ICE Concentration Linked with Extractive Stirrer (ICECLES)

SBSE "on the rocks" - David Benanou

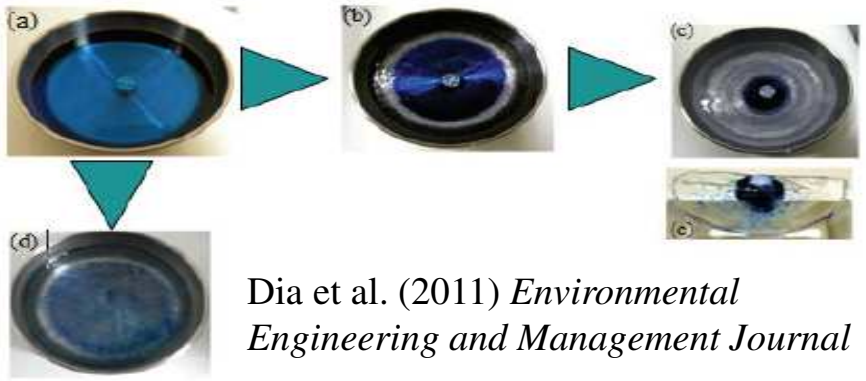
Brian A. Logue

South Dakota State University

Freeze Concentration (FC)

South Dakota State University

- Freeze concentration has been used for centuries, mainly in the food industry.
  - *Frozen concentrate orange juice*
  - *Ice beer*
  - *Ice wine*
- Sparingly evaluated for sample preparation.



Dia et al. (2011) *Environmental Engineering and Management Journal*

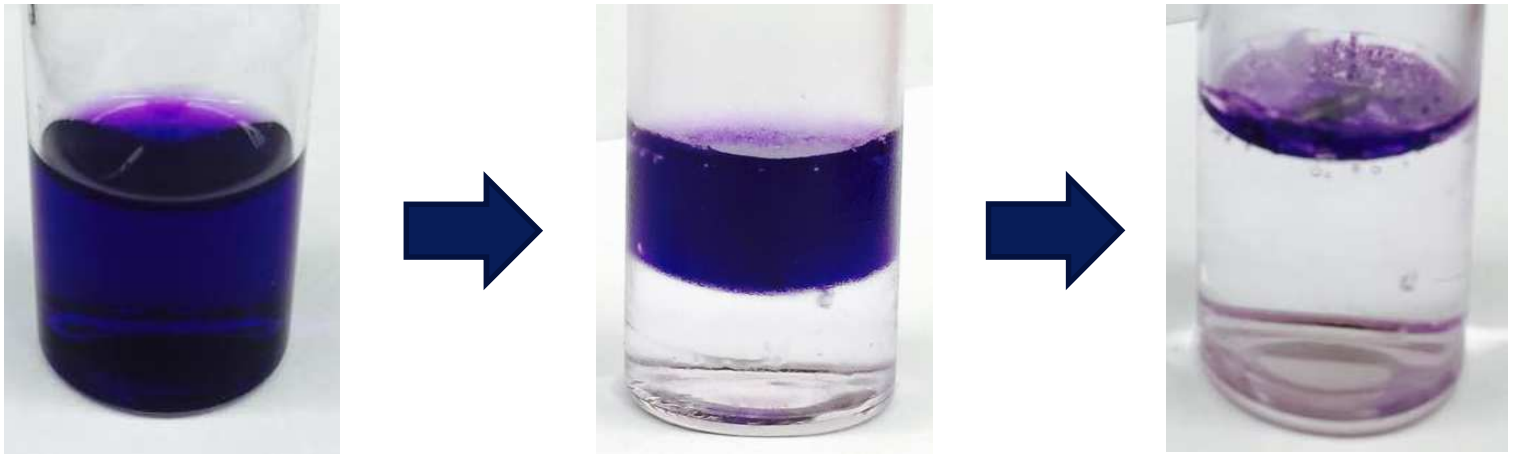
How does FC work?

South Dakota State University

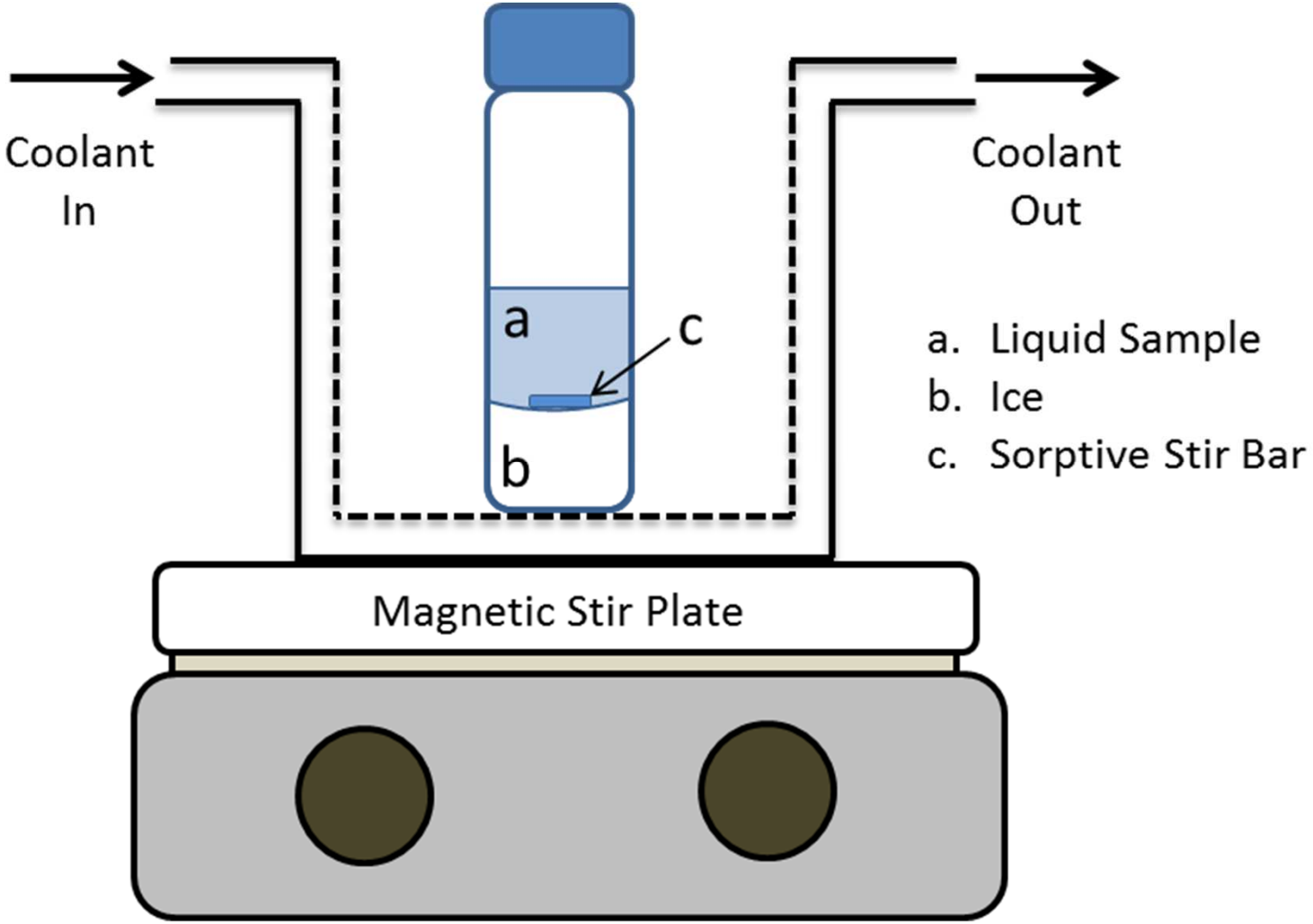
- Freeze concentration works through freezing point depression.

$$\Delta T_F = iK_F m$$

- A higher concentration of solute in a small area of volume causes lower freezing points.
- Therefore, lower concentration areas of solution freeze first and increase the concentration of the resulting fluid.
- Under the right conditions, almost pure solvent can be frozen out.
- In our lab, we found that under the right conditions, the stir bar will also stay stirring on top of the ice…creating an obvious link to SBSE.



ICECLES Apparatus



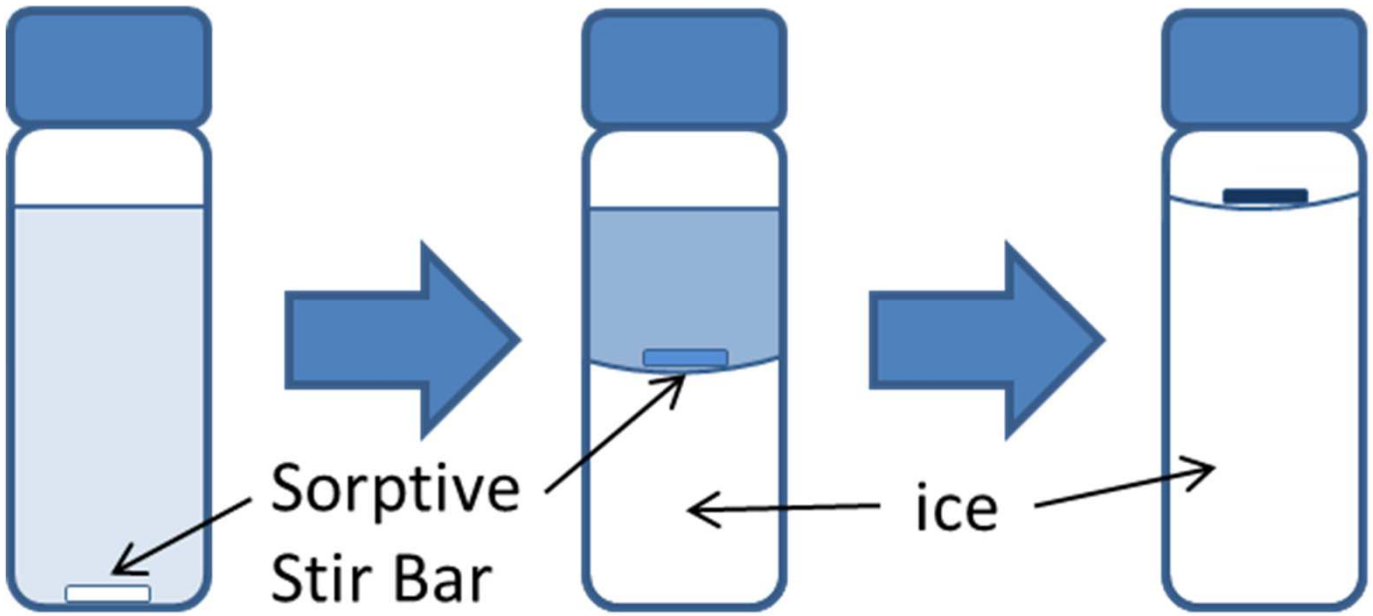
- Typical experimental...
  - *Coolant at -3 to -7 °C.*
  - *Start at 1200 rpm; 300 rpm after 2 hr.*
  - *Aqueous sample.*
  - *Freezing over 2-3 hours.*

ICECLES Sample Prep

South Dakota State University

- ICECLES was performed using…
  - *1200 rpm stirring.*
  - *Coolant at -5 °C.*
  - *Methylene blue dye.*
  - *Freezing over 3 hours.*

ICECLES Schematic



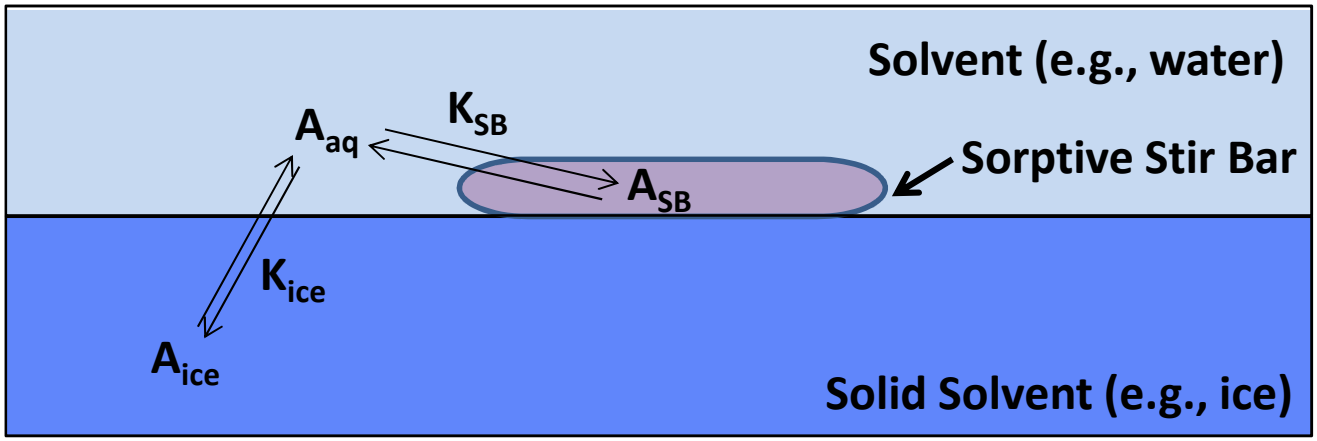
- White arrows designate the position of the stir bar.
- Stir bar is removed and typically…
  - *placed in a TDU tube for GC.*
  - *Back-extracted for LC.*

ICECLES "Equilibrium"

South Dakota State University

SBSE f_{extr}:

$$f_{extr} = \frac{K_{SB}V_{SB}}{K_{SB}V_{SB} + V_{aq}}$$

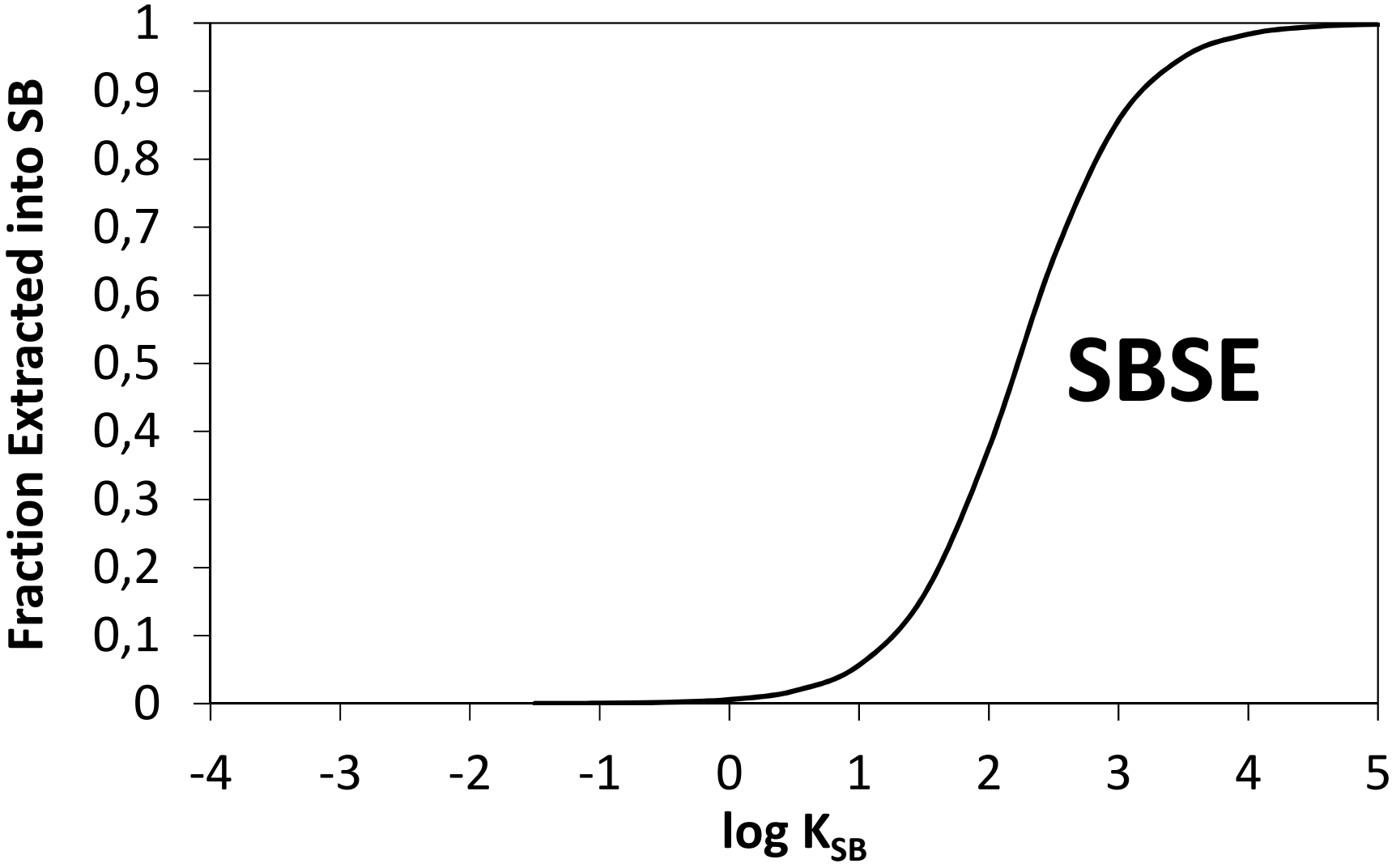


ICECLES f_{extr}:

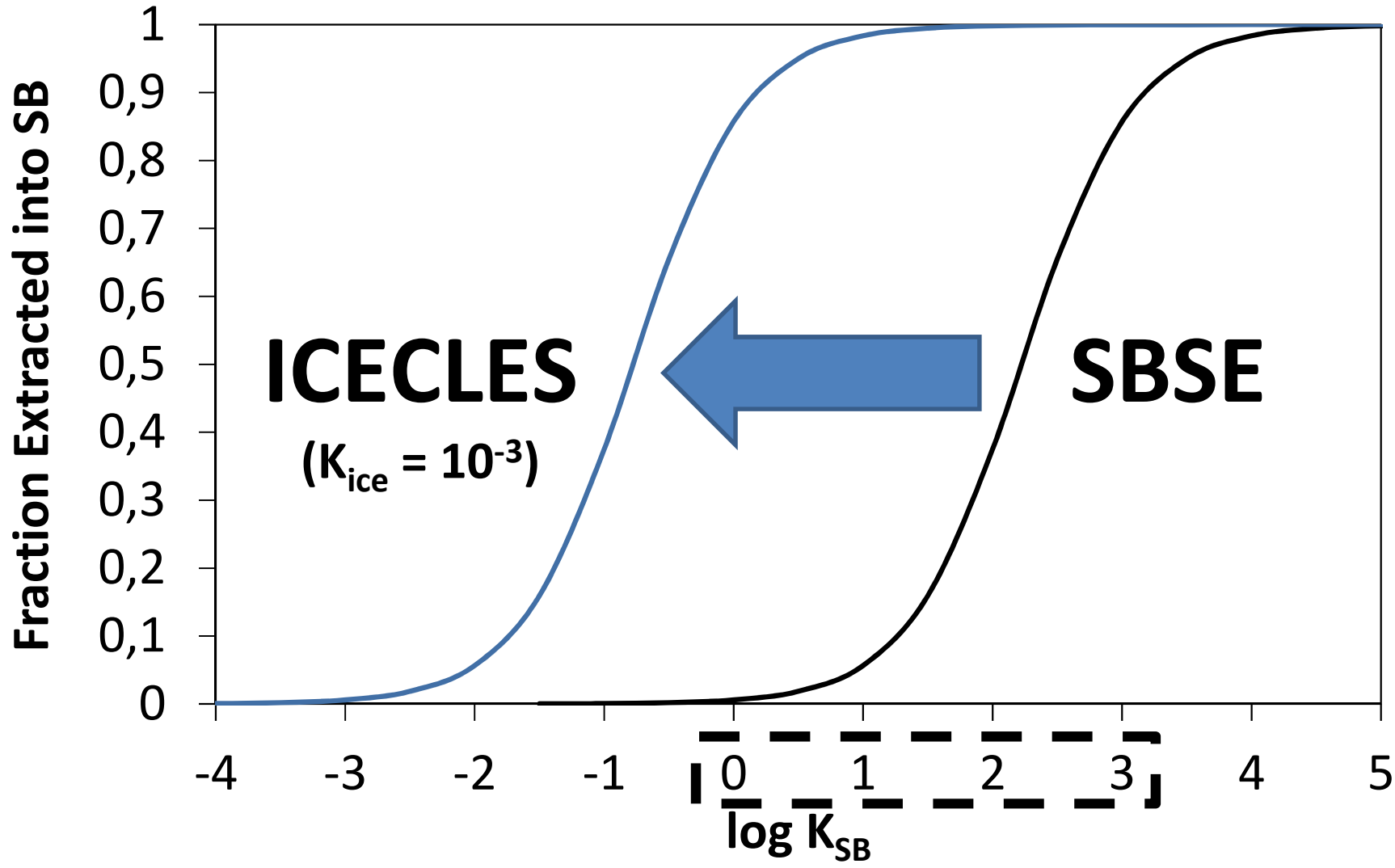
$$f_{extr} = \frac{K_{SB}V_{SB}}{K_{ice}V_{ice} + K_{SB}V_{SB} + V_{aq}} \rightarrow 0$$

- Need very small K_{ice} for large f_{extr}.
- Fortunately, K_{ice} is generally 10^{-2} to 10^{-4}.
- K_{ice} is a function of the rate of freezing, etc.

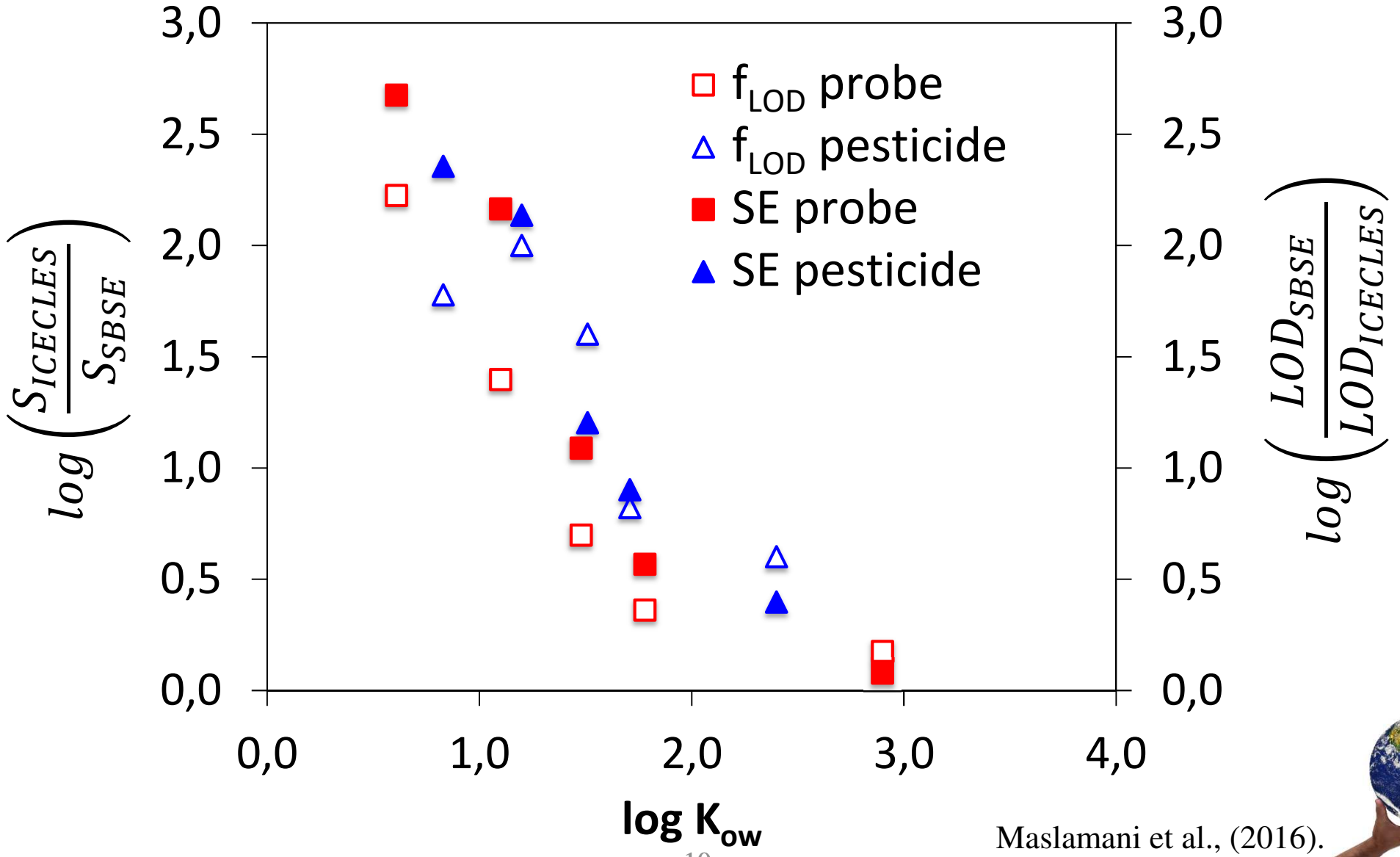
Fraction Extracted by ICECLES



Fraction Extracted by ICECLES

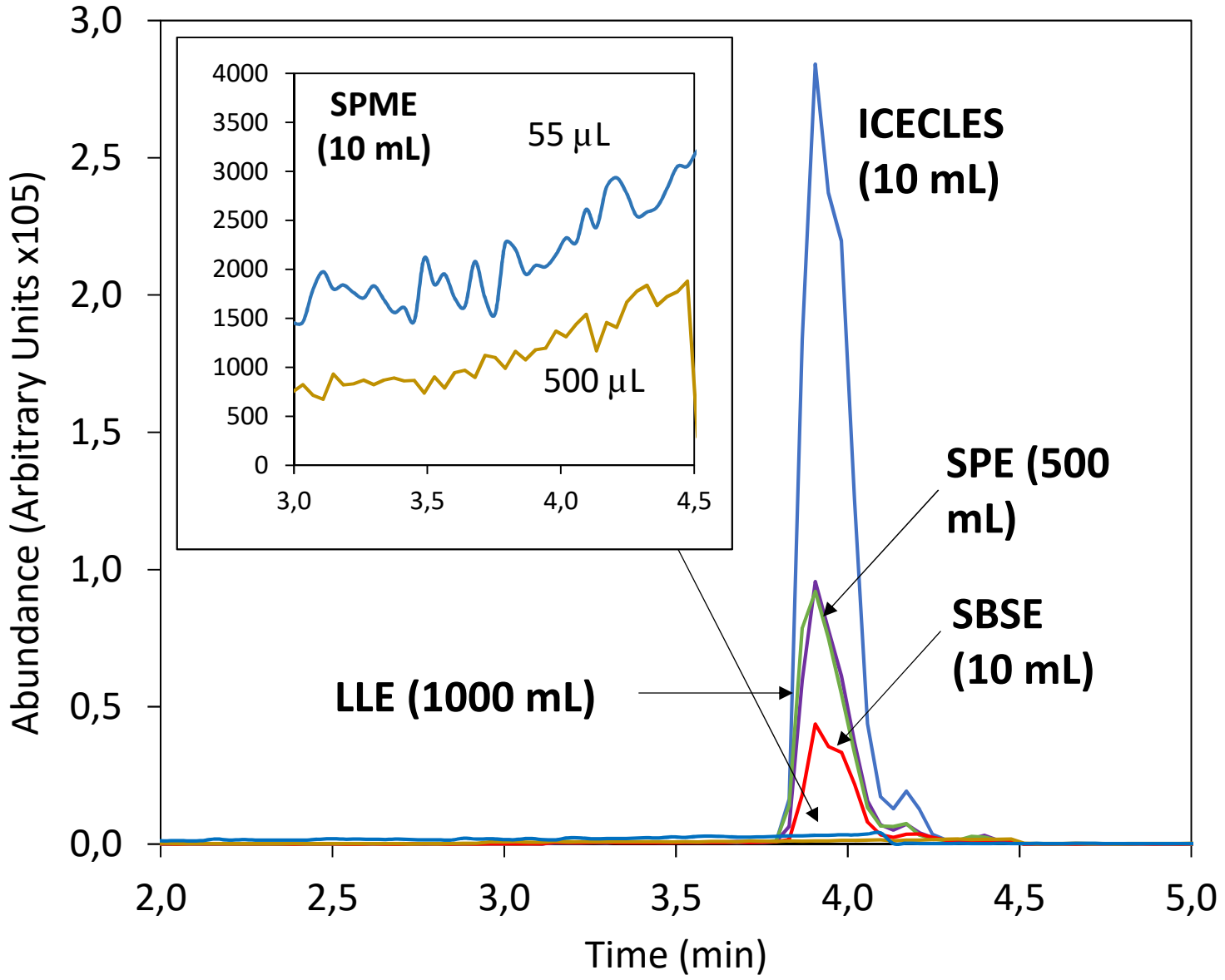


Signal Enhancement with ICECLES



Maslamani et al., (2016).

Atrazine (log K_{ow} = 2.4) Extraction



Extraction of Atrazine

South Dakota State University

Technique	Sample Size (mL)	Automated	Signal Relative to SBSE	Recovery (%)
SPE	1000	No	2.3	3.2
LLE	500	No	2.2	6.4
SBSE	10	Yes	1	14
SPME[1]	10	Yes	2.9×10^{-3}	ND[2]
SPME[3]	10	Yes	6.4×10^{-3}	ND[2]
ICECLES	10	Yes	4.9	70

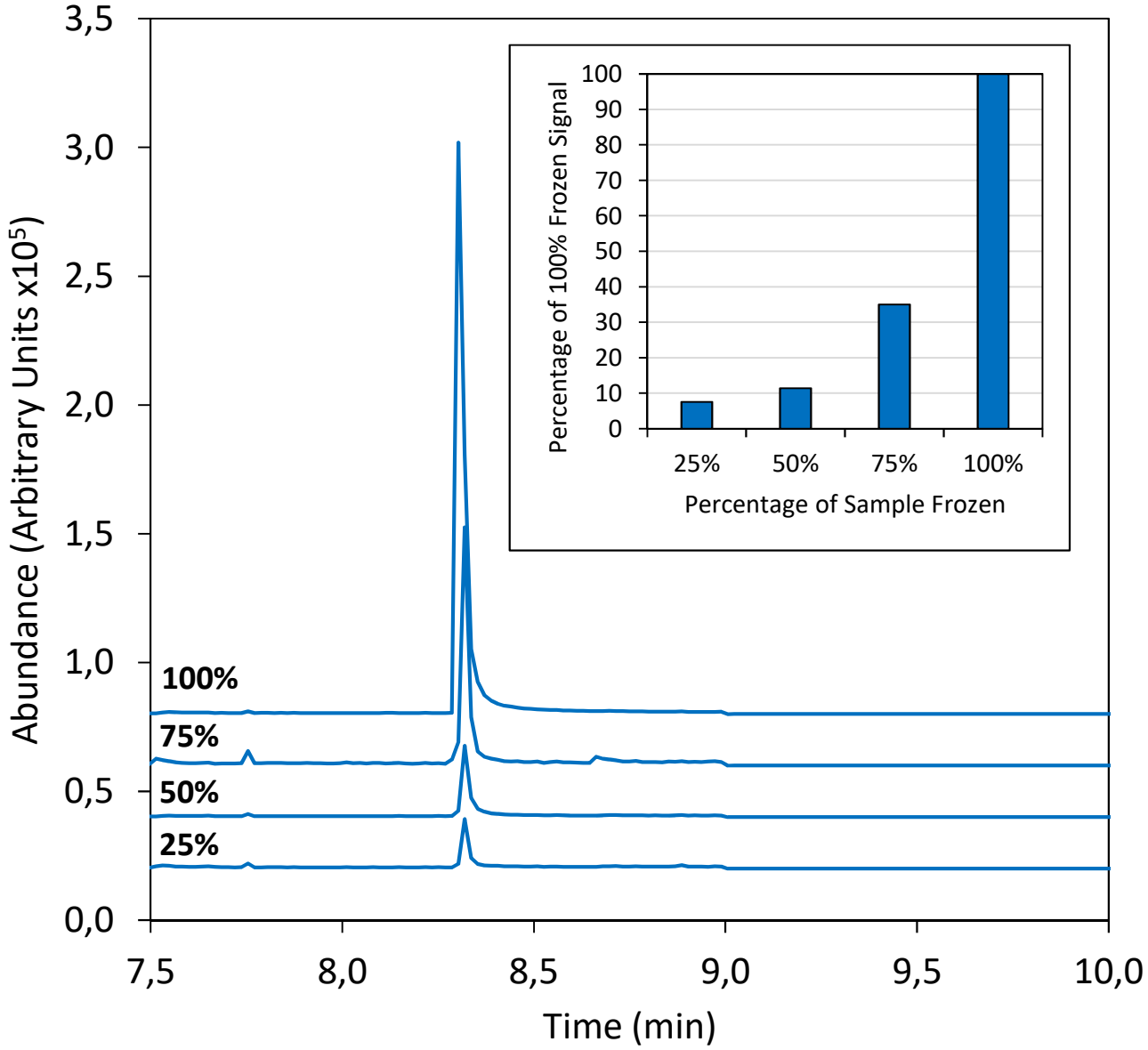
[1]Back-extracted with 500 µL

[2]ND = not detected

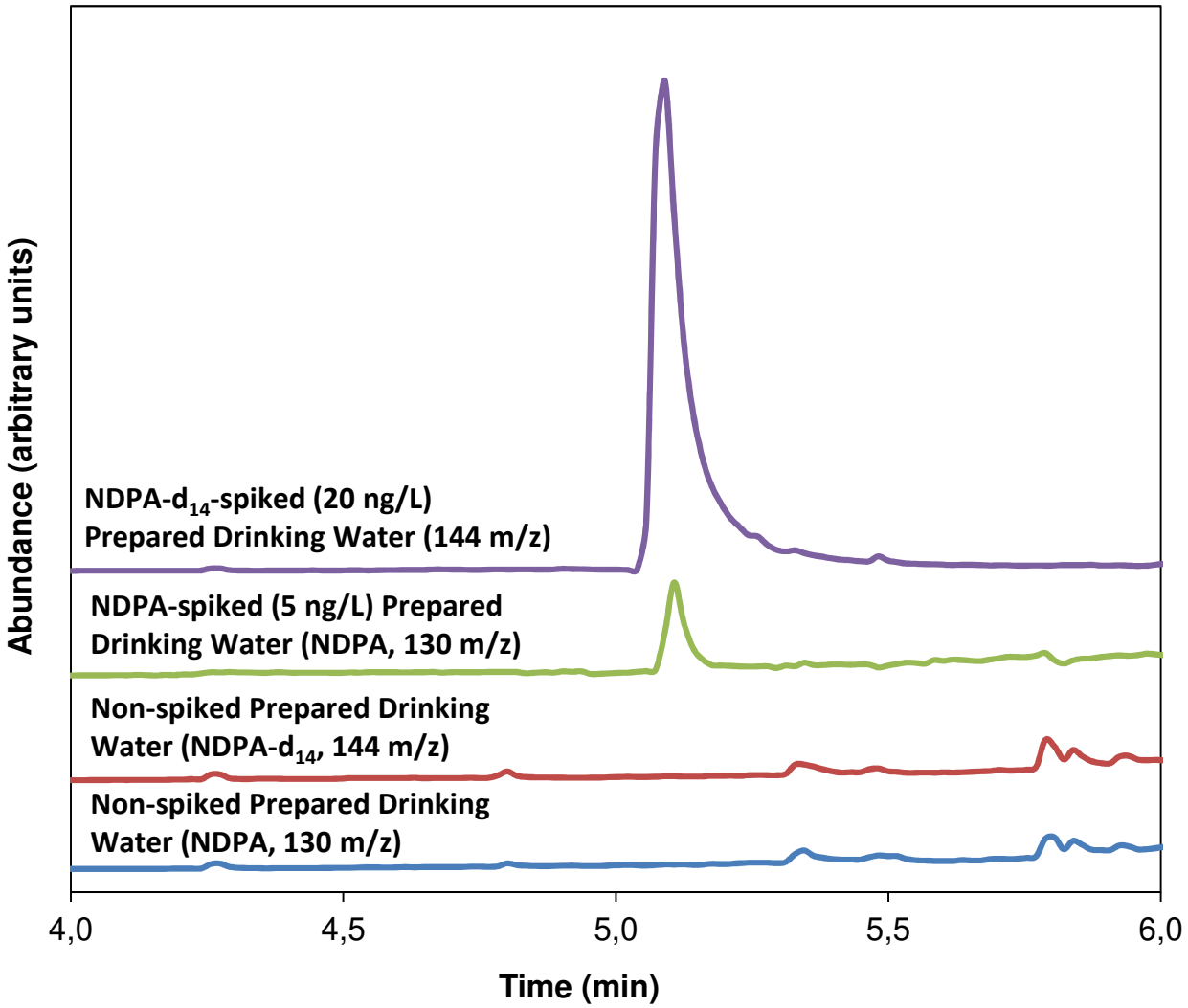
[3]Back-extracted with 55 µL

Atrazine Extraction During Freezing

South Dakota State University



Analysis of NDPA in Drinking Water

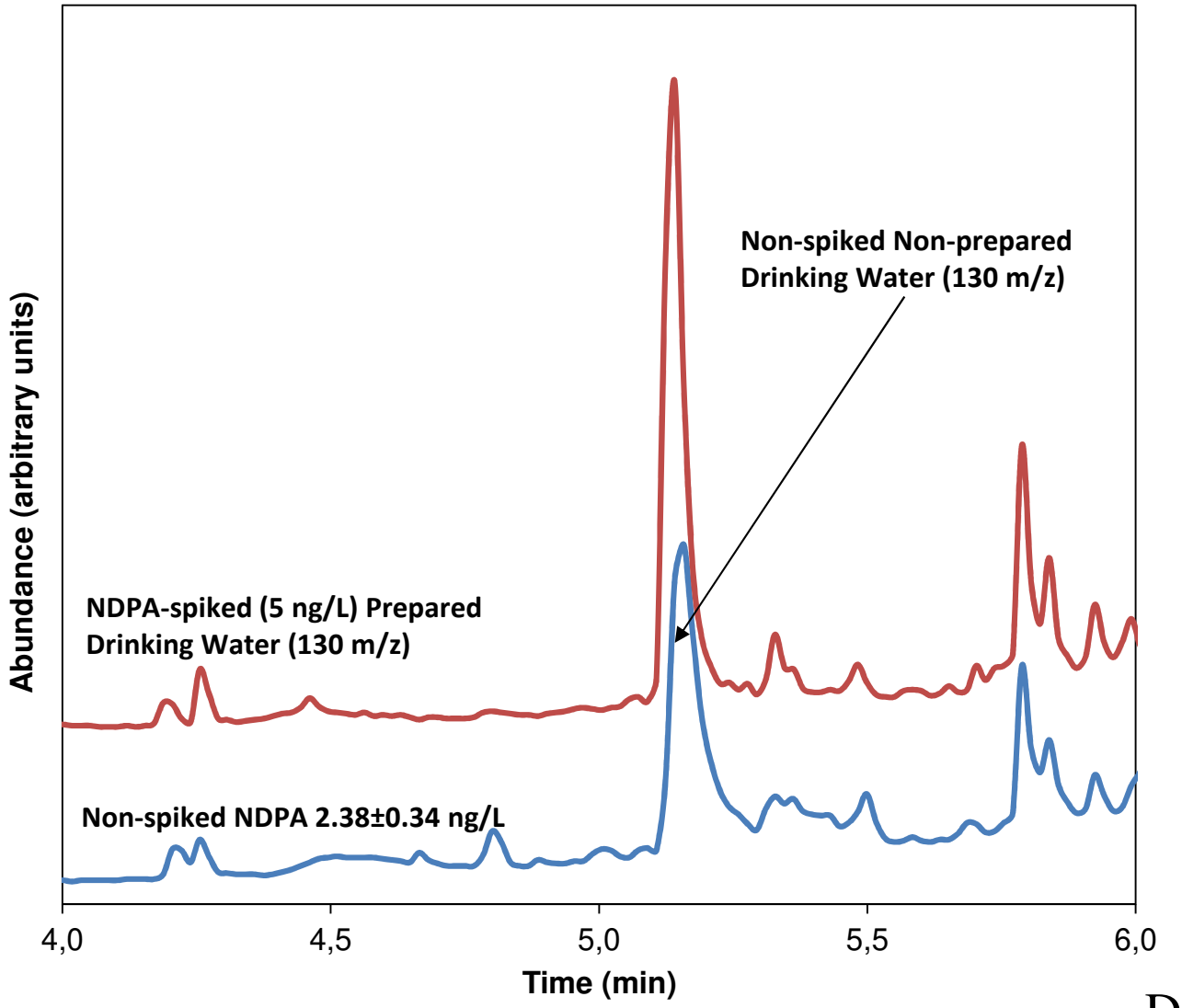


- NDPA (log K_{ow} = 1.4 est)
  - *Carcinogen.*
  - *EPA candidate contaminant.*
  - *EPA reporting limit = 7 ng/L.*
- Analysis of low ppt levels via a low-resolution GCMS

Dzisam and Logue (2019)

Analysis of NDPA in Drinking Water

South Dakota State University

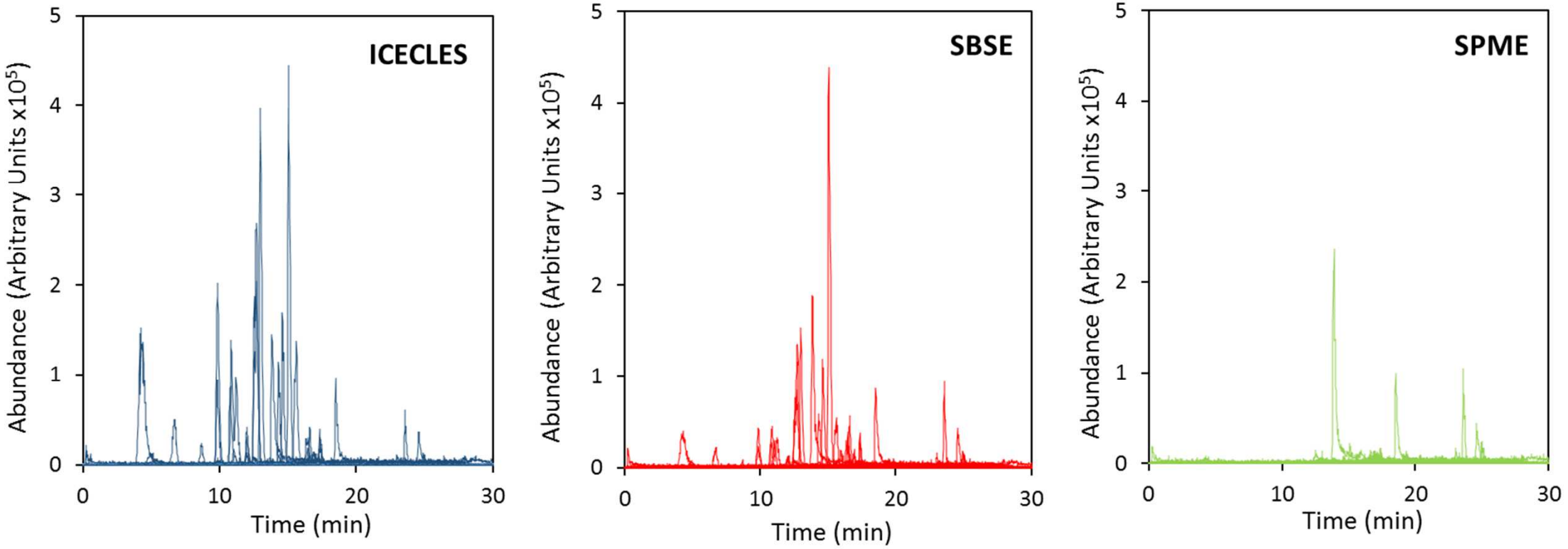


- ICECLES allows detection on a low resolution GCMS (SIM).
- Quantification of NDPA at 2 ng/L was achievable in one drinking water source.

Dzisam and Logue (2019)

Pesticide Analysis in Drinking Water

South Dakota State University



- ICECLES detects more compounds at a greater sensitivity than SBSE and especially better than SPME.
  - *ICECLES, SBSE, SPME (55 µL back-extract) were able to detect 53, 44, and 39 compounds, respectively at 10 ng/mL, and 32, 25, and 13 compounds, respectively, at 0.1 ng/mL.*

Skaggs, Alluhayb, and Logue (under review)

Pesticide Analysis In Drinking Water

South Dakota State University

Compound	Log K_{ow}	Concentration Detected (ng/mL)				Compound	Log K_{ow}	Concentration Detected (ng/mL)			
		ICECLES	SBSE	SPME[1]	SPME[2]			ICECLES	SBSE	SPME[1]	SPME[2]
Aldicarb	1.1	ND	ND	ND[3]	ND	Fuberidazole	2.7	0.1	0.1	1	10
Aldicarb-sulfoxide	1.4	10	ND	ND	ND	Furathiocarb	4.7	0.1	1	1	10
Aldicarb-sulfone	1.4	10	ND	ND	ND	Iprovalicarb	3.2	0.1	0.1	0.1	1
Aminocarb	1.9	ND	ND	ND	ND	Isopropalin	1.4	10	10	10	ND
Amitraz	5.5	10	ND	ND	ND	Isocarbamid	2.0	0.1	0.1	1	10
Acibenzolar-S-Methyl	3.1	0.1	0.1	1	10	Mepronil	0.6	0.1	0.1	0.1	0.1
Bendiocarb	1.7	0.1	1	ND	10	Methiocarb	2.9	ND	ND	ND	ND
Butylate	4.2	0.1	1	10	ND	Methomyl	0.1	10	ND	ND	ND
Carbaryl	2.4	0.1	0.1	1	10	Metolcarb	1.7	0.1	1	10	ND
Carbendazim	1.5	10	ND	ND	ND	Napropamide	3.4	0.1	0.1	1	10
Carbofuran	2.3	1	1	10	ND	Naproanilide	4.4	0.1	0.1	0.1	1
Chlorantraniliprole	2.8	0.1	1	1	10	Oxamyl	-0.5	10	ND	ND	ND
Chlorodimeform	2.9	10	10	10	ND	Oxamyl oxime	0.2	ND	ND	ND	ND
Chlorbufam	3.6	0.1	0.1	1	ND	Oryzalin	3.7	1	ND	10	ND
Chlorpropham	3.8	0.1	0.1	1	10	Phenmedipham	2.7	1	10	ND	ND
Cymiazole	2.5	ND	ND	ND	ND	Pirimicarb	1.7	0.1	0.1	1	10
Cycloate	3.9	10	ND	ND	ND	Promecarb	3.1	0.1	0.1	0.1	1
Desmedipham	3.2	1	1	ND	ND	Propamocarb HCl	4.9	ND	ND	ND	ND
Diallate	3.3	1	1	1	10	Propanil	3.1	0.1	0.1	0.1	1
Dimepiperate	5.6	10	10	10	ND	Propham	2.6	0.1	1	10	ND
Dioxacarb	4.9	1	10	ND	ND	Thiabendazole	2.5	0.1	0.1	0.1	1
Diphenamid	2.4	0.1	0.1	0.1	1	Thiodicarb	1.6	0.1	1	1	10
EPTC	3.2	10	ND	ND	ND	Triallate	4.6	1	1	1	10
Ethiofencarb	2.0	ND	ND	ND	ND	Trichlamide	5.6	0.1	0.1	0.1	1
Etobenzanid	4.3	0.1	0.1	0.1	1	2,3,5-Trimethacarb	2.5	0.1	0.1	1	10
Fenfuram	2.6	0.1	0.1	1	10	3,4,5-Trimethacarb	2.6	0.1	0.1	0.1	1
Fenoxycarb	4.3	0.1	0.1	0.1	1	Vernolate	3.8	1	1	1	10
Fenthiocarb	3.3	0.1	0.1	0.1	1	XMC	2.3	0.1	0.1	1	10
Fenoxanil	3.5	0.1	0.1	0.1	1	Xylylcarb	2.1	1	10	ND	ND
Formetanate HCl	4.6	1	1	ND	ND	Zoxamide	3.8	0.1	0.1	1	10

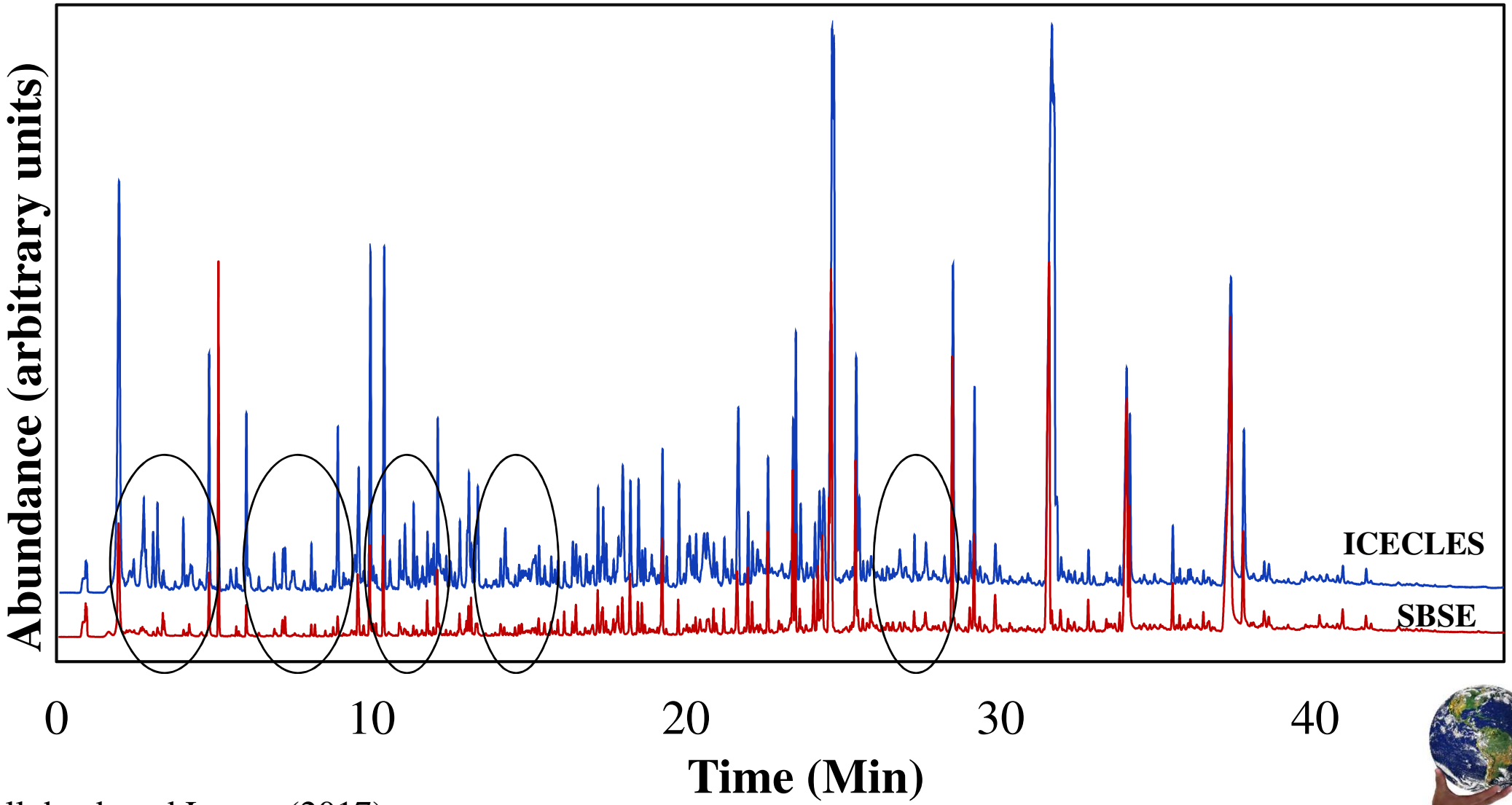
Pesticide Analysis In Purified Water

South Dakota State University

Compound	Log K_{ow}	Concentration Detected (ng/mL)				Compound	Log K_{ow}	Concentration Detected (ng/mL)			
		ICECLES	SBSE	SPME[1]	SPME[2]			ICECLES	SBSE	SPME[1]	SPME[2]
Aldicarb	1.1	10	10	ND[3]	ND	Fuberidazole	2.7	0.1	0.1	1	10
Aldicarb-sulfoxide	1.4	1	ND	ND	ND	Furathiocarb	4.7	0.1	0.1	0.1	1
Aldicarb-sulfone	1.4	1	ND	ND	ND	Iprovalicarb	3.2	0.1	0.1	0.1	1
Aminocarb	1.9	0.1	1	1	10	Isopropalin	1.4	10	10	10	10
Amitraz	5.5	10	10	ND	ND	Isocarbamid	2.0	0.1	10	10	ND
Acibenzolar-S-Methyl	3.1	0.1	0.1	1	10	Mepronil	0.6	0.1	0.1	0.1	1
Bendiocarb	1.7	0.1	1	1	10	Methiocarb	2.9	10	10	10	10
Butylate	4.2	0.1	0.1	0.1	1	Methomyl	0.1	0.1	ND	ND	ND
Carbaryl	2.4	0.1	0.1	1	10	Metolcarb	1.7	0.1	1	10	ND
Carbendazim	1.5	0.1	10	10	ND	Napropamide	3.4	0.1	0.1	0.1	0.1
Carbofuran	2.3	0.1	1	10	ND	Naproanilide	4.4	0.1	0.1	0.1	0.1
Chlorantraniliprole	2.8	0.1	1	10	10	Oxamyl	-0.5	10	ND	ND	ND
Chlorodimeform	2.9	0.1	0.1	1	ND	Oxamyl oxime	0.2	10	ND	ND	ND
Chlorbufam	3.6	0.1	0.1	1	ND	Oryzalin	3.7	0.1	1	10	ND
Chlorpropham	3.8	0.1	0.1	1	10	Phenmedipham	2.7	0.1	1	1	10
Cymiazole	2.5	0.1	0.1	0.1	1	Pirimicarb	1.7	0.1	0.1	1	10
Cycloate	3.9	0.1	0.1	0.1	1	Promecarb	3.1	0.1	0.1	0.1	1
Desmedipham	3.2	0.1	0.1	0.1	1	Propamocarb HCl	4.9	0.1	1	10	ND
Diallate	3.3	0.1	0.1	0.1	1	Propanil	3.1	0.1	0.1	1	10
Dimepiperate	5.6	0.1	0.1	0.1	0.1	Propham	2.6	0.1	1	10	ND
Dioxacarb	4.9	0.1	0.1	0.1	1	Thiabendazole	2.5	0.1	0.1	0.1	1
Diphenamid	2.4	0.1	0.1	0.1	1	Thiodicarb	1.6	0.1	1	10	ND
EPTC	3.2	0.1	0.1	1	10	Triallate	4.6	0.1	0.1	0.1	1
Ethiofencarb	2.0	10	10	10	ND	Trichlamide	5.6	0.1	0.1	0.1	1
Etobenzanid	4.3	0.1	0.1	0.1	1	2,3,5-Trimethacarb	2.5	0.1	1	1	10
Fenfuram	2.6	0.1	0.1	1	10	3,4,5-Trimethacarb	2.6	0.1	1	1	10
Fenoxycarb	4.3	0.1	0.1	0.1	0.1	Vernolate	3.8	0.1	0.1	0.1	1
Fenthiocarb	3.3	0.1	0.1	0.1	0.1	XMC	2.3	0.1	1	1	10
Fenoxanil	3.5	0.1	0.1	0.1	1	Xylylcarb	2.1	10	10	ND	ND
Formetanate HCl	4.6	0.1	1	10	ND	Zoxamide	3.8	0.1	0.1	0.1	1

ICECLES of Green Tea

South Dakota State University



Alluhayb and Logue (2017).

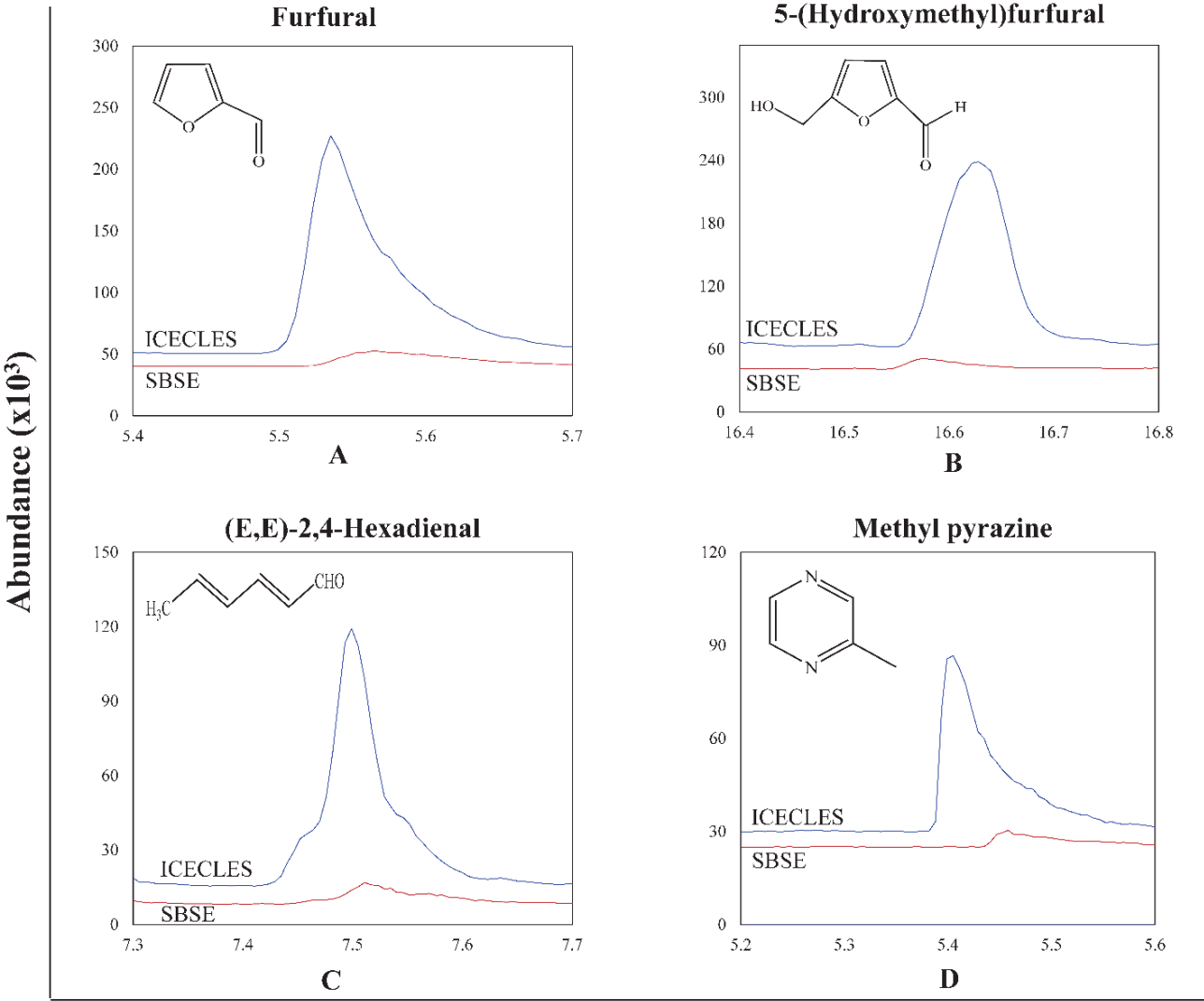
ICECLES of Green Tea

SOUTH DAKOTA STATE UNIVERSITY

Peak No./Category	Name	Odor	Log K_{ow}
Alcohol			
14	1-Pentanol	Fruity	1.33
15	2-Penten-1-ol, (Z)	Rubber	0.9*
84	Phenylethyl Alcohol	Rose	1.57
105	α-Terpineol (α,α4-trimethyl 3-Cyclohexene-1-methanol)	Floral	3.28
Heterocyclic			
21	Methyl pyrazine	Nut	0.49
38	2,5-dimethyl pyrazine	Nut	1.03
Aldehyde			
22	Furfural	Caramel	0.83
37	(E,E)-2,4-Hexadienal	Citrus	1.37[c]
111	5-(hydroxymethyl) furfural (5-(hydroxmethyl)-2-Furancarboxaldehyde)	Carmel	-0.09[c]
Ketone			
82	Maltol	Caramel	0.02
91	Ketoisophorone (2,6,6-Trimethyl-2-cyclohexene-1,4-dione)	Floral	1[b]
Ester			
95	Benzyl acetate	Fruit	1.96[b]
66	γ-Undecalactone (5-heptyldihydro-2-(3H)-Furanone)	Fruit	0.7[b]
Phenol			
136	Syringol (2,6-dimethoxy phenol)	Phenol	1.1[b]
138	Eugenol	Clove	2.49

[b]log K_{ow} values were calculated by using the difference between a log K_{ow} value of known compound and the query compound then estimated by an additive model with well-defined correction factors [26].

[c]log K_{ow} values were calculated by using an atom/fragment contribution method via KOWWIN™ program [27].



Alluhayb and Logue (2017).

Potential of ICECLES

South Dakota State University

- Advantages:
  - *Can achieve extremely high concentration factors.*
  - *Well-suited for trace targeted analysis and comprehensive analysis.*
  - *Extends SBSE to compounds with log K_{ow} < 3. This polarity range is difficult to analyze for most sample preparation techniques.*
  - *Well-suited for more thermally labile and volatile compounds.*
  - *Easier to back-extract compounds, making ICECLES more amenable for LC analysis.*
- Areas of improvement:
  - *Lengthy sample preparation times (depending on sample volume).*
  - *Simple implementation requires small sample volumes.*

  } Addressed by automated large volume system.

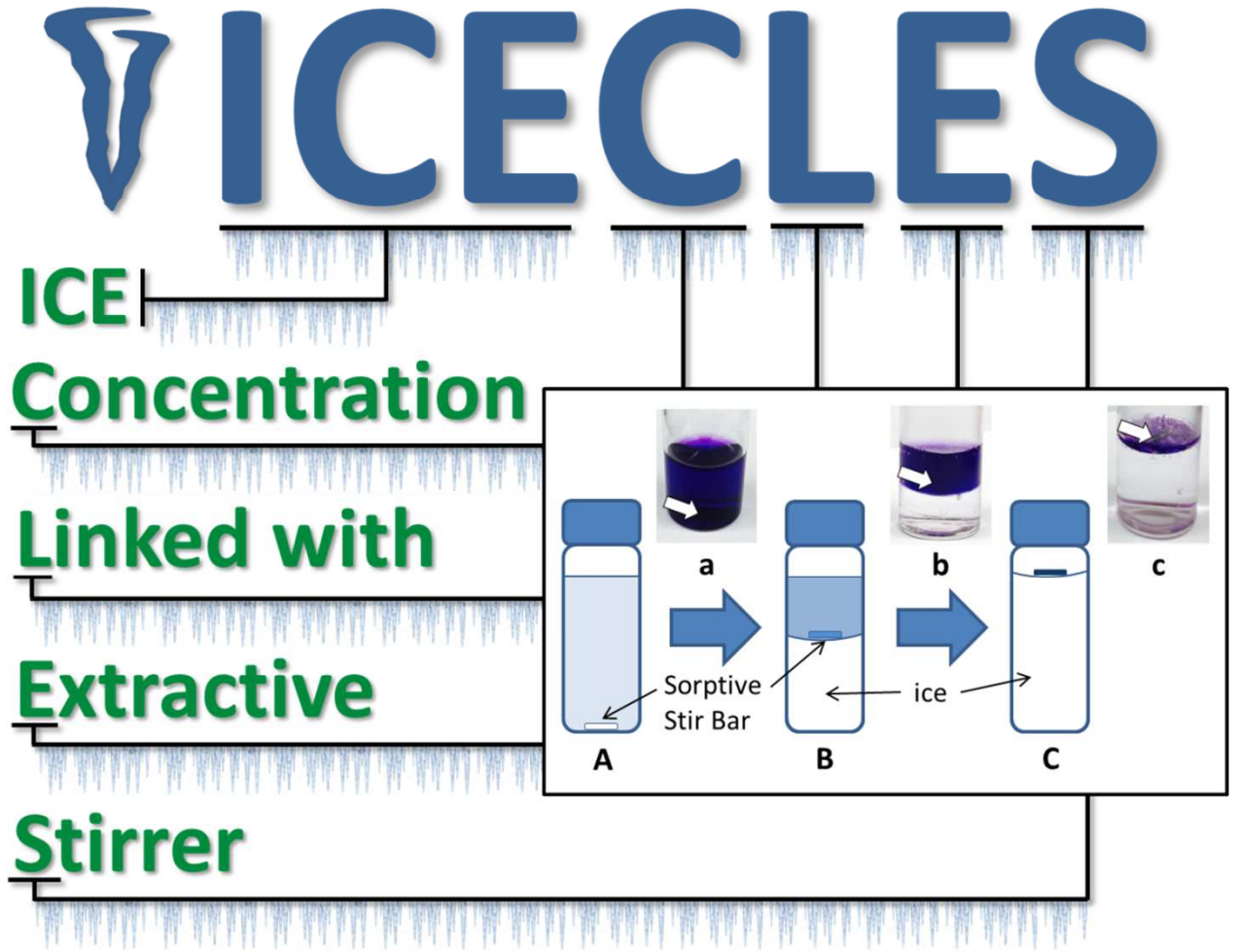
  - *Precipitation of some compounds more likely under freezing temps.*
  - *Extra equipment, compared with SBSE, necessary to freeze the sample.*
  - *More difficult for low freezing point solvents.*

Acknowledgements

- LARGE group members.
- SACM and Quasim University.
- U.S. Joint Executive Office for Chem Bio Defense, Joint Program Management Protection W911SR-09-0059.
- Meeting organizers and participants.
- South Dakota winters, soda, and my laziness.

Questions???

SOUTH DAKOTA STATE UNIVERSITY



brian.logue@sdstate.edu
https://www.sdstate.edu/chemistry-biochemistry/brian-logue