Electronic Supplementary Information (ESI) for:

Speciation of Organotins in Poly Vinyl Chloride Pipe via X-Ray Absorption Spectroscopy and in Leachates by Ethylation/Derivitization

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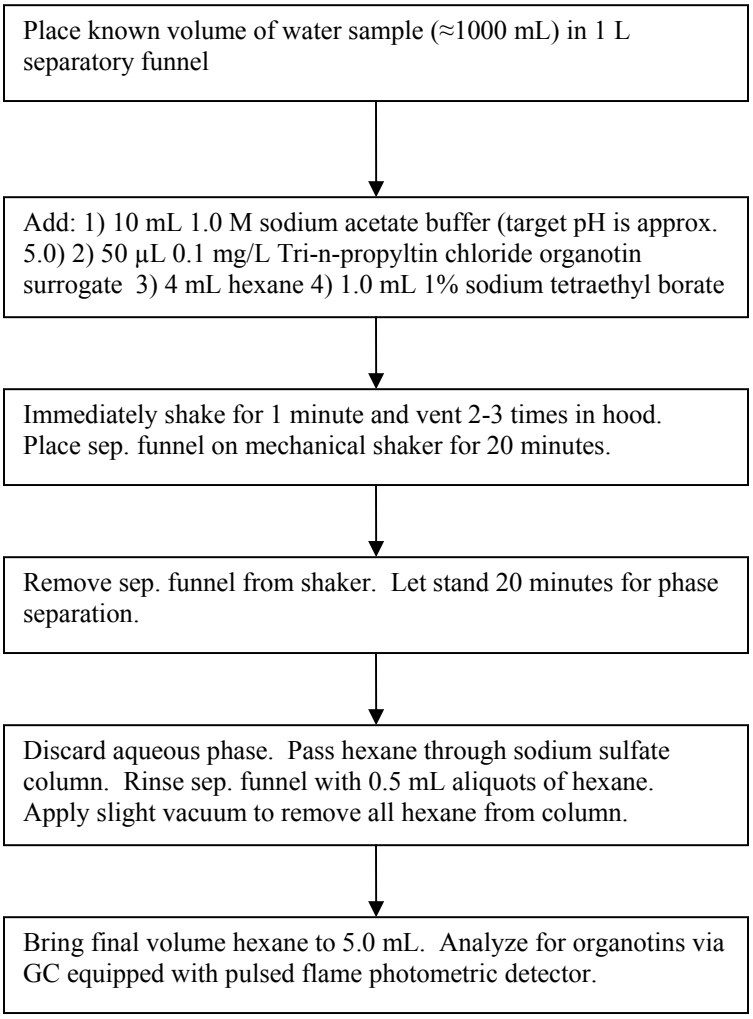
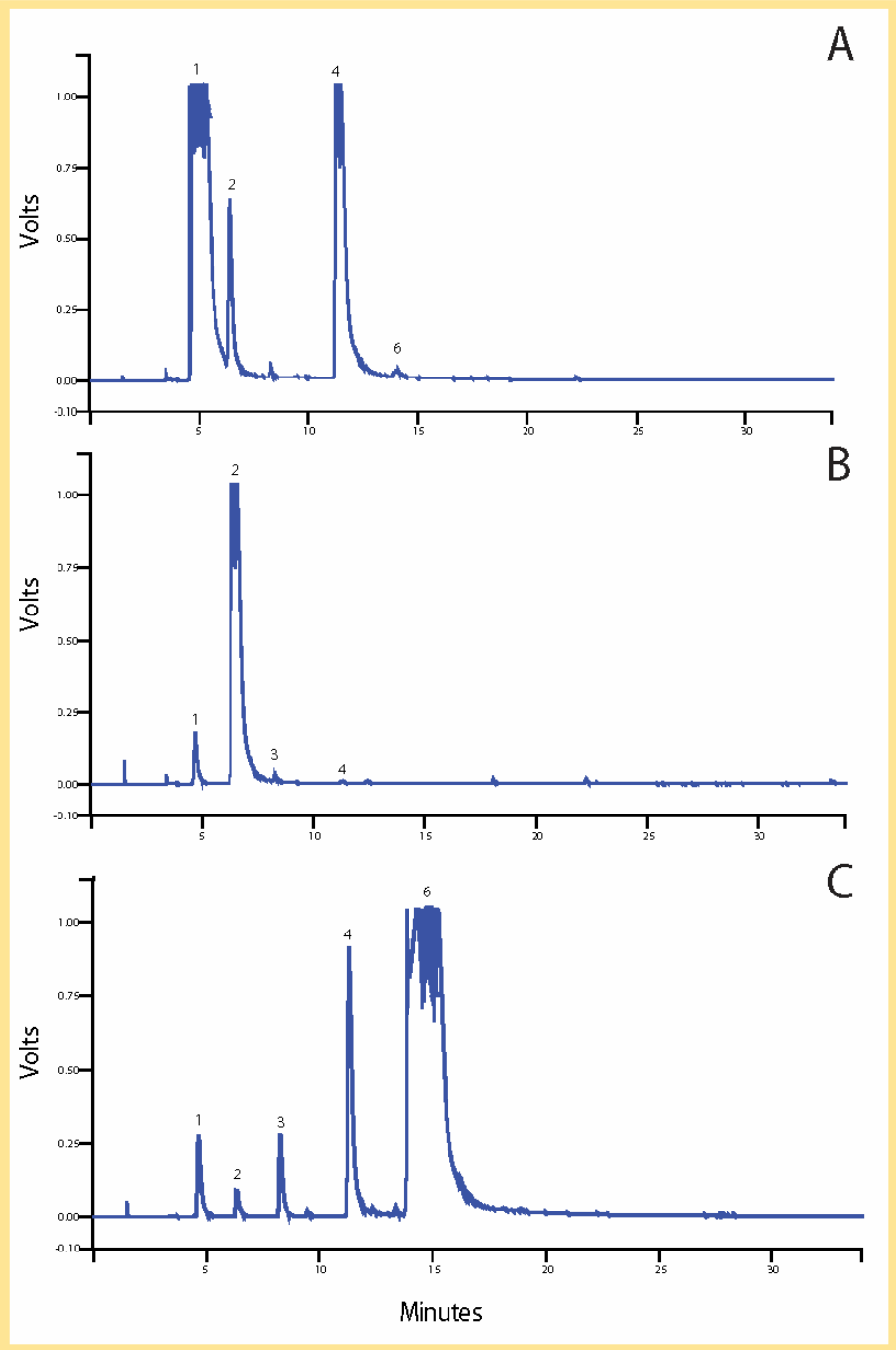
Analytical method for ethylation/extraction of organotins in water.





Example chromatogram for leachates in Charlotte pipe (A), IPEX pipe (B), and FlowGuard Gold pipe (C). Analytes are DMT (1), MMT (2), tetraethyl tin (3), MBT (4), DBT (6).

XAS parameters/methodology

Organotin standards, inorganic tin standards, and PVC pipe samples were analyzed via X-ray absorption near-edge spectroscopy (XANES) and X-ray absorption fine structure (XAFS). Sn (29.2 KeV) K-XANES and XAFS data were collected at beamline 10-ID (Materials Research Collaborative Access Team (MRCAT)) at the Advanced Photon Source at Argonne National Laboratory, Argonne, IL. The electron storage ring operated at 7 GeV. A liquid nitrogen cooled double crystal Si(111) monochromator was used to select incident photon energies and a platinum-coated glass mirror was used for harmonic rejection. Three to five scans were collected at ambient temperature in transmission mode. XANES and XAFS spectra were collected in both transmission and fluorescence modes using ionization chambers for the incident, transmitted, fluorescence, and reference channels. Reference samples of stannous chloride (Sn(II), liquid-l), SnO_2 (Sn(IV), solid-s), MMT (s), DMT (s), MBT (l), DBT (s), TPHT (s), TBT (l), TCHT, MPHT (l) were collected for comparison with the pipe sample XANES spectra. Solid reference materials were diluted with boron nitride (final concentration approximately 10,000 mg kg^{-1} Sn) and placed in Teflon sample holders with a thickness 5 mm. Liquid samples were placed in 5 mL glass vials (1 mm wall thickness) and diluted with hexane (final concentration approximately 10,000 mg L^{-1} Sn). The collected scans for a particular sample were aligned using a reference tin foil and averaged. The averaged data were then normalized and the background was removed by spline fitting using Athena (see text, reference 21). The background-subtracted EXAFS data were converted from energy (E) to photoelectron wavenumber (k), windowed, and Fourier transformed to R-space for Figure 7 in the main text.

To verify that the data for the organotin standards was fully understood, these data were analyzed using the Artemis program (see text, reference 21) and theoretical standards computed using FEFF 6L (S. I. Zabinsky, J. J. Rehr, A. Ankudinov, R. C. Albers, and M. J. Eller, *Multiple-Scattering Calculations of X-ray-Absorption Spectra*, Physical Review **B52**:4 (1995) 2995 – 3009). For each organotin species R_nSnCl_{4-n} input data for Feff 6L was generated from cartesian coordinates found at the UC Irvine ChemDB website (http://cdb.ics.uci.edu/CHEM/Web/cgibin/ChemicalSearchWeb.py). In each case, the structure with n=2 was used to compute the theory. For each alkyl or aryl group, R, the data for that group were co-refined. For example, the EXAFS data collected on MMT and DMT were analyzed simultaneously. For each R, six parameters were measured: (1) an amplitude intended to measure the so-called passive amplitude reduction factor S_0^2 as well as any systematic distortions to the measured amplitude, (2) an energy phase shift ΔE_o, (3) a change in bond length for the carbon scatterer, (4) a mean-square deviation σ^2 in bond length for the carbon, (5) a change in bond length for the chlorine scatterer, and (6) a mean-square deviation σ^2 in bond length for the chlorine. Continuing with the example of the methyltin species – for the MMT, three chlorine scatterers were used in the fit along with one carbon from the single methyl group, while for the DMT, two chlorine and two carbon scatterers were used. In this way, the six parameters could be fit to the MMT and DMT simultaneously. The results along with measured uncertainties for each parameter and each R are shown in Table 1ESI.

From the results in Table 1ESI, we see that results for carbon and chlorine bond lengths are quite consistent for each R, although the strengths of the bonds vary somewhat

between R groups, as seen by the values for σ^2. The one troubling aspect of these otherwise high quality fits is the large values for the passive amplitude reduction factor S_0^2, a number that should not be larger than 1. In each case, the refined values are larger than 1, even outside their error bars. The most likely cause of this discrepancy is the relatively primitive energy loss model available in Feff 6L.

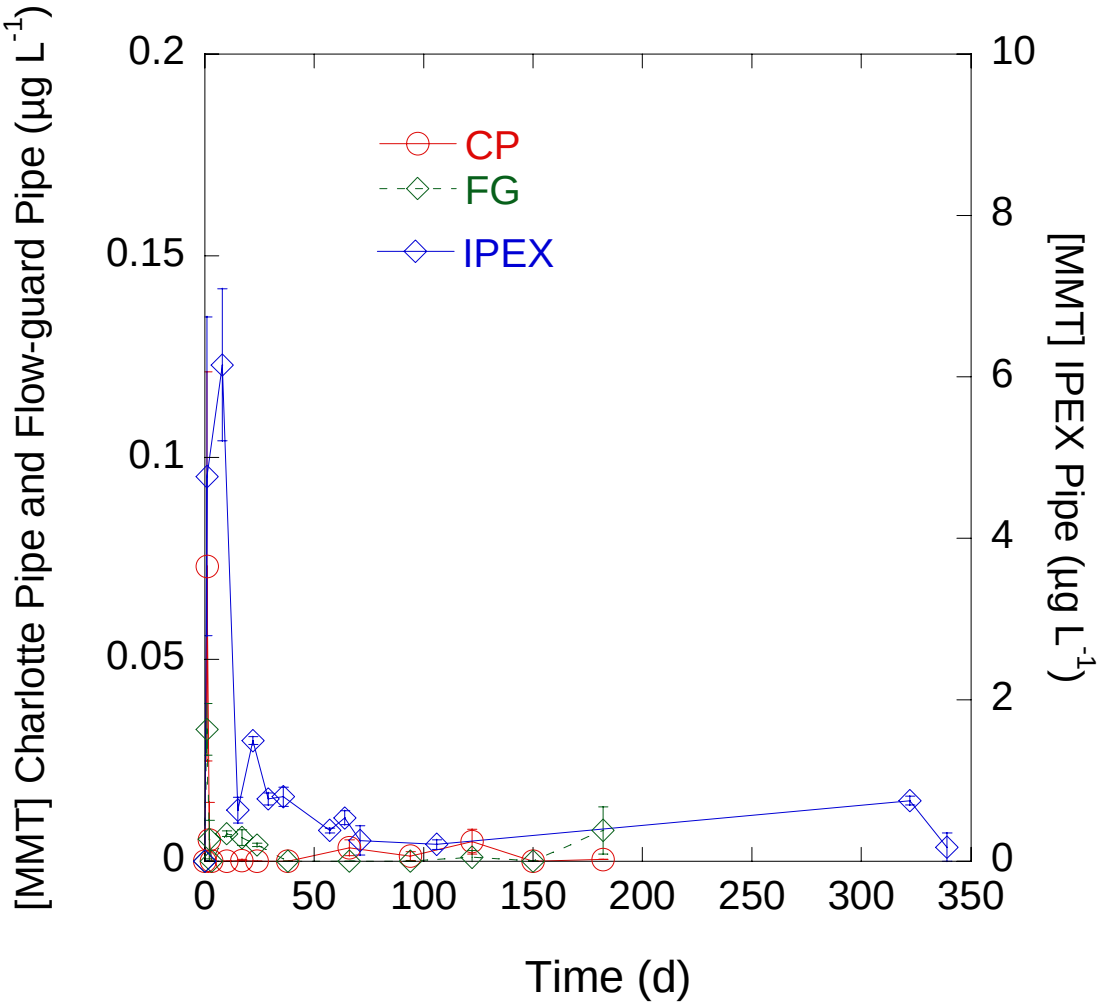


Fig. 1ESI – Leaching of MMT from PVC pipes. 0-180 days for Charlotte pipe (CP) and FlowGuard Gold (FG). 0-350 days for IPEX pipe. Please note different scales on y-axes.

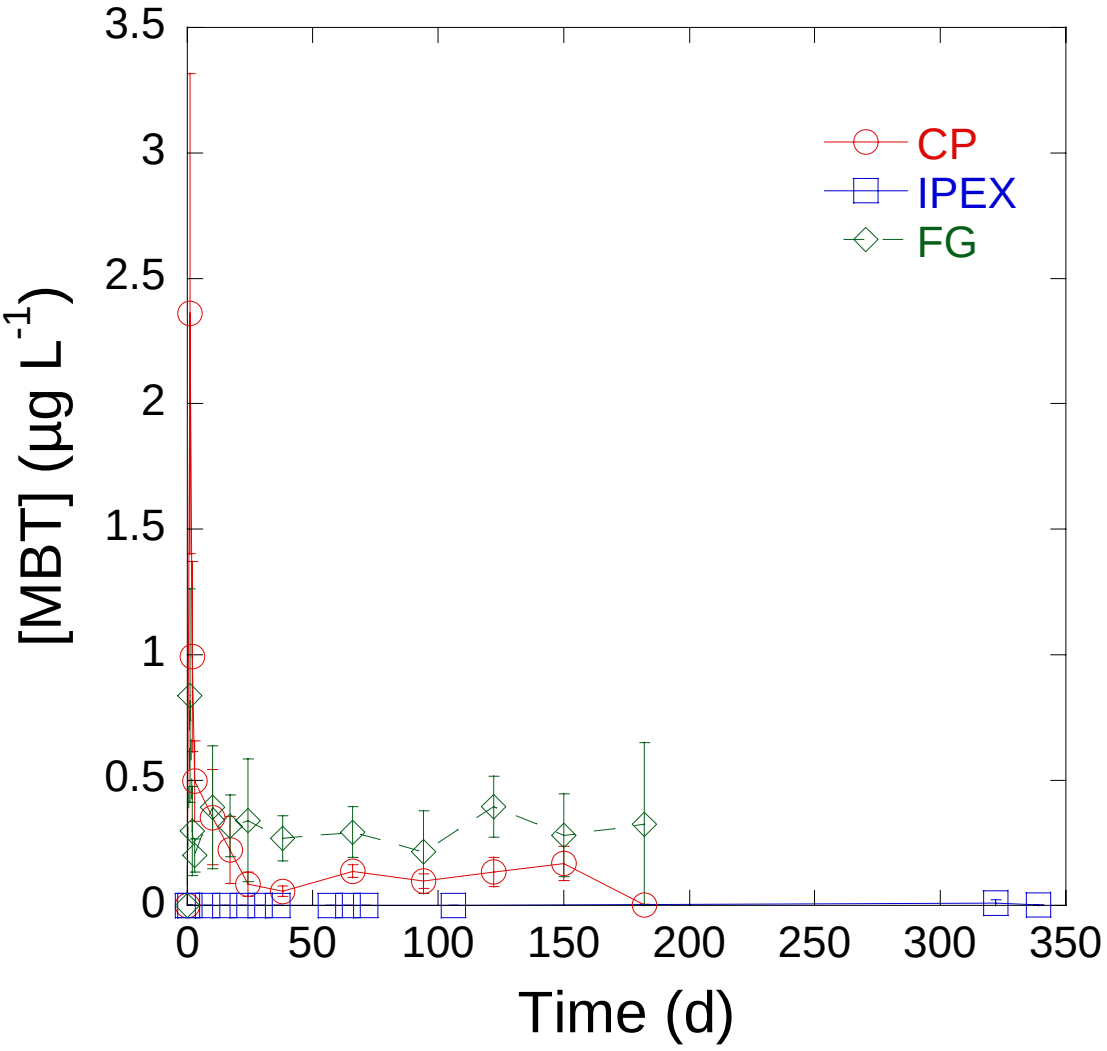


Fig 2ESI – Leaching of MBT for PVC pipes. 0-180 days for Charlotte pipe (CP) and FlowGuard Gold (FG). 0-350 days for IPEX pipe.

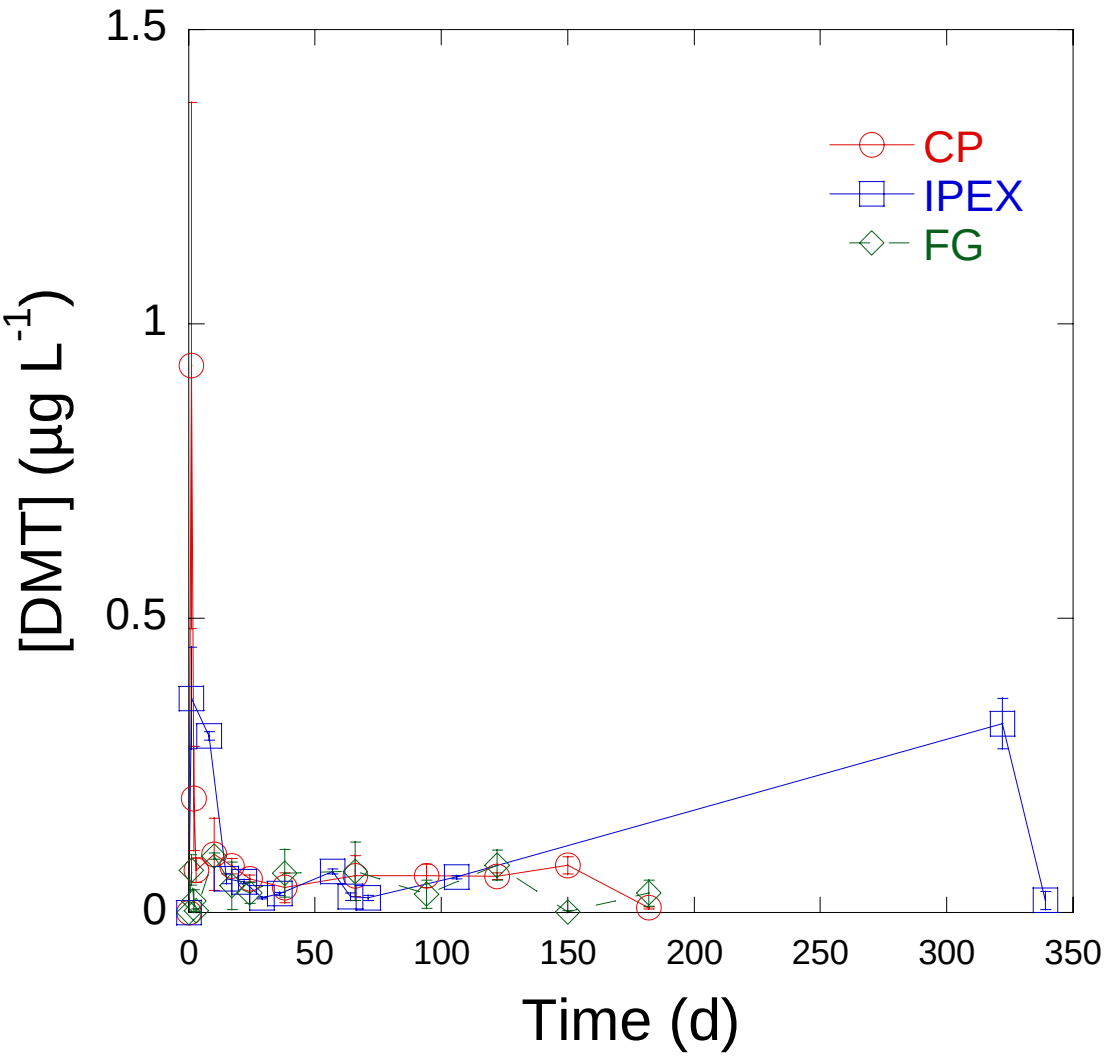


Fig. 3ESI – Leaching of DMT from PVC pipe. 0-180 days for Charlotte pipe (CP) and FlowGuard Gold (FG). 0-350 days for IPEX pipe.

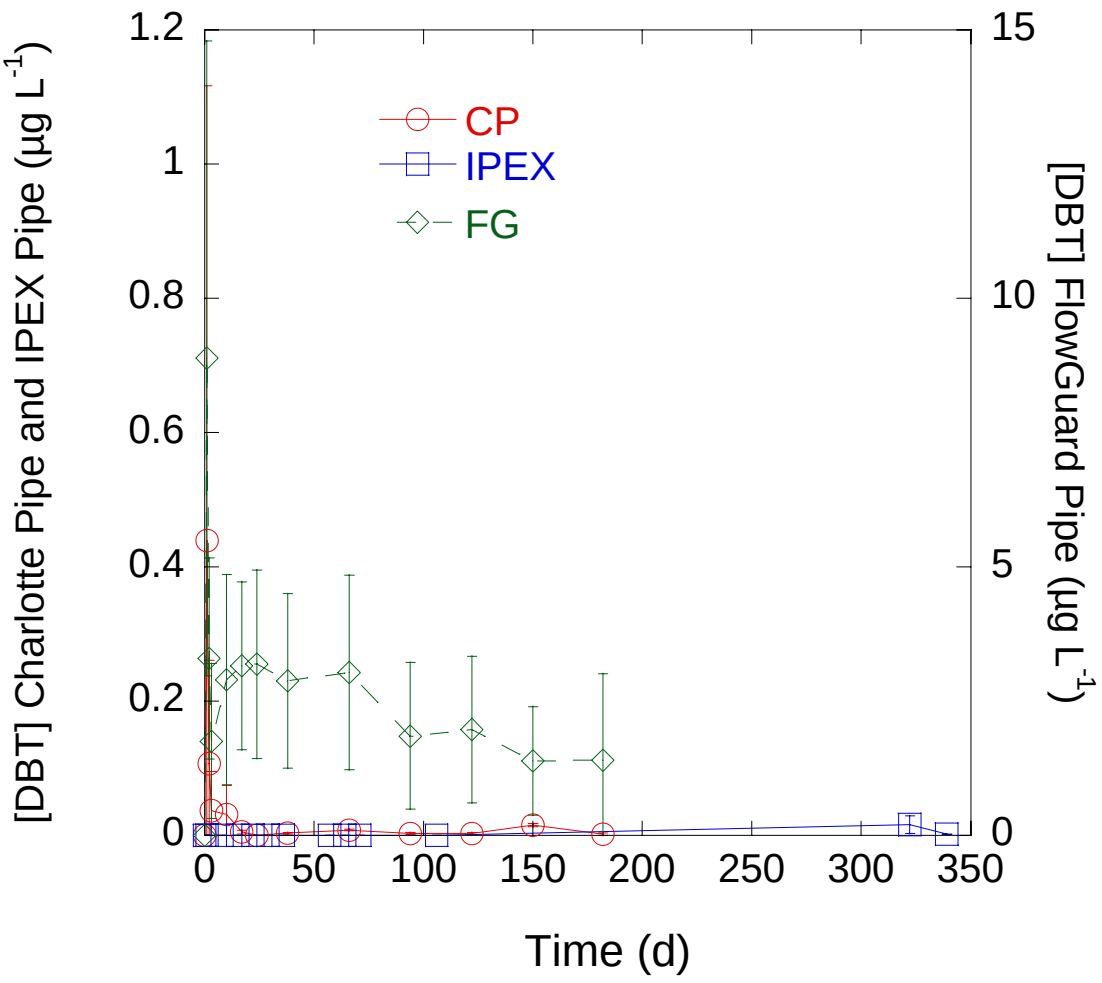


Fig 4ESI – Leaching of DBT from PVC pipes. 0-180 days for Charlotte pipe (CP) and FlowGuard Gold (FG). 0-350 days for IPEX pipe. Please note different scales on y-axes.

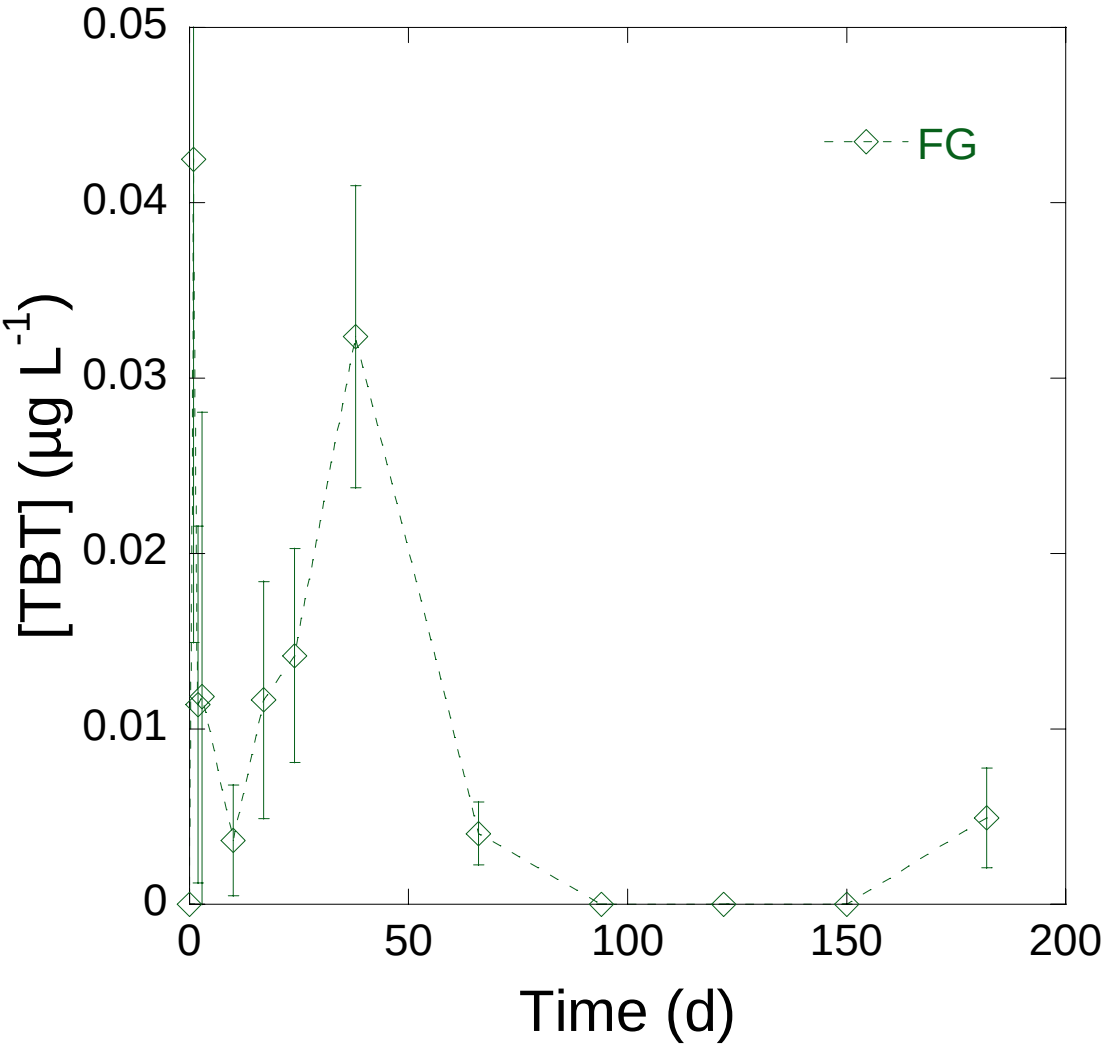


Fig. 5ESI – Leaching of TBT from FlowGuard Gold pipe. 0-180 days.

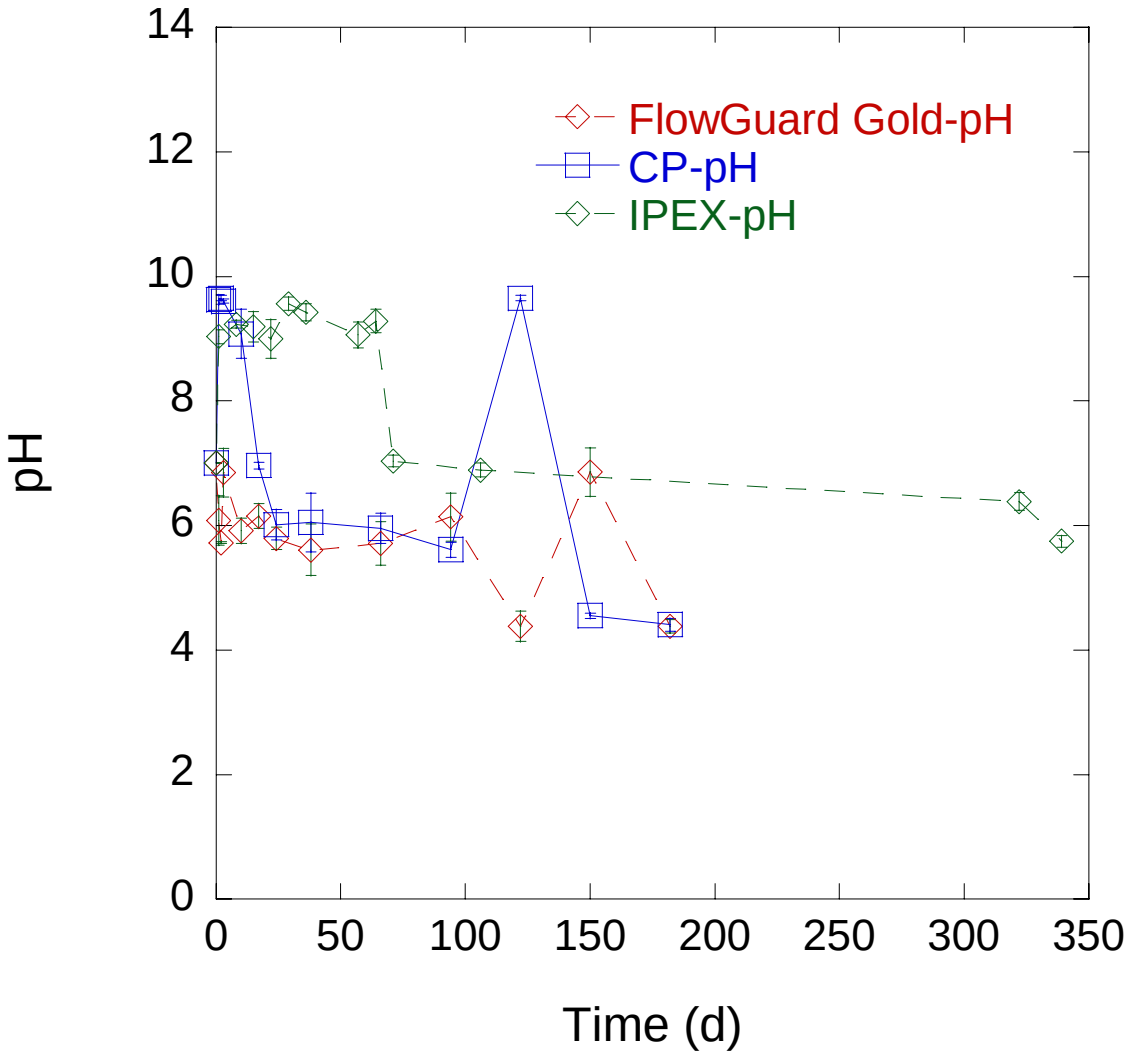


Fig 6ESI – pH data for the leaching experiments.

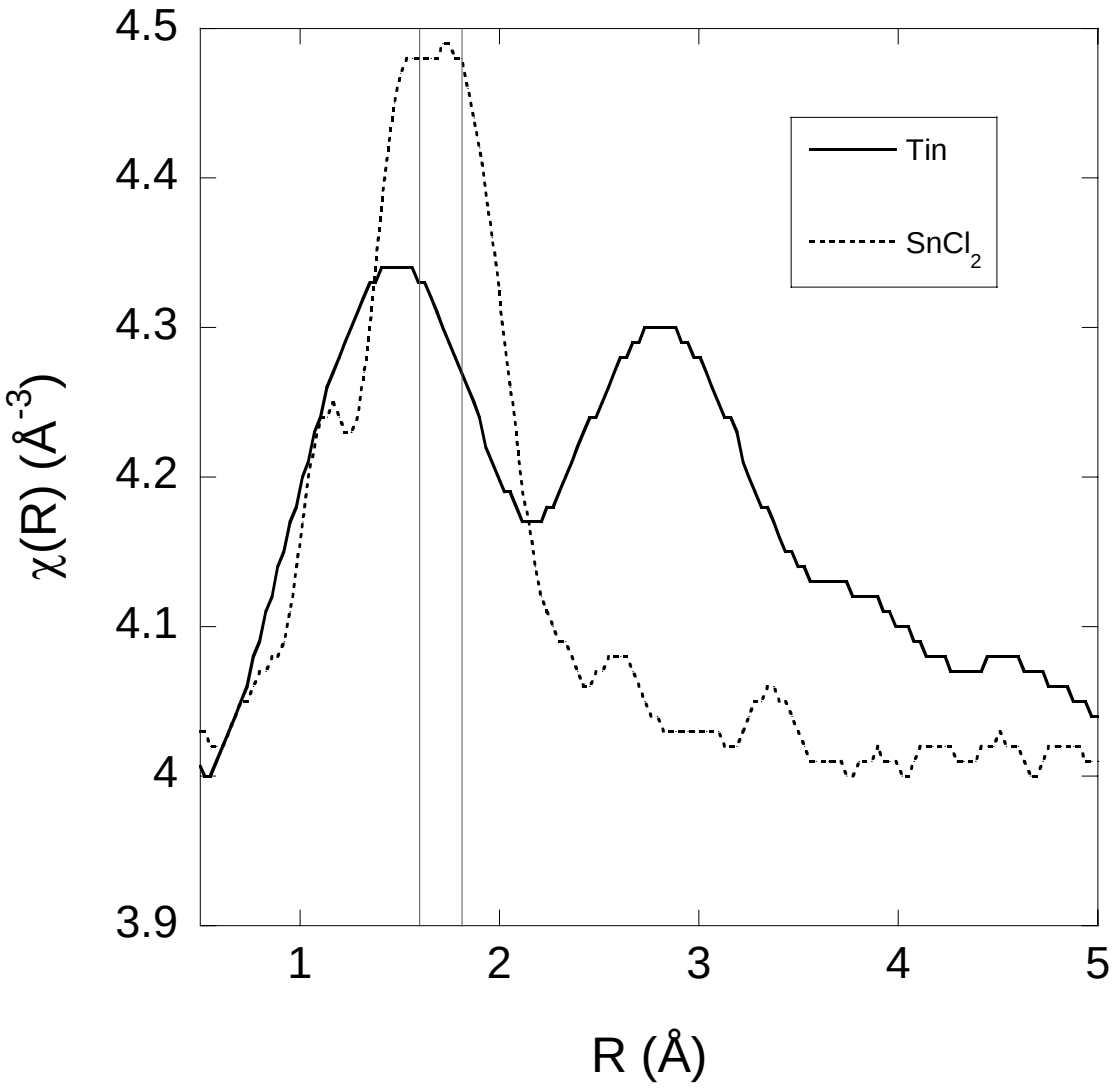


Fig. 7ESI – Peak positions for inorganic tin standards in R-space.

Carbon group	S_0^2	E_0 (eV)	R (C) (Å)	σ^2 (C) (Å^2)	R (Cl) (Å)	σ^2 (Cl) (Å^2)
Methyl	1.40 (19)	4.41 (1.76)	2.107 (23)	0.00379 (313)	2.397 (14)	0.00724 (187)
Phenyl	1.47 (30)	4.63 (2.05)	2.108 (26)	0.00568 (412)	2.392 (58)	0.00574 (196)
Butyl	1.27 (22)	4.56 (2.28)	2.116 (33)	0.00800 (550)	2.384 (18)	0.00559 (234)
Cyclohexyl	1.74 (38)	5.41 (2.52)	2.127 (25)	0.00496 (359)	2.384 (34)	0.00911 (591)

Table 1ESI. The results of fitting the organotin compounds using the fitting model described in the text, including the amplitude reduction factor (S_0^2), the energy shift aligning theory to data (E_0), bond length (R), and mean square variation in bond length (σ^2). Uncertainties determined from the evaluation of the covariance in the fit are given in parentheses.