Chemical Regeneration and Reuse of Pesticide-Spent Granular Activated Carbon

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2024 Chlorinated Conference

June 6, 2024

Denver, CO

Problem statement

Active and Standby Public Wells with at least one detection of DBCP above the MCL of 0.2 µg/L, 156 wells (2006-2016)

Fumigants: 1,2-dibromo-3-chloropropane (DBCP), 1,2-dichloropropane (DCP), 1,2-dibromoethane (EDB), 1,2,3-trichloropropane (TCP)

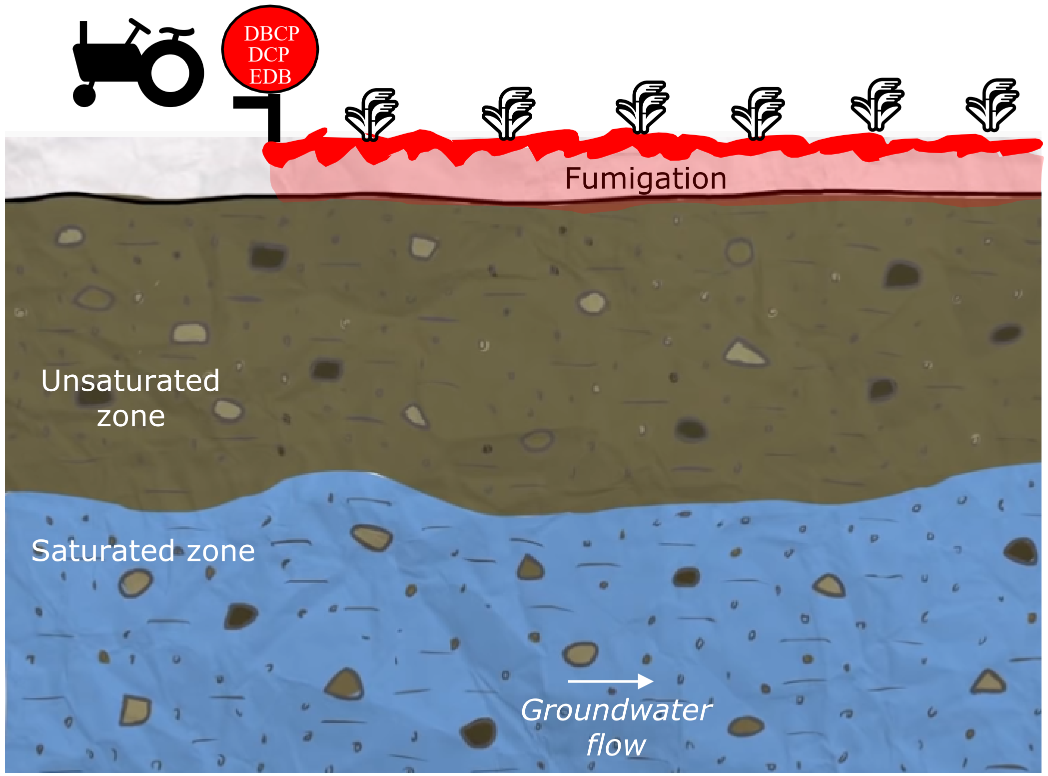
- Banned from agricultural application in 1979 (widespread detection in GW and drinking water sources and reported adverse health effects)
- Persistent in the environment & resistant to conventional in-situ treatment amendments
- Very low maximum contaminant levels (MCLs) established by EPA for DBCP, EDB, DCP

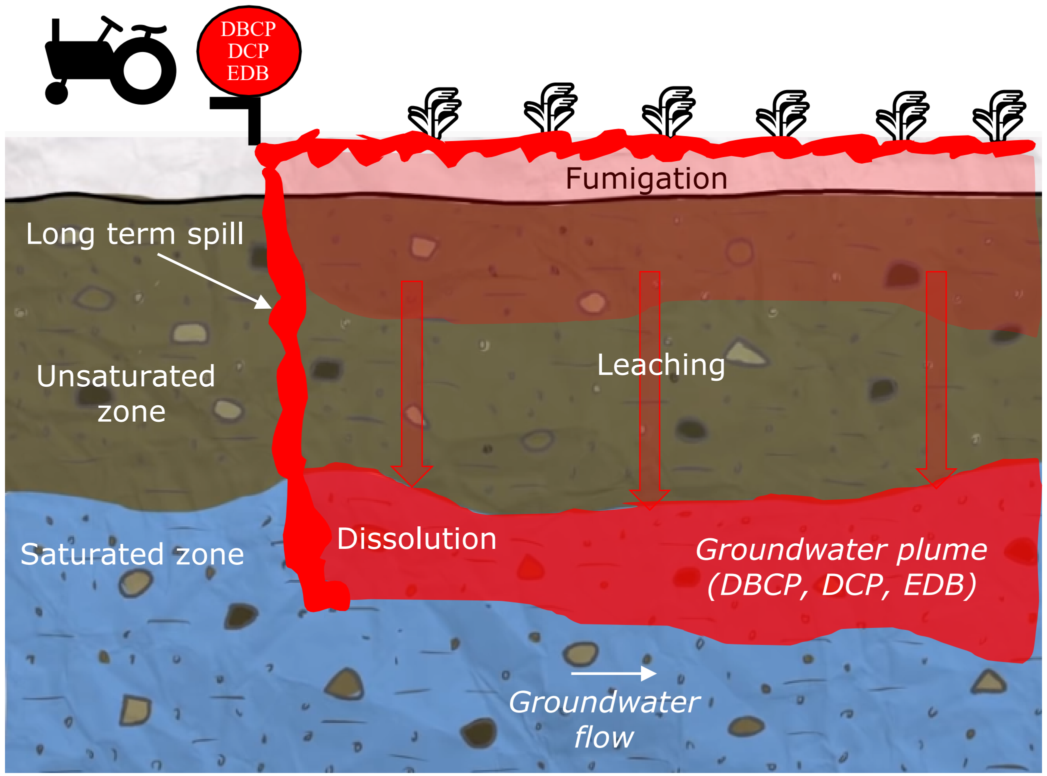
Why so persistent?

Physico-chemical characteristics of the fumigant compounds

	high	rel. high	DNAPL	low-moderate	low
Name	**Solubility in water (mg/L)**	**Vapor Pressure (mm Hg)**	**Density (g/cm^3)**	**Henry's Constant (atm m^3/g mol)**	**K_{OC} (Log K_{OC}) (L/kg)**
DBCP	2240	0.8; 0.58	2.05	$2.49\ 10^{-4}$	431 (2.11)
EDB	4310	11.0	2.18	$7.06\ 10^{-4}$	47 (1.67)
DCP	4500	49.67	1.16	$2.30\ 10^{-3}$	14-160 (1.15-2.20)
TCP	1750	3.1 – 3.69	1.39	$3.17\ 10^{-4}$	50.1-97.7 (1.70-1.99)

Simplified schematic of pesticide fumigants fate and transport





Treatment approaches

- Current: pump & treat; adsorption of pesticide fumigants onto granular activated carbon (GAC) and subsequent thermal regeneration
  - GAC not ideal, but lack of other viable and cost-effective treatment options
  - thermal regeneration is costly, requires transportation, not environmentally friendly

- Proposed: pump & treat; adsorption onto GAC and chemical base hydrolysis instead of thermal regeneration:
  - Applicable to halogenated (Cl^- and Br^-) alkanes
  - On-site and in-situ GAC regeneration
  - Reduce carbon footprint & cost

Laboratory 3-step proof of concept

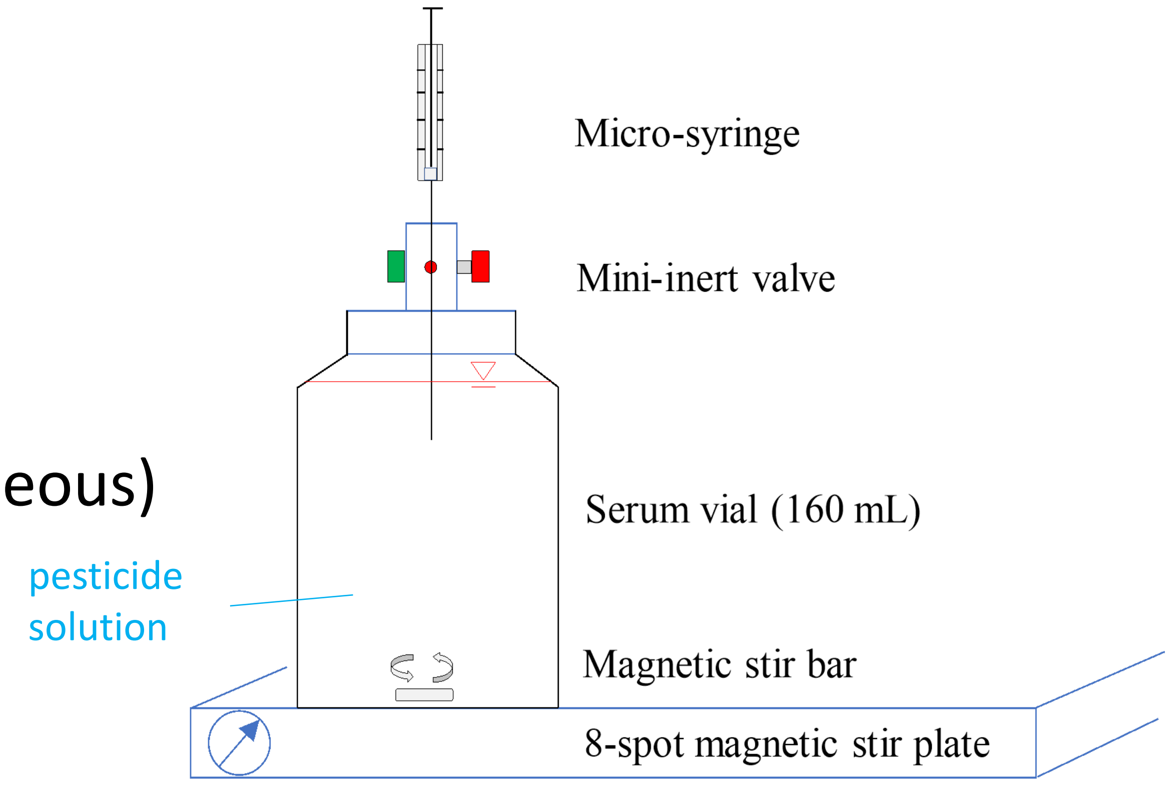
1) Adsorption

- GAC: COC L55 (coconut shell), F400 (bituminous)

2) Base hydrolysis (homogeneous)

- Kinetics of DBCP, EDB, TCP and DCP
- pH (NaOH)
- (by)products, Cl^-, Br^-

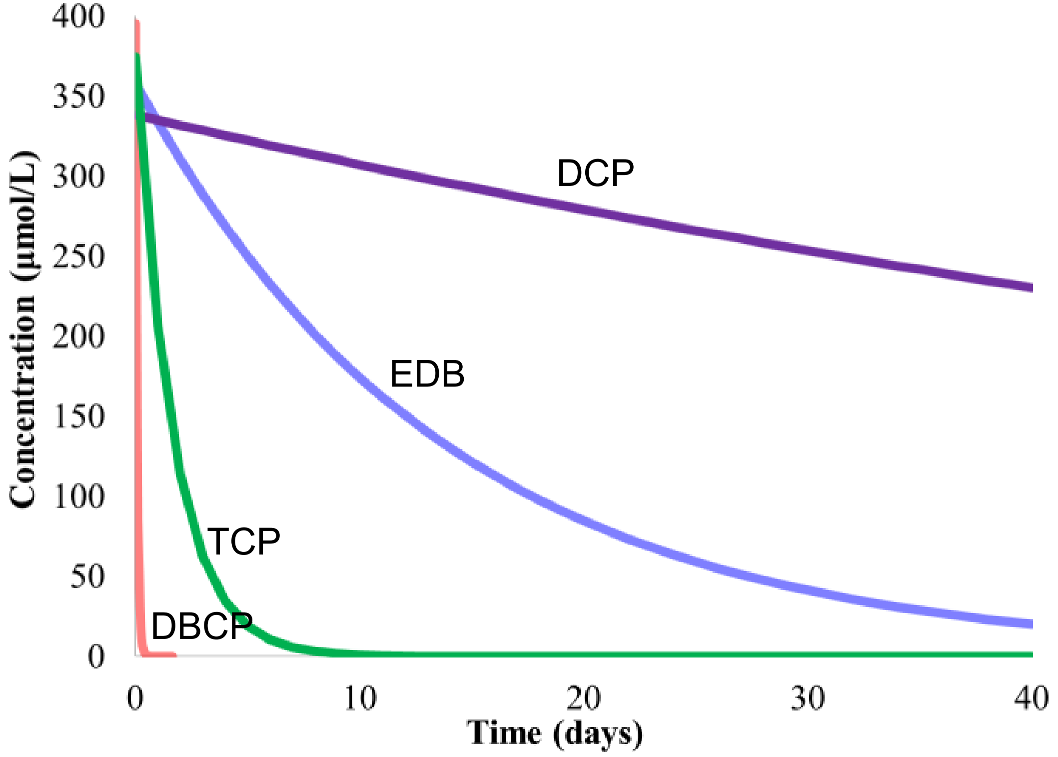
3) Adsorption & base hydrolysis (heterogeneous)



Serum vial (160 mL) with mini-inert valves for aq. phase sampling with micro-syringe placed on magnetic stir plate

Analytical:
Aq. samples – diluted and neutralized prior analysis
Pesticides conc. – automated headspace GC/MS; standard curve 0.5-372 µg/L ($r^2 > 0.99$)

Aqueous phase base hydrolysis of pesticides (homogeneous)



Hydrolysis Kinetic Parameters (aq.)	DBCP	TCP	EDB	DCP
k (1/h)	0.49	0.025	0.003	0.0002
k (1/d)	11.7	0.595	0.072	0.0048
$t_{1/2}$ (h)	1.45	27.9	231	3465
$t_{1/2}$ (d)	0.06	1.16	9.6	144
Cl^- Recovery (%)	16.8	41.0	-	3.7
Br^- Recovery (%)	52.1	-	49	-

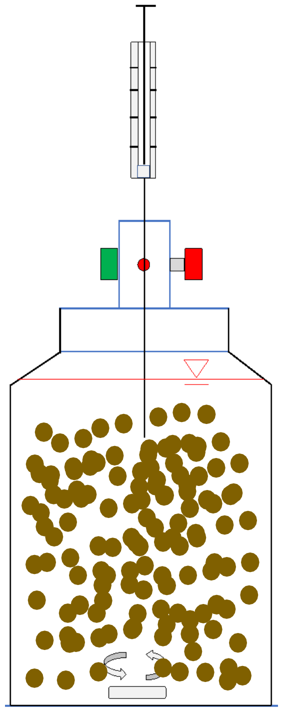
$[\text{Pesticide}]_{\text{AQUEOUS}}$ ~ 350 - 400 µM; pH 12-12.5

DBCP >> TCP >> EDB >> DCP

Rate-determining

Crincoli, K.R. and Huling, S.G., Chemosphere, 2023.

Solid phase base hydrolysis of pesticide-spent GAC (heterogeneous)



Parameters:
3-d sorption; followed by 30-d alkaline treatment,
pH 12-12.5

$[\text{Pesticide}]_{\text{initial}} = [\text{Pesticide}]_{\text{AQUEOUS}}$

$[\text{Pesticide}]_{\text{final}} = [\text{Pesticide}]_{\text{AQUEOUS}} + [\text{Pesticide}]_{\text{GAC}}$

negligible

measured in methanol extract

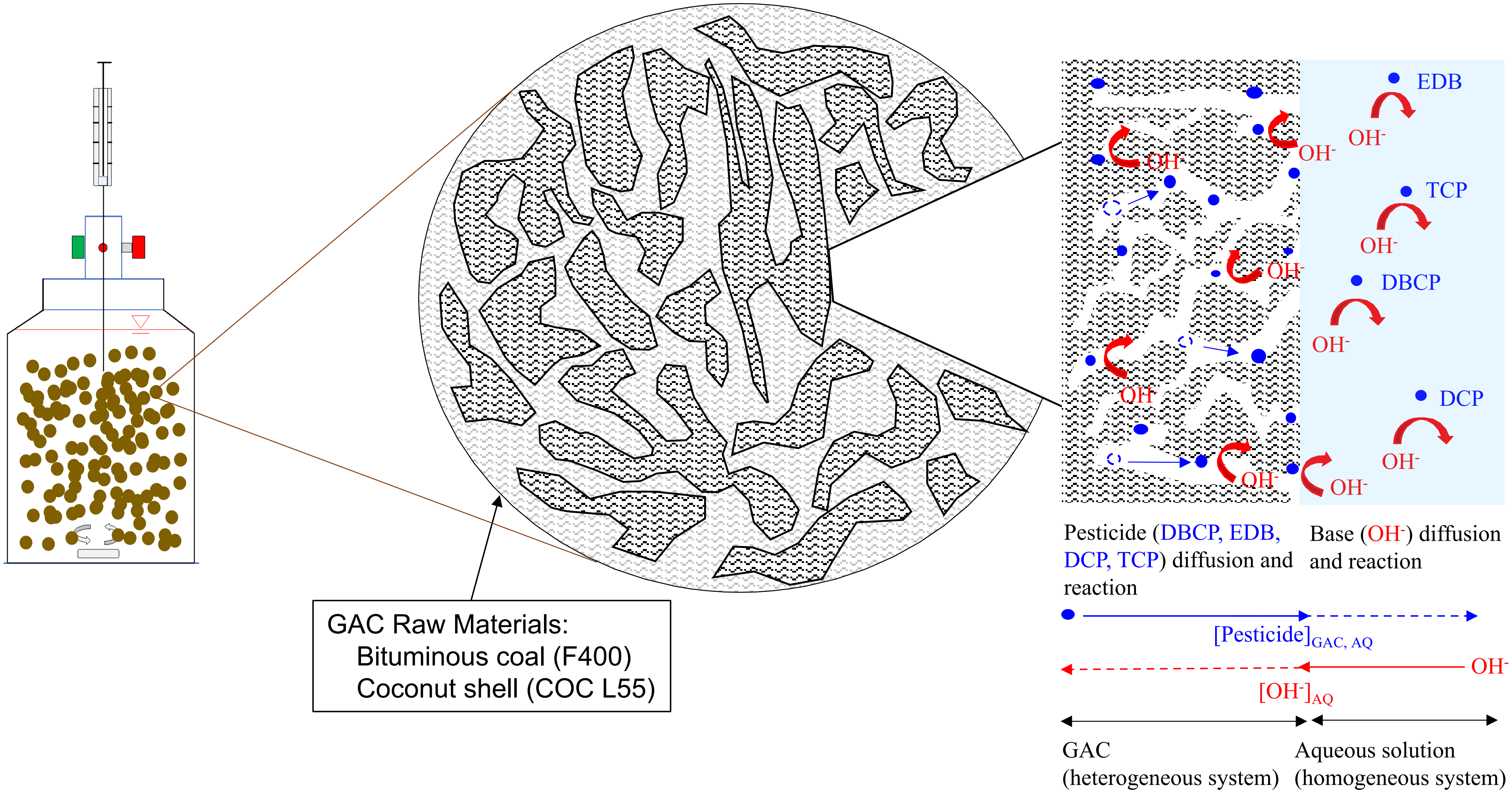
GAC	Initial $[\text{Pesticide}]_{AQ}$ (mg/L)	Initial $[\text{Pesticide}]_{GAC}$ (µg/g)	Final $[\text{Pesticide}]_{GAC}$ (µg/g)	Base Hydrolysis Removal of Pesticide (%)
F400				
DBCP	90.6	213.7	< 0.0046	> 99.98
EDB	67.4	154.3	< 6.2	> 95.97
TCP	55.2	119.5	< 3.5	> 97.04
COC-L55				
DBCP	90.6	194.4	< 0.039	> 99.98
EDB	69.8	160.2	< 5.9	> 96.34
TCP	63.9	145.0	< 7.3	> 94.95

95-99.98% loss of pesticides within 30 d

Crincoli, K.R. and Huling, S.G., Chemosphere, 2023.

Conceptual model

Pesticide and base (NaOH) mass transport and reaction in heterogeneous (predominant) and homogeneous systems

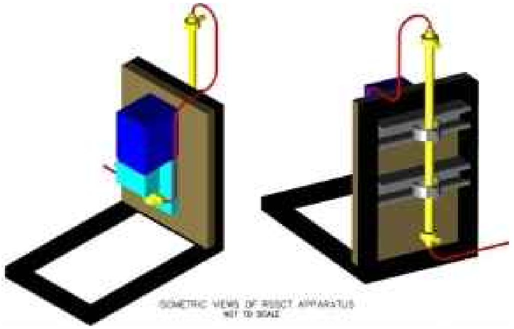


Proposed (and identified in blue) list of potential haloalkane pesticide byproducts after base hydrolysis treatment

Pesticide	Formula	Molar Mass (g/mol)	Byproducts	Molar Mass (g/mol)
1,2-dibromo-3-chloropropane (DBCP)	$C_3H_5Br_2Cl$	236.3	2-bromoallyl alcohol 2,3-dibromopropene 2-bromo-3-chloropropene	137.0 199.9 155.4
1,2-dibromoethane (EDB)	$C_2H_4Br_2$	187.9	ethylene glycol 2-bromoethanol 1-bromoethene	62.1 125.0 107.0
1,2-dichloropropane (DCP)	$C_3H_6Cl_2$	111.0	2-chloropropene 3-chloro-1-propene propen-2-ol	76.5 76.5 58.1
1,2,3-trichloropropane (TCP)	$C_3H_5Cl_3$	147.3	2,3-dichloro-1-propene 1,2-dichloro-1-propene 2-chloro-2-propen-1-ol 3-chloro-2-propen-1-ol	111.0 111.0 92.5 92.5

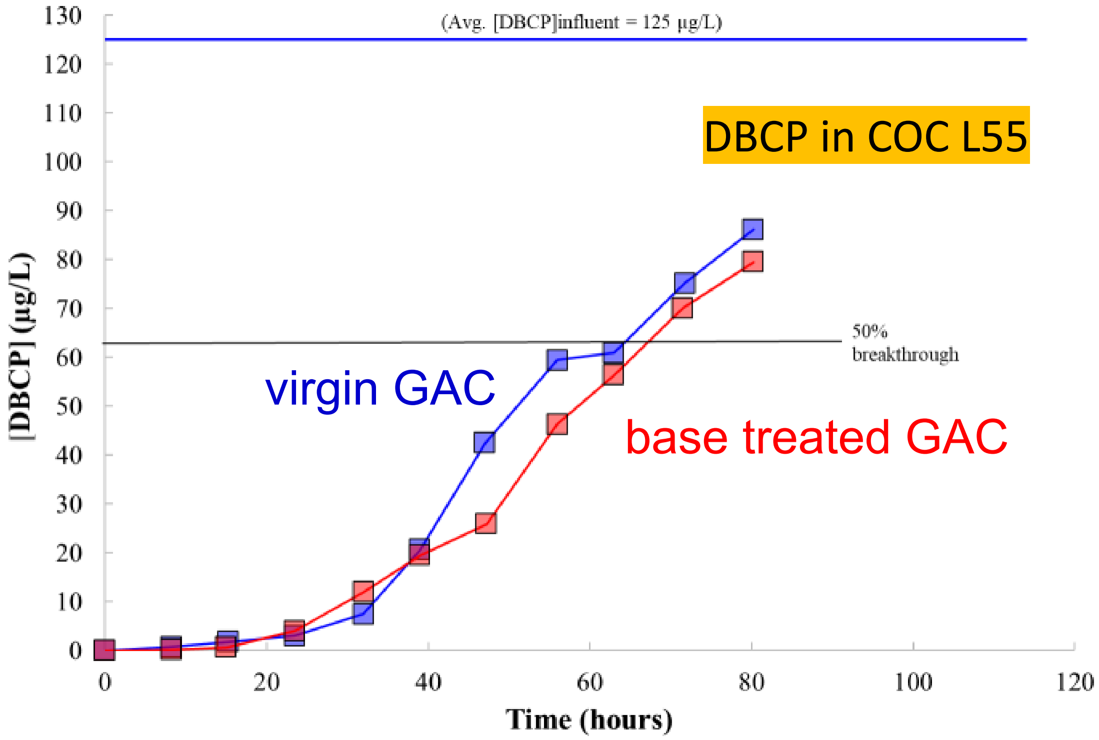
Literature indicates further hydrolysis leads to complete dehalogenation of the pesticides

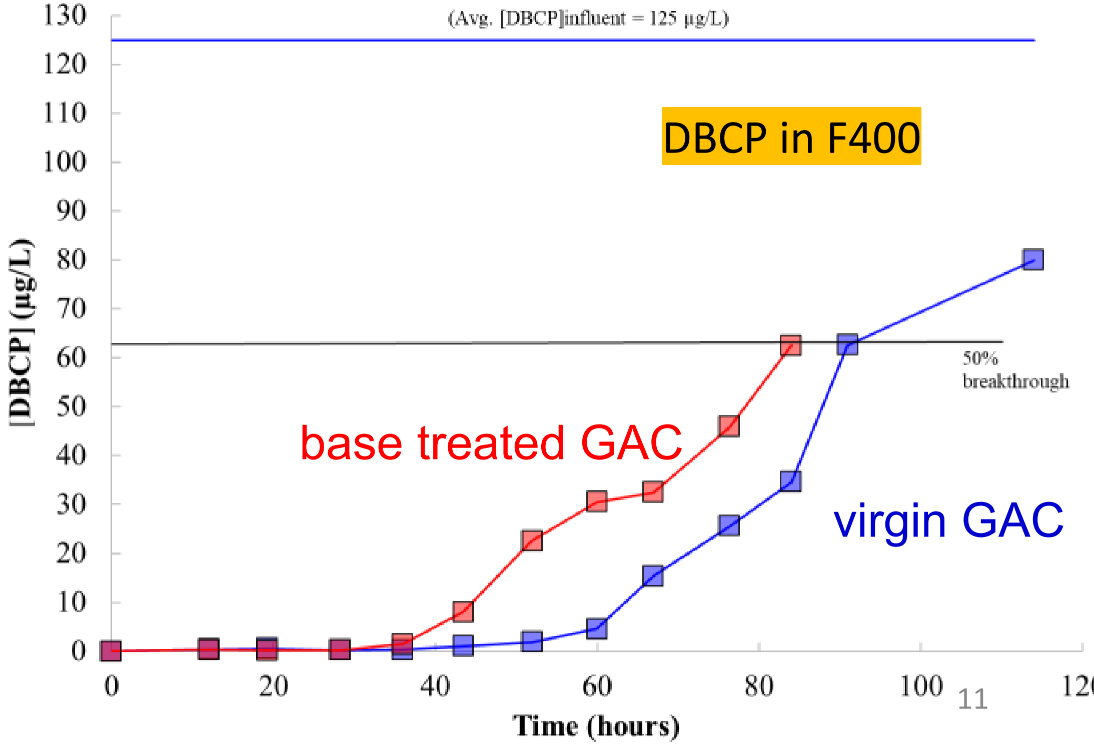
Rapid Small-Scale Column Tests



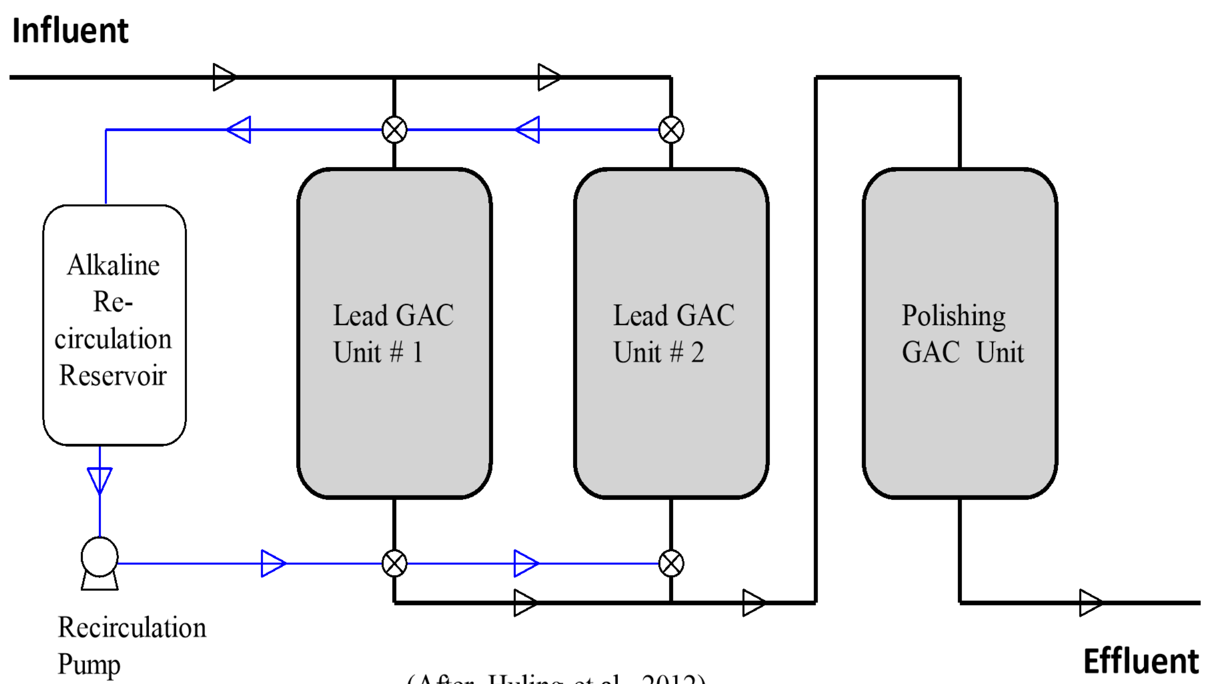
Westerhoff, 2008, EPA/600/R-08/051

- Used to determine impact of NaOH treatment on GAC sorption properties
- Contrasting 50% pesticide breakthrough times between alkaline-treated GAC and virgin, untreated (i.e., NaOH-free) GAC





Simplified conceptual schematic of 3-reactor GAC, and alkaline treatment of pesticide-spent GAC



(After, Huling et al., 2012)

- Lead units (#1 and #2) alternate between on-line (sorption) and stand-by mode, followed by a polishing unit
- Contaminated GW moves in a downflow direction; effluent continuously monitored
- Once the GAC in lead unit #1 is spent it is taken off-line and recirculation of the base takes place
- Meanwhile, the standby lead unit #2 containing clean GAC is now placed online
- Produced alkaline-spent solution - determination of possible haz. waste, or reuse/recycle

Summary & observations from the experiments

- ✓ **Alkaline (NaOH)** treatment of pesticide-spent GAC
- ✓ **Two types of GAC** were tested – bituminous (F400) and coconut shell (COC L55)
- ✓ The alkaline hydrolysis (pH 12.0-12.5) of pesticides in the homogeneous system occurred at significantly different rates (**DBCP >> TCP >> EDB >> DCP**)
- ✓ **95-99.98% loss** of DBCP, TCP, and EDB were measured within 30 d in both the F400 and COC L55 GAC
- ✓ Halogenated reaction byproducts indicated incomplete dehalogenation of the pesticide fumigants
- ✓ **Sorption properties** of F400 and COC L55 GAC **marginally impacted** by the base treatment

We gratefully appreciate

Bianca Handley – US EPA Region 9
Matt Small – US EPA Region 9
Charlotte Mooney – US EPA OLEM/ORCR
DHL Analytical Inc., Round Rock TX
Engineering Performance Solutions, Jacksonville FL

for their support and collaboration.

Crincoli, K. R., Huling, S.G. 2023. A new method to treat fumigant pesticides-spent granular activated carbon utilizing alkaline hydrolysis. *Chemosphere*, 330, 138648.