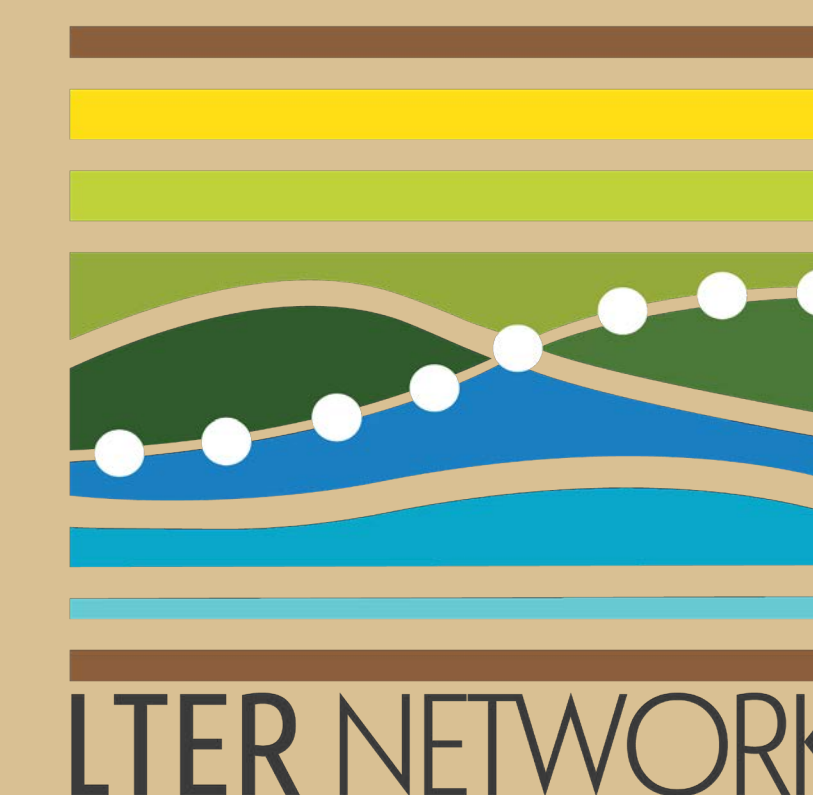


Ultra-Trace Analysis of Plastic Additives in the Tres Rios Wetlands



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What Are Plasticizers?

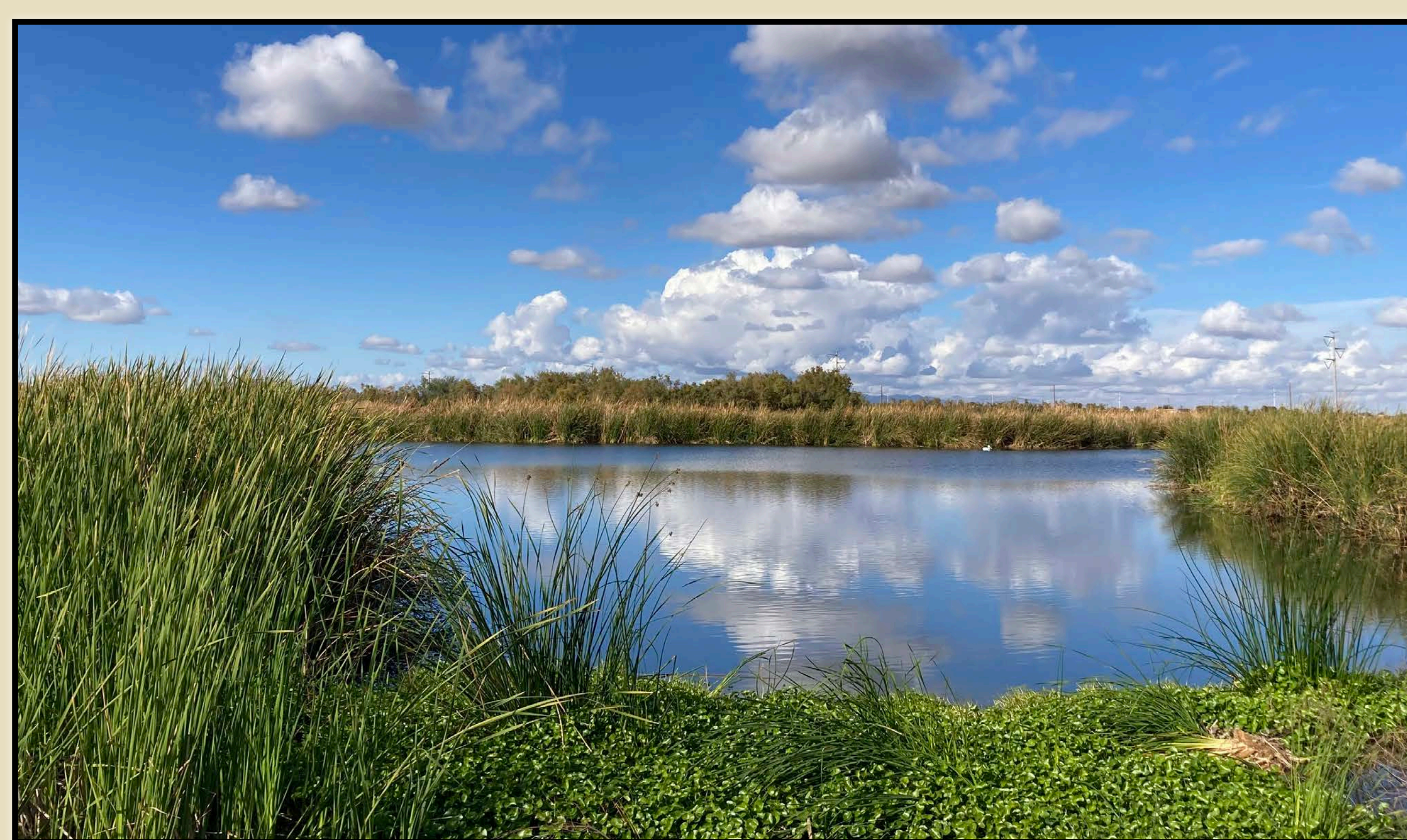
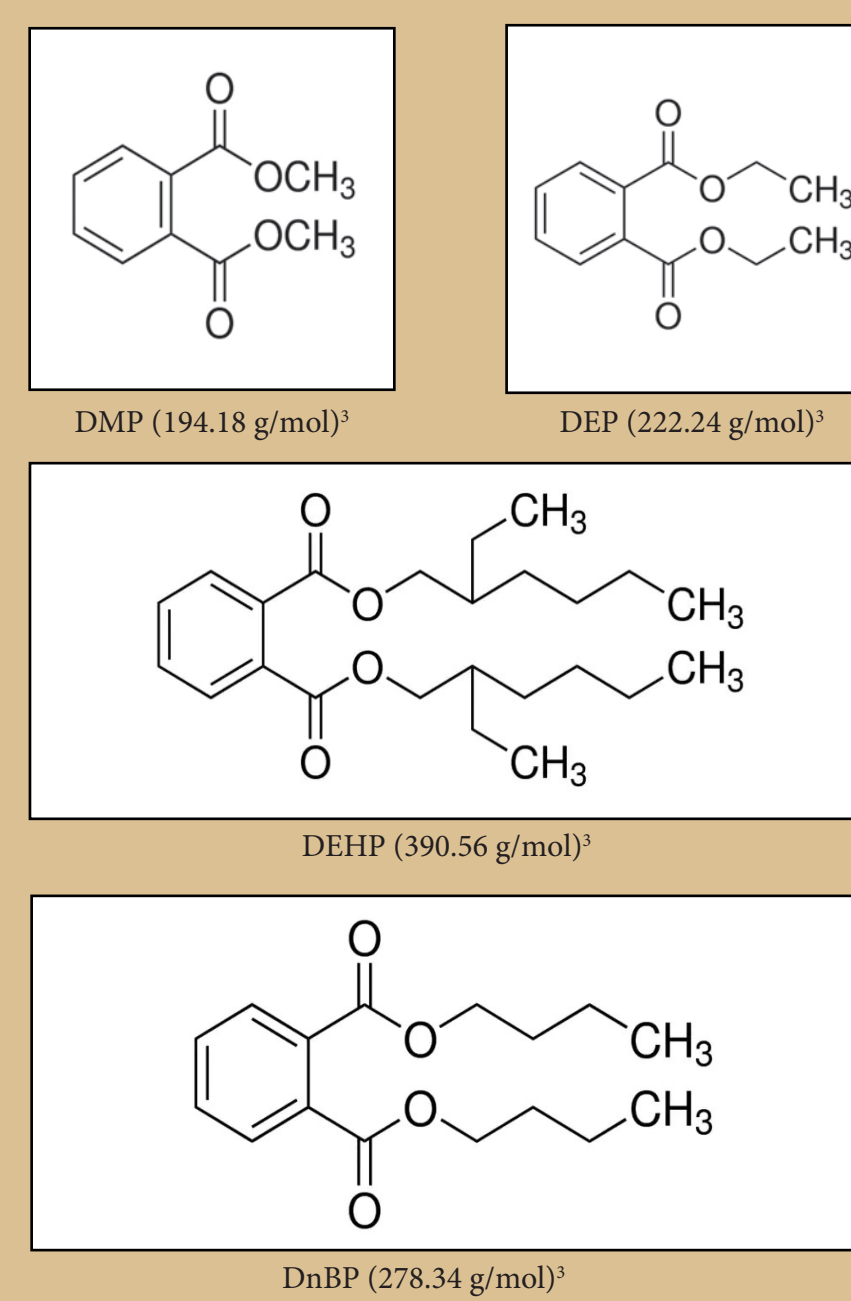
Plasticizers are a type of plastic additive used in plastics to enhance their flexibility.

They are persistent in the environment and are deposited through:

- Leaching from plastic products
- Atmospheric deposition
- Wastewater effluent into treatment wetlands¹

Determining the fate of these contaminants of emerging concern is critical since even low concentrations can lead to bioaccumulation, acute toxic effects, and long-term ecosystem disruption².

The objective of this study is to perform ultra-trace quantification of these four phthalate plasticizers in the Tres Rios constructed wetland ecosystem to help understand their fate in the environment.



Results

All concentrations are measured in nanograms/liter.

	DNBP	DEHP	DMP	DEP
LOD	55	47	18	13
Minimum	< 6	< 4	< 1	< 9
25%	< 29	< 38	< 2	< 9
50%	74	109	< 8	< 9
75%	774	891	< 15	< 9
Maximum	7349	27876	3447	2480

Site	DnBP	DEHP	DMP	Overall
Blank	6	9	1	5
Inflow	654	3770	6	1477
M4N	331	361	8	233
M1E	463	1417	867	916
M4S	1331	427	16	591
Outflow	1406	491	14	637

Concentrations for all spatial and temporal data.

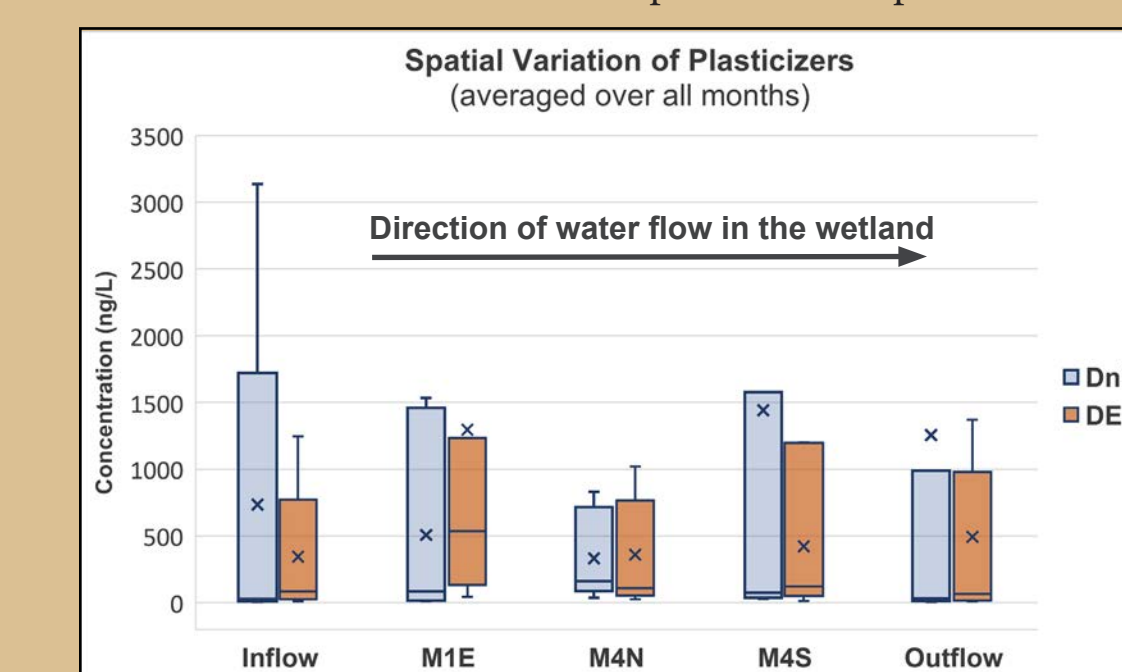
Month	March	May	July	September
LOD	55	55	55	55
Minimum	< 6	372	226	< 10
25%	< 14	635	614	< 27
50%	< 28	1246	990	< 38
75%	< 41	1966	1628	58
Maximum	162	7349	7291	94

Temporal concentrations of DnBP.

Month	March	May	July	September
LOD	47	47	47	47
Minimum	< 31	110	614	< 4
25%	< 38	783	792	< 12
50%	58	1199	969	30
75%	77	1369	1108	78
Maximum	149	27876	1246	536

Temporal concentrations of DEHP.

Concentrations for all spatial and temporal data.



DMP and DEP were not included here since a large amount of the values were below the detection limit. Outliers such as the DEHP maximum were excluded for chart clarity.

Sampling Methodology

Two water samples were gathered at each of the following sites: inflow, M-1-E, M-4-N, M-4-S, and the outflow.

This represents 10 samples per sampling run, with 2 replicates per site. Forty total samples were taken in the study.

Decontaminated and baked amber glass bottles were used and kept in a cooler until stored in a lab refrigerator.

A standard triple-rinse procedure was used and samples were taken at surface level just past where the greenery ended and the water began.

Samples were taken in March, May, July, and September of 2022.

These locations were chosen to maximize spatial resolution of data while balancing accessibility.



Quantification/Specifications

Solid Phase Extraction:

- Extracts target analytes from complex aqueous matrix into a suitable solvent
- Samples and procedural blanks spiked with an internal standard (deuterated DMP)
- Caliper LifeScience AutoTrace SPE with Oasis HLB 6cc (500mg) LP Extraction Cartridges

Standard Calibration:

- Allows for concentration to be calculated from analyte signal/internal standard signal
- This helps correct for losses in the extraction and procedure
- 99% pure analytical standards of analytes from Sigma-Aldrich used for calibration curves
- 99% pure deuterated DMP used for the internal standard
- Constructed in the range of 2ug/mL to 200 ug/mL and had r^2 greater than 0.990

GC/MS Method:

- Allows for separation of complex mixtures and quantification of individual ions
- ThermoFisher TRACE 1310 gas chromatograph and TSQ 9000 triple quad mass spec
- Agilent HP-5MS nonpolar capillary column used with MS running in scanning mode
- Runs lasted 56 minutes with a ramp from 65 °C to 300 °C for effective separation

Discussion

Overall Concentrations:

- Higher molecular weight plasticizers like DnBP and DEHP are present at consistently higher concentrations in the wetland than those of lower molecular weight like DMP and DEP. DEP was rarely present in detectable concentrations

Temporal Trends:

- Concentrations of each analyte increase during the summer season and hottest temperatures and decrease during the end of spring and beginning of fall

Spatial Trends:

- Concentrations tended to be highest at the inflow of the wetland, decreasing around M4N, and increasing around M1E and M4S

Future Work:

- Since plasticizers are lipophilic, they may be accumulating in the plant material at the site. Further study will include sampling and analysis of plasticizers in plant material, as well as more surface water samples to better understand the variability of the inflow concentrations, which may be impacting these trends
- Tres Rios is a constructed wetland used to ecologically filter wastewater effluent. If the plant species at the site can safely break down or sequester these compounds, the utility of the site will be increased

References

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- (2) Jambeck, J. R., Geyer, R., Wilcox, C., Siegler, T. R., Perryman, M., Andrady, A., Narayan, R., & Law, K. L. . Plastic waste inputs from land into the ocean. *Science (American Association for the Advancement of Science)* 2015, 347(6223), 768–771.
- (3) Chemical structures and molecular weight data obtained from Sigma Aldrich.

Acknowledgements

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