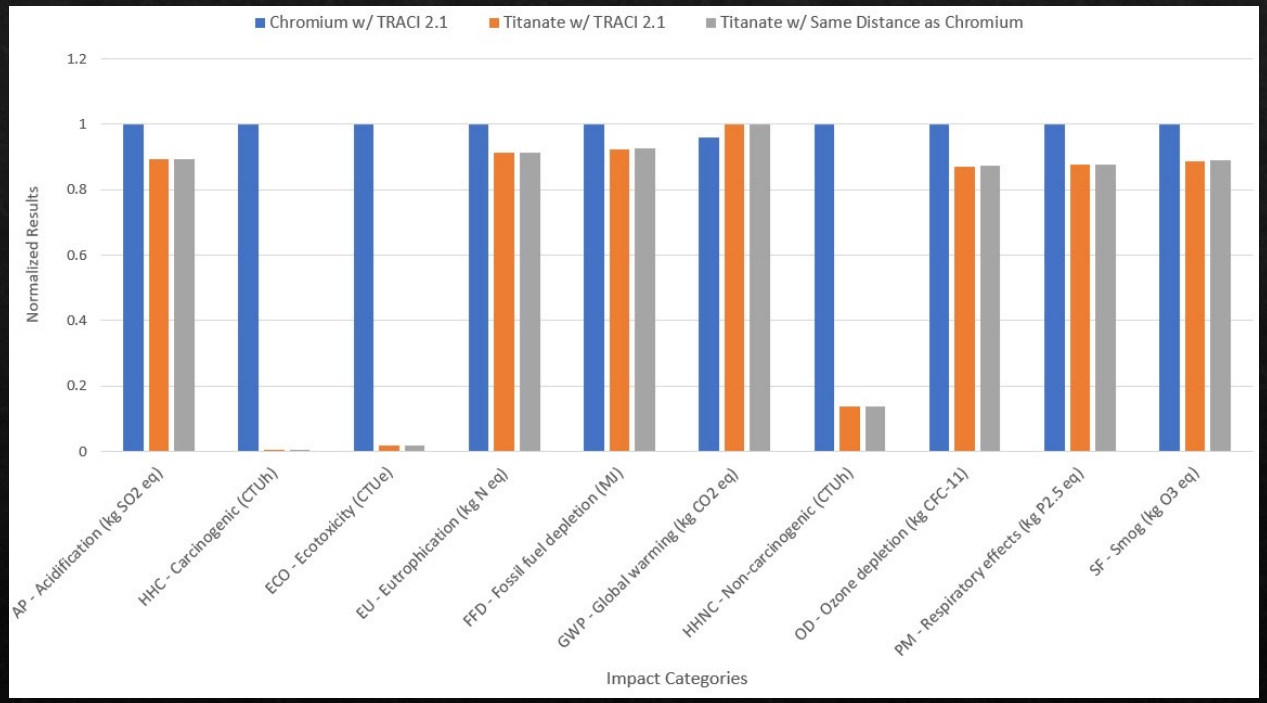
Overall Impact Comparison

Impact category	Chromium w/ TRACI 2.1	Titanate w/ TRACI 2.1
Acidification (kg SO2 eq)	708	632
Carcinogenic (CTUh)	1.920	0.00268
Ecotoxicity (CTUe)	1.69E+07	2.78E+05
Eutrophication (kg N eq)	238.5	217.6
Fossil fuel depletion (MJ)	1.73E+05	1.60E+05
Global warming (kg CO2 eq)	1.45E+05	1.51E+05
Non-carcinogenic (CTUh)	0.11162	0.01539
Ozone depletion (kg CFC-11)	0.01654	0.01440
Respiratory effects (kg P2.5 eq	62.31	54.55
Smog (kg O3 eq)	5749	5101

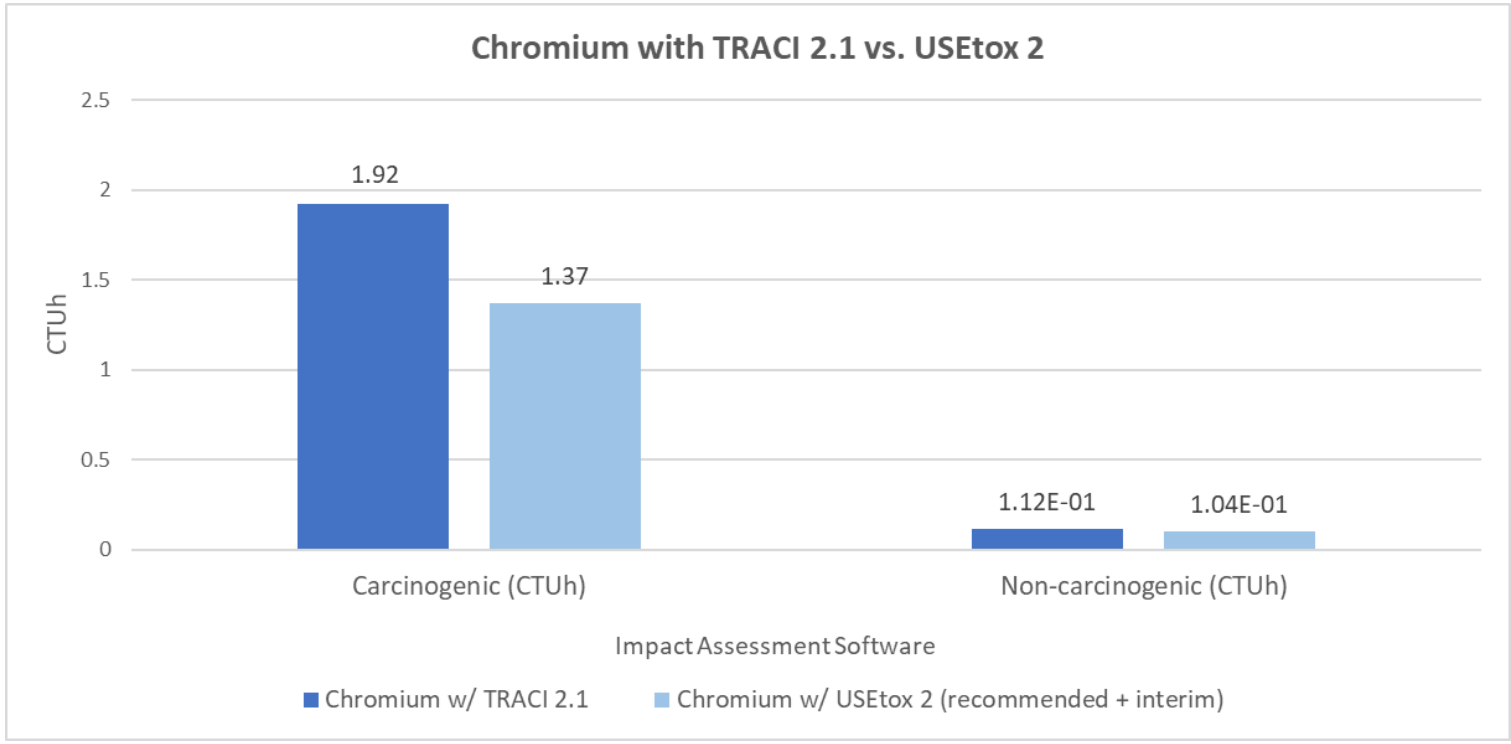


Sensitivity Analysis

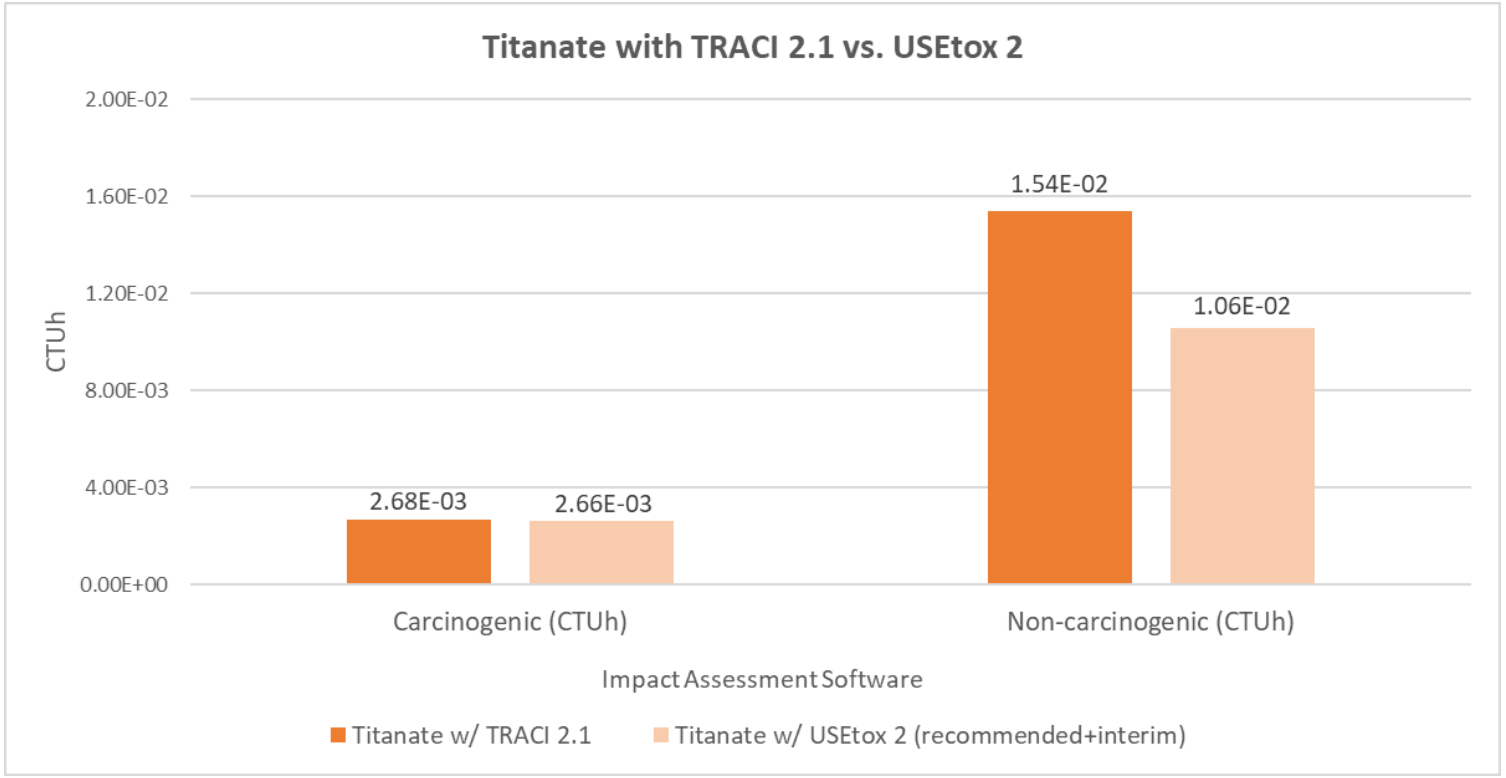
Impact category	Chromium w/ TRACI 2.1	Titanate w/ TRACI 2.1	Titanate w/ Same Distance as Chromium
Acidification (kg SO2 eq)	708	632	633
Carcinogenic (CTUh)	1.920	0.00268	0.00269
Ecotoxicity (CTUe)	1.69E+07	2.78E+05	2.79E+05
Eutrophication (kg N eq)	238.5	217.6	217.8
Fossil fuel depletion (MJ)	1.73E+05	1.60E+05	1.60E+05
Global warming (kg CO2 eq)	1.45E+05	1.51E+05	1.51E+05
Non-carcinogenic (CTUh)	0.11162	0.01539	0.01540
Ozone depletion (kg CFC-11)	0.01654	0.01440	0.01442
Respiratory effects (kg P2.5 eq	62.31	54.55	54.61
Smog (kg O3 eq)	5749	5101	5124



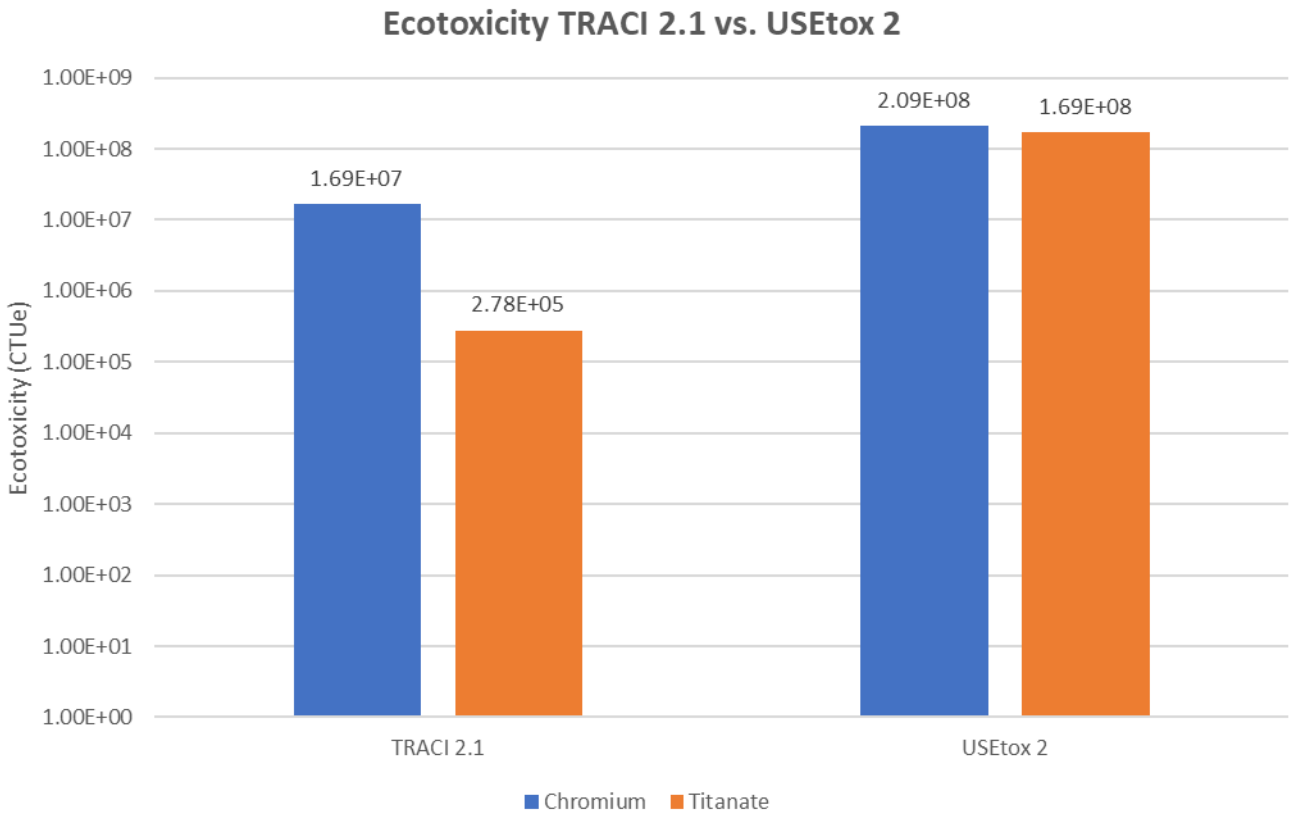
Chromium: TRACI 2.1 vs. USEtox 2



Titanate: TRACI 2.1 vs. USEtox 2



Ecotoxicity: TRACI 2.1 vs. USEtox 2



Winner: Titanate

Titanate process had lower impacts in every category except CO_2 emissions which was supported by literature

What's Next?

- LCA's are critical to a sustainable future because they allow users to envision a more efficient and environmentally safe alternative.
- Long-term benefits and cost savings from employee health, metal performance, environmental compliance, disposal.

Thank You!

Hexavalent Chromium in South Carolina

- EPA Toxic Releases Inventory (TRI) Data built into tableau

The Science Behind the Harm

- Cells confuse -2 charge of chromate and dichromate for Sulfates (SO_4^{-2})
- Reduced by compounds in the cell
- Damages proteins, lipids, and most importantly leads to DNA damage

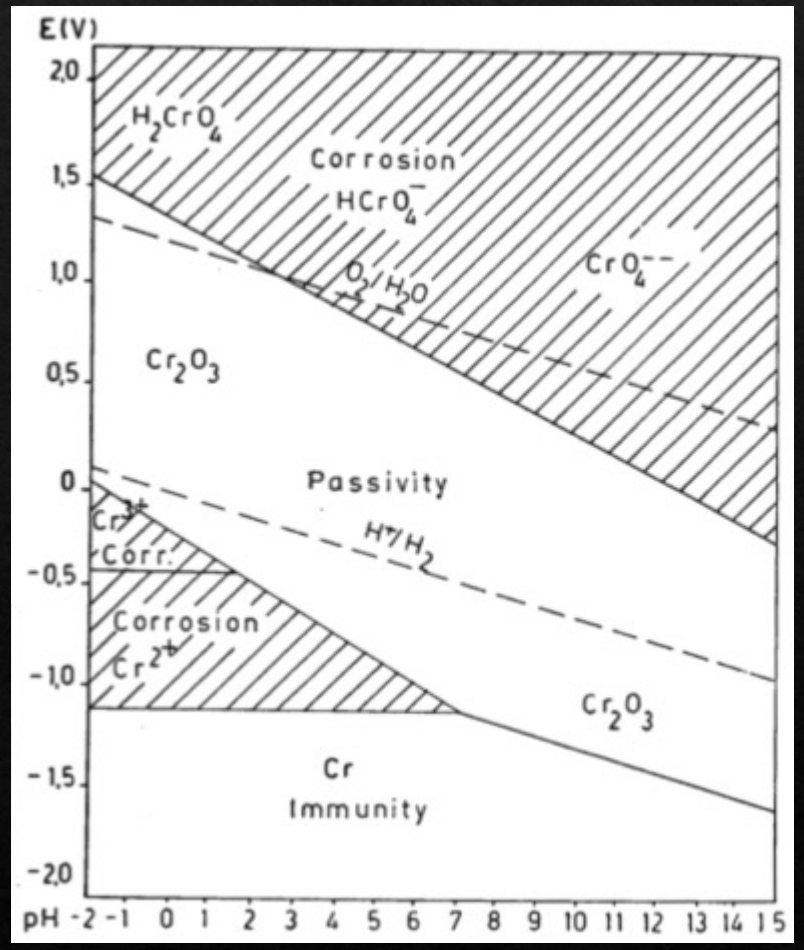
Main Industry Contributors

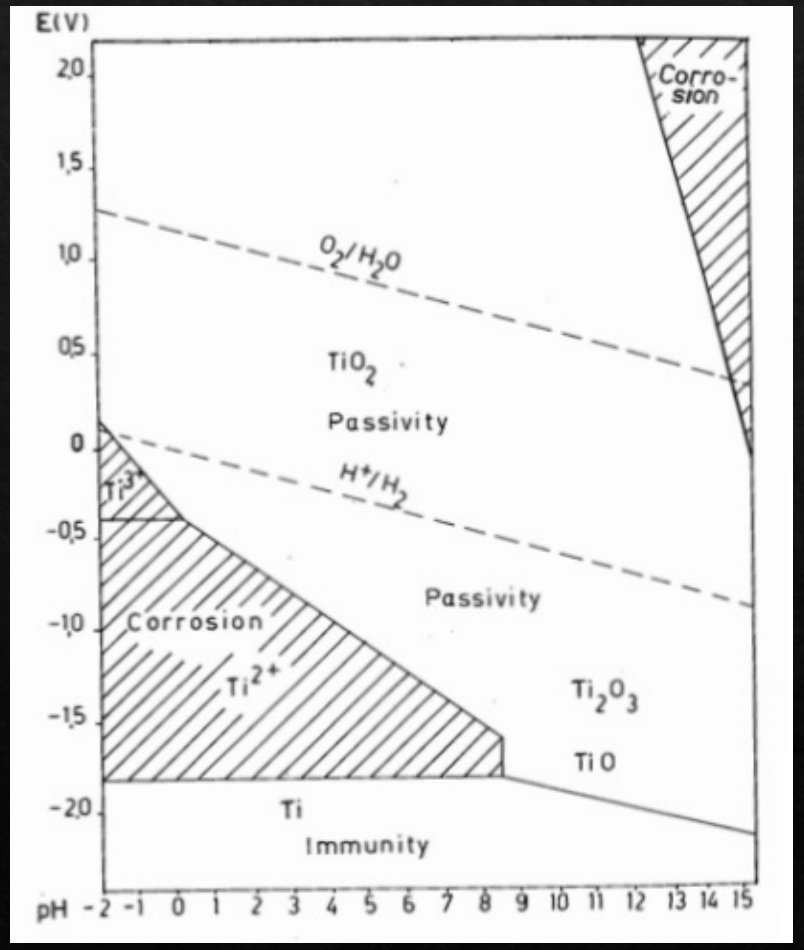
- Primary and fabricated metals production make up roughly 67% of hexavalent chromium emissions during study period
  - Study to focus on source reduction in metals production
- Electric power production was second largest producer but largely due to electricity produced by coal.

Trivalent Chromium Cr(III)

- Stable state of chromium found naturally in $FeCr_2O_4$ and $MgCr_2O4$ ores
- Trace element in many living organisms including humans
- Mostly insoluble and not mobile

Pourbaix Diagrams





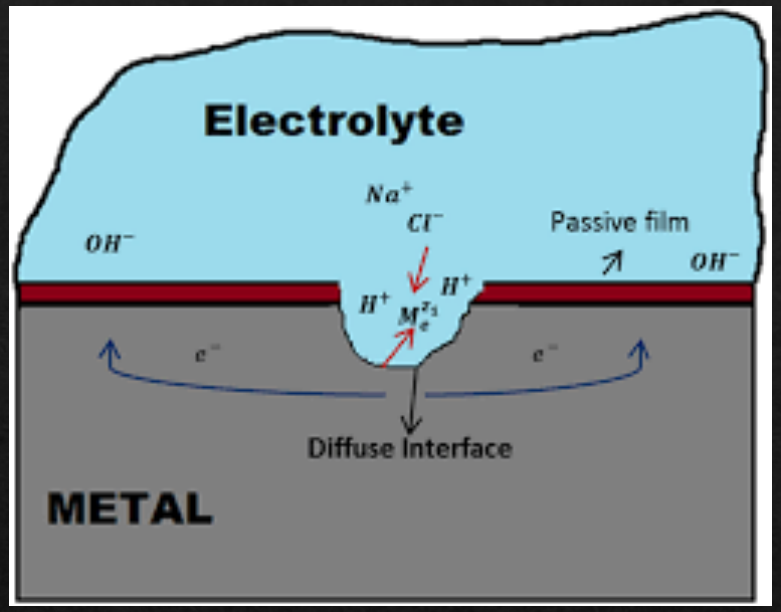
Pit and Crevice

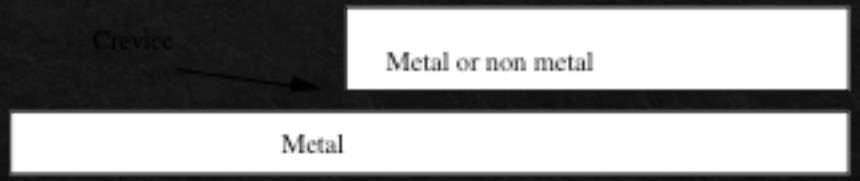
$O2 + 2H_2O + 4e^- \Rightarrow 4OH^-$

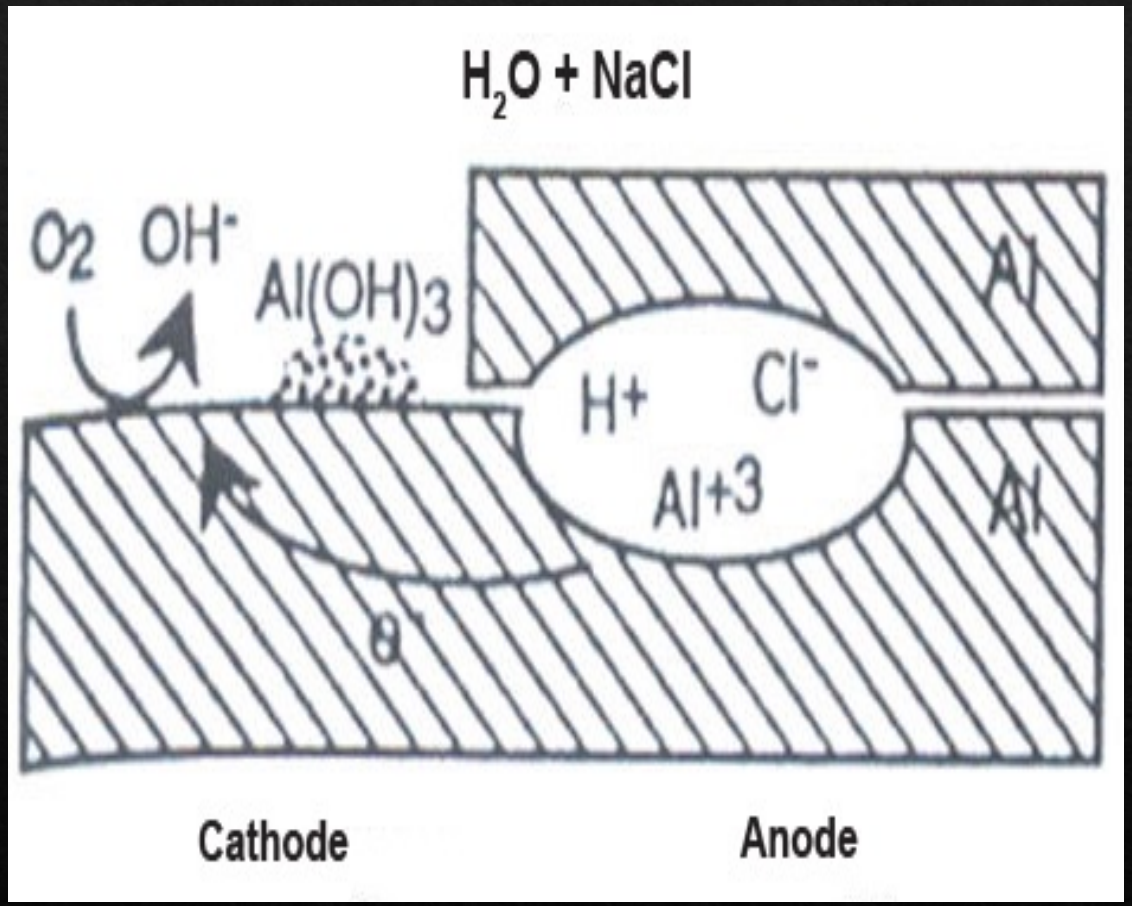
$Al \Rightarrow Al^{3+} + 3e^-$

$Al^{3+} + Cl^- \Rightarrow AlCl_3$

$AlCl_3 + 3H_2O \Rightarrow Al(OH)_3 + 3HCl$

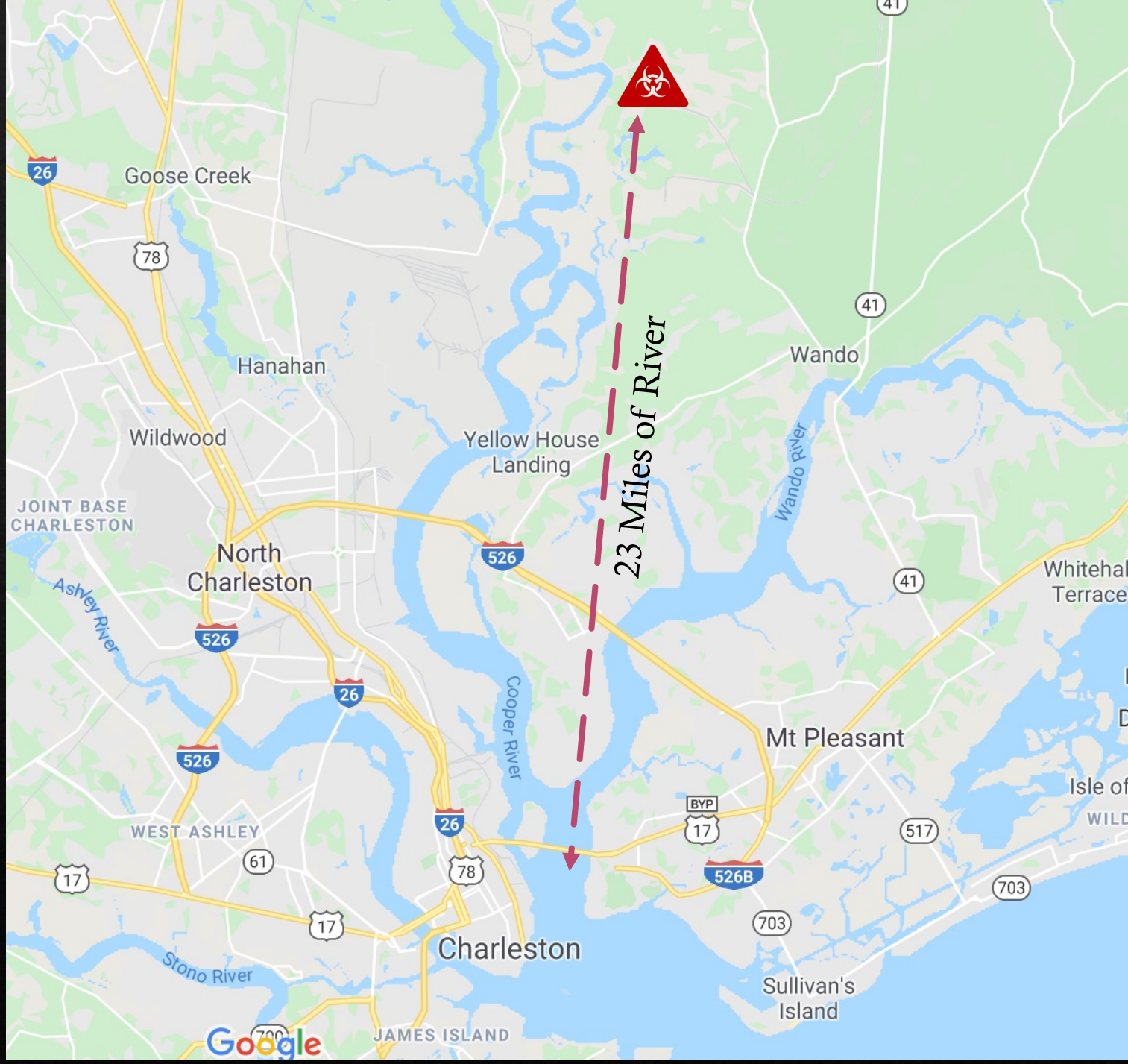

Electrolyte
Na^+
Cl^-
Passive film
OH^-
OH^-
H^+
H^+
H^+
M_e^{z+}
e^-
e^-
Diffuse Interface
METAL

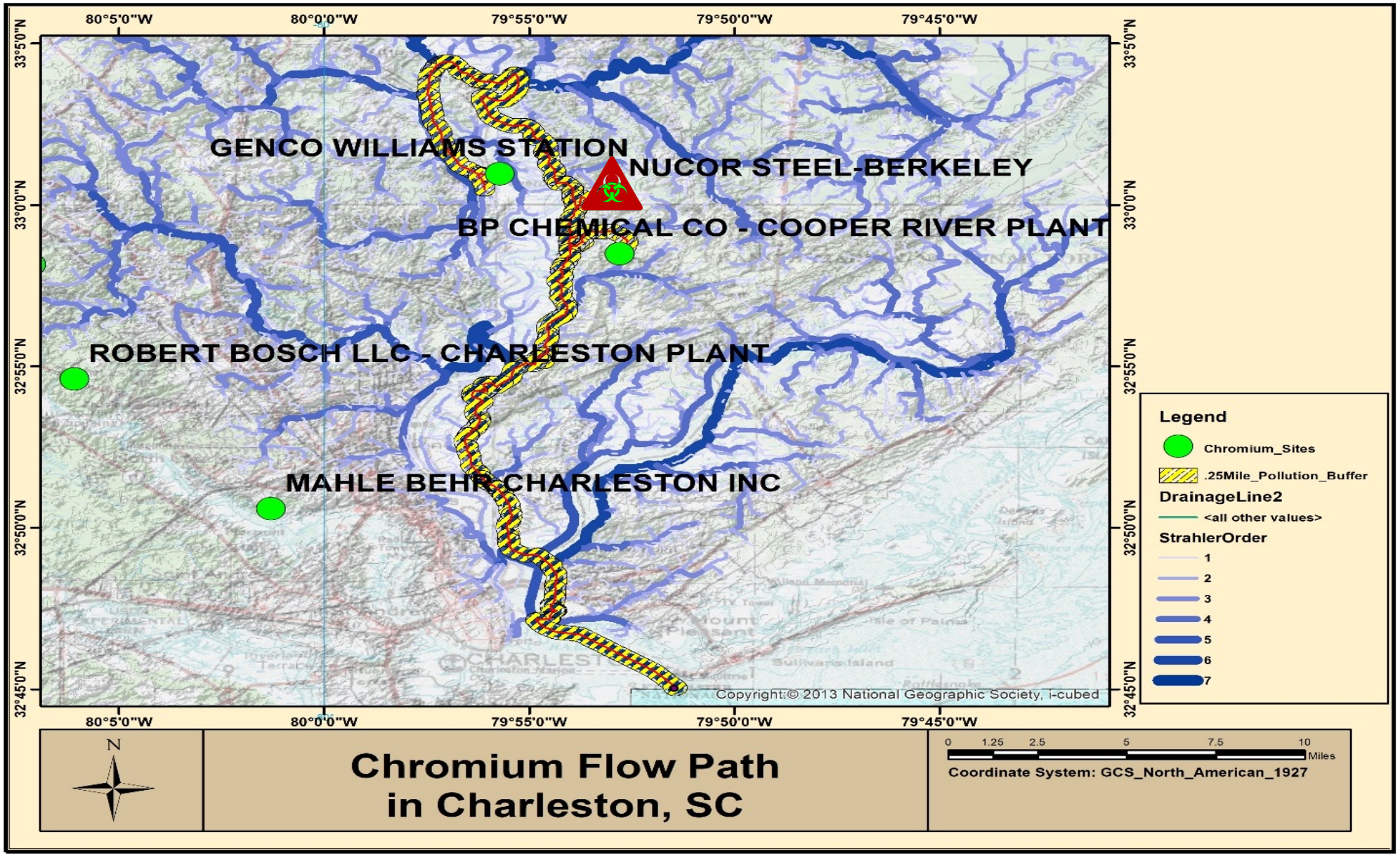

Crevice
Metal or non metal
Metal


$H_2O + NaCl$
O_2
OH^-
$Al(OH)_3$
Al
H+
Cl^-
Al+3
Al
θ
Cathode
Anode

Site Risk Assessment

Charleston Bay Area/ Cooper River




80°5'0"W
80°0'0"W
79°55'0"W
79°50'0"W
79°45'0"W
33°5'0"N
33°0'0"N
32°55'0"N
32°50'0"N
32°45'0"N
GENCO WILLIAMS STATION
NUCOR STEEL-BERKELEY
BP CHEMICAL CO - COOPER RIVER PLANT
ROBERT BOSCH LLC - CHARLESTON PLANT
MAHLE BEHR CHARLESTON INC
Copyright:© 2013 National Geographic Society, i-cubed
Legend
Chromium_Sites
.25Mile_Pollution_Buffer
DrainageLine2
<all other values>
StrahlerOrder
1
2
3
4
5
6
7
N
Chromium Flow Path
in Charleston, SC
0 1.25 2.5 5 7.5 10
Miles
Coordinate System: GCS_North_American_1927

Risk Analysis Goals

- Estimate concentration in river with semi-infinite step emissions vs. instantaneous emissions
  - Drinking water link
- Calculate dose and risk from drinking
- Calculate dose and risk from consuming fish

Charleston Water System Chromium-6 testing from 2013-2015

Chromium-6 Testing Summary

California's Public Health Goal for chromium-6 is 0.02 parts per billion (ppb)

Samples:	8
Detects:	8
Average :	0.062 ppb
Range:	0.053-0.079 ppb

Chromium-6 Tests

Sample Date	Sample Facility	Sample Point	Result
2013-07-08	Distribution System	St. Pauls Fire Department	0.073 ppb
2013-07-08	Hanahan WTP	EPTDS from Hanahan WTP	0.079 ppb
2013-10-07	Distribution System	St. Pauls Fire Department	0.056 ppb
2013-10-07	Hanahan WTP	EPTDS from Hanahan WTP	0.07 ppb
2014-01-06	Distribution System	St. Pauls Fire Department	0.054 ppb
2014-01-06	Hanahan WTP	EPTDS from Hanahan WTP	0.057 ppb
2014-04-07	Distribution System	St. Pauls Fire Department	0.056 ppb
2014-04-07	Hanahan WTP	EPTDS from Hanahan WTP	0.053 ppb

Fish Consumption

Cooper River	East Fork Cooper River Quinby Creek to The "T"	Chain Pickerel	1 meal a week
		Largemouth Bass	1 meal a week
		Blue Catfish	No Restrictions
		Bluegill	No Restrictions
		Bowfin (Mudfish)	No Restrictions
		Redear Sunfish	No Restrictions
		Spotted Sunfish	No Restrictions
		Warmouth	No Restrictions
	West Fork Cooper River From Lake Moultrie Dam to The "T"	Bowfin (Mudfish)	1 meal a week
		Black Crappie	No Restrictions
		Blue Catfish	No Restrictions
		Bluegill	No Restrictions
		Chain Pickerel	No Restrictions
		Largemouth Bass	No Restrictions
		Redear Sunfish	No Restrictions
		Warmouth	No Restrictions
	The "T" to Bushy Park	Bowfin (Mudfish)	1 meal a month
		Black Crappie	No Restrictions
		Blue Catfish	No Restrictions
		Bluegill	No Restrictions
		Chain Pickerel	No Restrictions
		Largemouth Bass	No Restrictions
		Redear Sunfish	No Restrictions
		Warmouth	No Restrictions
	Downstream of Bushy Park	Red Drum	No Restrictions
		Spotted Sea Trout	No Restrictions
		Southern Flounder	No Restrictions
		Striped Mullet	No Restrictions

References

- Cited in Thesis