The Beaumont-Port Arthur of Texas Passive Sampling of Ambient Concentrations of Volatile Organic Compounds

Final Report

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Section 1 – Introduction

The goal of this project was to gain a more complete overview of volatile organic carbon (VOCs) levels in the area around Beaumont and Port Arthur, Jefferson County, Texas. To accomplish this, passive monitoring devices (PSDs) for the pollutants of interest were deployed at twelve sites across the study area. Around Port Arthur, six sites were established at existing sites used by the Texas Commission on Environmental Quality (TCEQ) for routine air pollution monitoring. In Beaumont, two existing TCEQ sites were also employed, and the remaining four sites for the project were located at Beaumont fire stations.

The use of TCEQ sites and fire stations offered several advantages. First and foremost, they are well-distributed across the area from a geographic standpoint. Secondly, only two agencies needed to be consulted for permission to conduct the sampling. Fire stations typically would be expected to have enough open physical space to accommodate the samplers, and physical access to the collectors would not generally be difficult. Finally, the potential for vandalism of the samplers would be low. The TCEQ sites were all well-established with good data capture records; the fire stations did not have enough open space or other features (e. g., playground equipment) to attract people who might be tempted to disturb the samplers, and the stations are staffed around the clock. Figure 1 displays the study area, the location of the sampling sites, and other relevant features such as the Neches Sabine Canal, emissions sources, major roads, and population density. Sites labeled 1-8 are TCEQ locations and sites 9-12 are at fire stations. The emissions levels indicated in Figure 1 are for total VOCs, based on EPA's National Emissions Inventory (NEI) for 2005 for Jefferson County.

The sampling was conducted between October 3, 2007 through November 7, 2007. Five week long (Wednesday to Wednesday) samples were collected at each site. Duplicate samples were collected at two locations each week with the duplicate sampling rotating among the sites over the five week period. The VOCS were sampled with Carbopack X diffusive sampling tubes. Alion personnel installed the sampling devices and collected the weekly samples. Upon collection, the samples were shipped to Alion personnel at the EPA facility in Research Triangle Park, NC for chemical analysis. Details of all quality assurance related topics including standard operating procedures for both field and laboratory are provided in the Quality Assurance Project Plan (Alion, 2007) developed at the beginning of the project. (This document was provided earlier.)

The chemical analysis results from this project were furnished electronically to EPA. Section 2 of this report describes the results of the statistical analyses of the data obtained. All concentration units discussed here are in parts per trillion (volume), denoted as pptv.

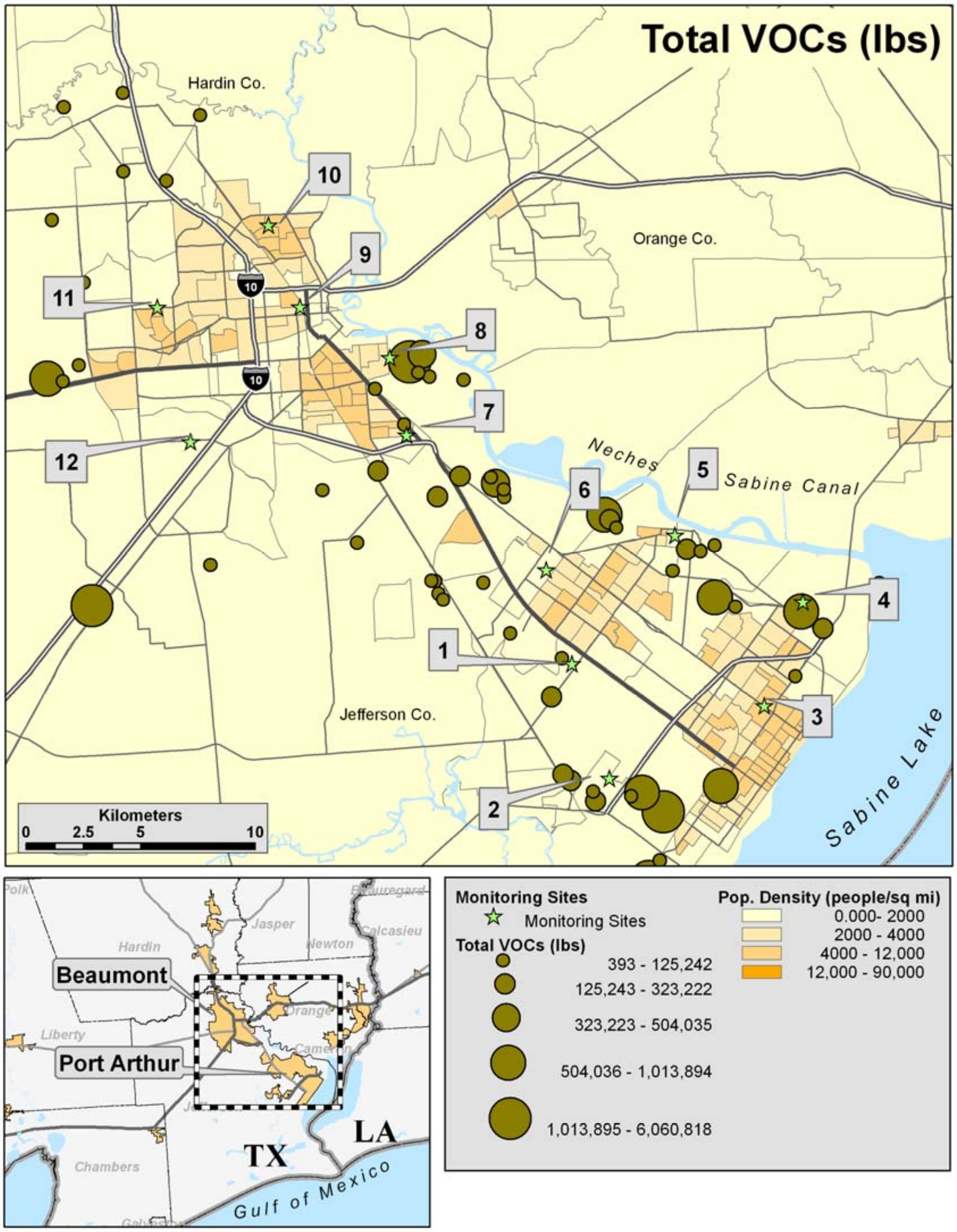

Figure 1. Beaumont Monitoring Sites and 2005 Total VOC Emissions.

Section 2 – Results

The monitoring generally went quite smoothly. Including duplicates, seventy weekly samples were possible over the five week period, and all samples were valid. Generally, levels were quite low. Table 1 provides the method detection limits (MDL) and the below detection limit (BDL) counts for each of the twenty-five monitored VOCs; the nonzero BDL counts indicate values that were below the MDL, but above the analytical detection limit. One observes that for five of the VOCs no sample was ever measured as above the detection limit. These were: Freon 114; *cis*-1,2-dichloroethene; 1,2-dichloropropane; *m*-dichlorobenzene; *o*-dichlorobenzene. In addition, three other compounds were almost always below the detection limit: trichloroethene; 1,1-dichloroethane; chlorobenzene.

Table 1. MDLs and BDL Counts.

Compound	MDL (pptv)	BDL Count	Nonzero BDL Count
Benzene	8	0	0
Toluene	25	0	0
Ethylbenzene	8	0	0
m,p-xylene	16	0	0
o-xylene	8	1	1
4-ethyltoluene	21	3	3
1,3,5-trimethylbenzene	15	1	1
Chlorobenzene	8	68	62
m-dichlorobenzene	8	70	29
p-dichlorobenzene	9	2	2
o-dichlorobenzene	9	70	39
Styrene	16	1	0
1,1-dichloroethane	12	68	1
1,2-dichloropropane	23	70	1
1,1-dichloroethene	8	0	0
cis-1,2-dichloroethene	25	70	2
Trichloroethene	22	65	22
Tetrachloroethene	9	0	0
1,1,1-trichloroethane	9	1	0
Carbon tetrachloride	18	1	0
Freon 113	8	1	1
Freon 114	8	70	0
Freon 11	40	1	0
1,2-dichloroethane	14	15	9
1,3-butadiene	33	0	0

Table 2 reports the precision from the duplicate monitoring sites for all species measured. The table presents precision in the form of the mean absolute difference both in terms of concentration units and as a percentage. For purposes of the precision calculations, all values below the method detection limit were set to one half the detection limit. Precision was generally quite good as evidenced by the very low absolute differences. Note that while a few of the percentage differences are quite high, this was driven by the fact that the actual concentrations were very low.

Table 2. Precision Results.

Compound	MDL (pptv)	BDL Count SA	BDL Count DU	Mean Abs Diff (pptv)	Mean % Difference
Benzene	8	0	0	29	5
Toluene	25	0	0	27	4
Ethylbenzene	8	0	0	12	10
m,p-xylene	16	0	0	50	13
o-xylene	8	0	0	18	13
4-ethyltoluene	21	0	1	10	33
1,3,5-trimethylbenzene	15	0	0	9	24
Chlorobenzene	8	10	9	1	4
m-dichlorobenzene	8	10	10	0	0
p-dichlorobenzene	9	0	0	5	21
o-dichlorobenzene	9	10	10	0	0
Styrene	16	0	0	15	13
1,1-dichloroethane	12	10	10	0	0
1,2-dichloroethane	14	2	2	3	11
1,1-dichloroethene	8	0	0	0	4
cis-1,2-dichloroethene	25	10	10	0	0
Trichloroethene	22	9	9	0	0
Tetrachloroethene	9	0	0	3	15
1,1,1-trichloroethane	9	0	0	2	11
Carbon tetrachloride	18	0	0	23	24
Freon 113	8	0	0	3	3
Freon 114	8	10	10	0	0
Freon 11	40	0	0	12	8
1,2-dichloropropane	23	10	10	0	0
1,3-butadiene	33	0	0	48	11

For the chemicals considered for further statistical analysis, Table 3 provides the minimum, median, mean and maximum values of the weekly means over all twelve sites. That is, the weekly sample observations were averaged (after averaging the duplicate samples, where applicable) across weeks for each site. The summary statistics for these twelve site means are then reported in Table 3. Table 4 provides the actual site means themselves.

Table 3. Summary Statistics (pptv) of the Weekly Means over 12 Sites.

COMPOUND	MIN	MEDIAN	MEAN	MAX
Benzene	414	649	736	1670
Toluene	448	741	856	1882
Ethylbenzene	82	110	143	326
m,p-xylene	233	358	511	1490
o-xylene	91	138	190	522
4-ethyltoluene	27	35	41	73
1,3,5-trimethylbenzene	25	38	47	92
p-dichlorobenzene	11	20	23	42
Styrene	27	44	100	728
1,2-dichloroethane	16	24	23	30
1,1-dichloroethene	10	10	10	10
Tetrachloroethene	15	21	31	140
1,1,1-trichloroethane	11	17	16	20
Carbon tetrachloride	70	102	104	134
Freon 113	62	81	80	88
Freon 11	118	139	149	289
1,3-butadiene	124	318	442	1280

Table 4. Site Means (pptv).

COMPOUND	SITE MEANS											
	Site_1	Site_2	Site_3	Site_4	Site_5	Site_6	Site_7	Site_8	Site_9	Site_10	Site_11	Site_12
Benzene	769	695	603	1,151	474	572	717	1,670	596	705	465	414
Toluene	724	683	845	1,882	448	623	758	1,439	858	937	593	484
Ethylbenzene	99	116	150	326	96	95	103	245	162	147	100	82
m,p-xylene	303	363	527	1,490	233	320	352	869	562	514	337	267
o-xylene	119	145	198	522	91	123	127	307	214	199	130	100
4-ethyltoluene	33	36	39	70	27	31	31	73	48	46	35	28
1,3,5-trimethylbenzene	34	37	43	90	25	31	33	92	56	53	39	31
p-dichlorobenzene	14	19	37	28	11	11	21	25	30	42	18	16
Styrene	44	36	59	54	728	47	27	44	44	32	31	51
1,2-dichloroethane	25	22	25	28	26	18	23	27	30	16	20	21
1,1-dichloroethene	10	10	10	10	10	10	10	10	10	10	10	10
Tetrachloroethene	30	15	18	21	18	17	22	21	140	32	18	27
1,1,1-trichloroethane	17	18	18	20	17	16	16	17	18	11	14	14
Carbon tetrachloride	106	98	92	98	98	106	123	113	134	70	93	120
Freon 113	81	84	84	88	82	79	80	84	84	62	77	78
Freon 11	132	147	289	153	128	121	123	144	152	118	139	139
1,3-butadiene	346	291	360	570	1,280	357	244	1,244	207	146	124	140

Figures A1-A12 in Appendix A display the observed concentrations by week at each site for several of the chemicals measured during the project. Similar plots appear in Appendix B for the rest of the chemicals monitored. It is noteworthy that, with a few exceptions during the latter weeks, sites 4 and 8 exhibited higher concentrations than the other sites for benzene (Figure A1), toluene (Figure A2), ethylbenzene (Figure A3), *m*,*p*-xylene (Figure A4), *o*-xylene (Figure A5), 4-ethyltoluene (Figure A6), and 1,3,5-trimethylbenzene (Figure A7).

Similarly, higher levels of 1,3-butadiene (Figure A8) were found at sites 4 and 8, but site 5 also reported higher levels of this chemical. Site 10 saw the highest levels of *p*-dichlorobenzene (Figure A9) in weeks 1, 3, and 4 and the second highest level in week 2; however, site 10 was the lowest of all sites for *p*-dichlorobenzene (in fact, below the method detection limit) during week 5. Styrene (Figure A10) was always considerably higher at site 5 than at any other site, and tetrachloroethene (Figure A11) was always highest at site 9. For 1,2-dichloroethane (Figure A12), most sites were generally higher during week 1, but all sites reported their lowest values (all being below the method detection limit) during week 3.

In the early morning hours of Thursday during week 3 of the sampling, an explosion caused two pipelines to catch fire. The conflagration was located roughly between sites 1 and 2 in Figure 1. However, with the possible exception of 1,2-dichloroethane, no signature of this was seen in the data collected during the project. Some other chemicals in Figures A1-A12 show decreases (at least at some sites), but these declines seem to be within the overall variability exhibited across all weeks of sampling.

In the time plots shown in Appendix B, no salient features appear in the figures for carbon tetrachloride, Freon 11, Freon 113, 1,1-dichloroethene, or 1,1,1-trichloroethane. For the remainder of the chemicals, the time plots in Appendix B simply indicate that these species were almost always below the method detection limit. Even when values for these were reported as above the method detection limit, the concentrations were low.

Figures 2-8 display the concentrations of the BTEX species (benzene, toluene, ethylbenzene, and the xylenes), 1,3,5-trimethylbenzene, and 1,3-butadiene averaged over all sampling periods at each site. It is interesting to note that these figures suggest a general tendency for the concentrations of these chemicals to decline with the distance of the site from the Neches Sabine Canal. This is perhaps not too surprising considering the role of this canal in transporting oil to the Port Arthur-Beaumont petrochemical facilities for processing into a variety of products. As discussed below, the levels of the monitored chemicals were statistically compared between groups of sites.

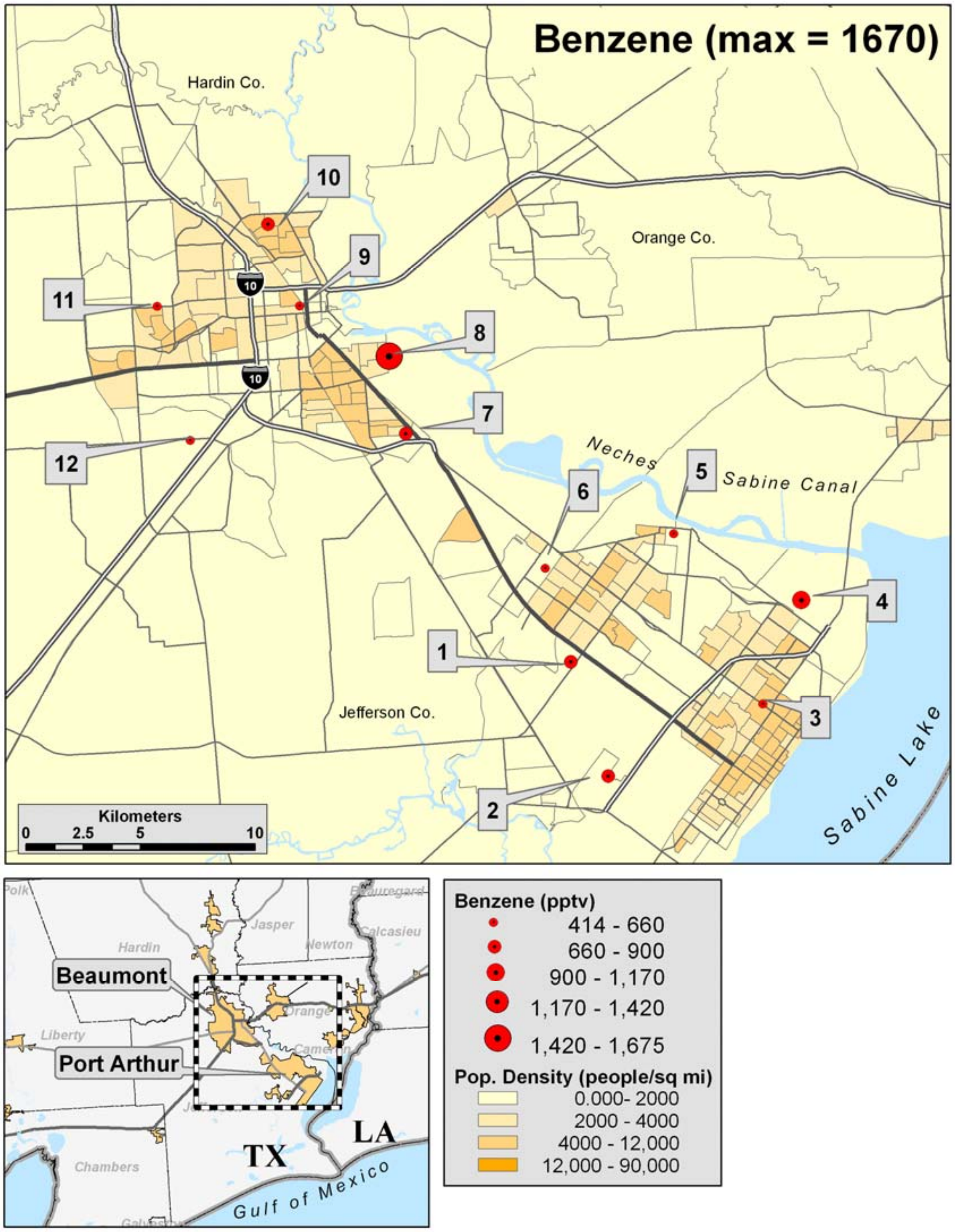

Figure 2. Average Monitored Benzene Concentration.

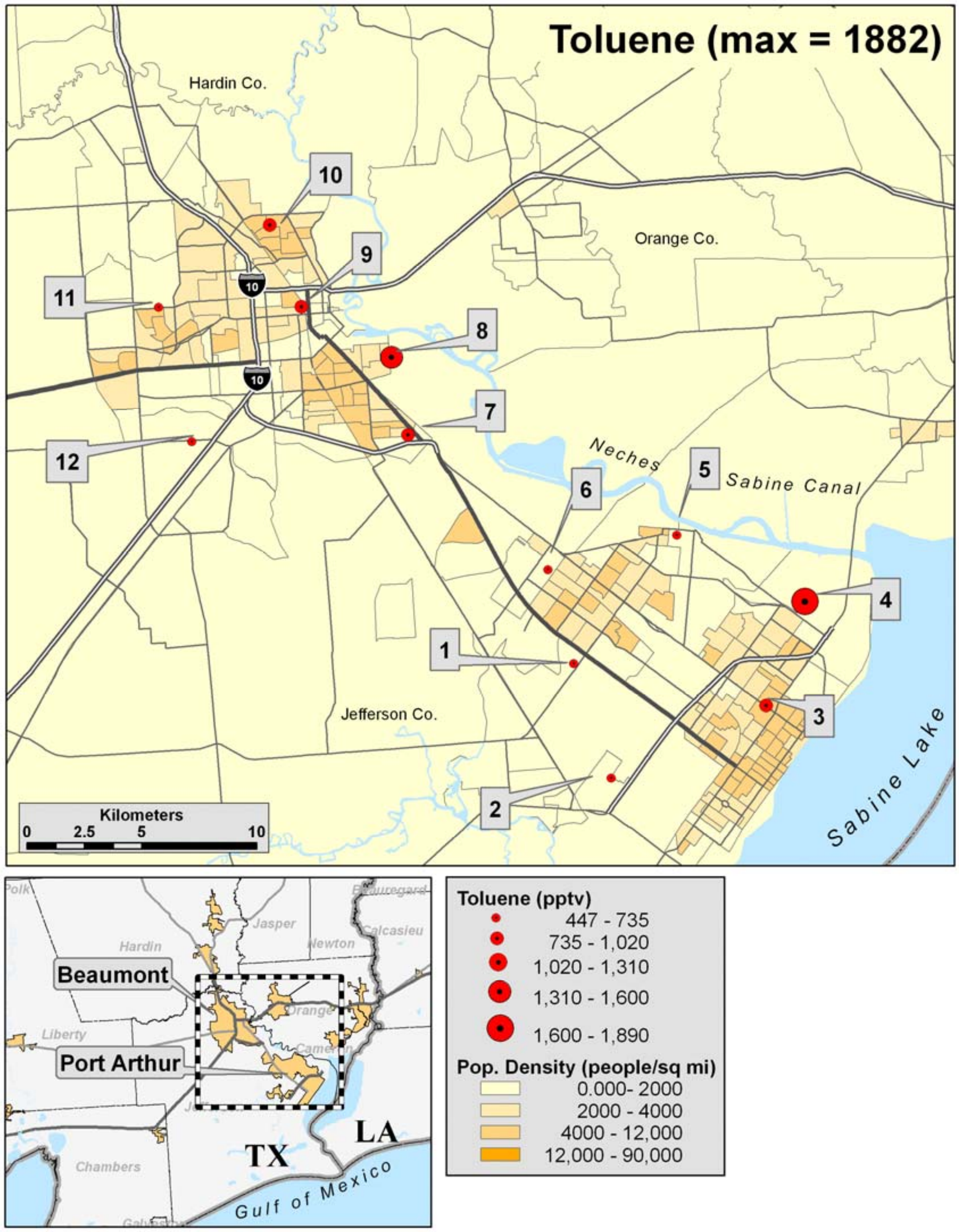

Figure 3. Average Monitored Toluene Concentration.

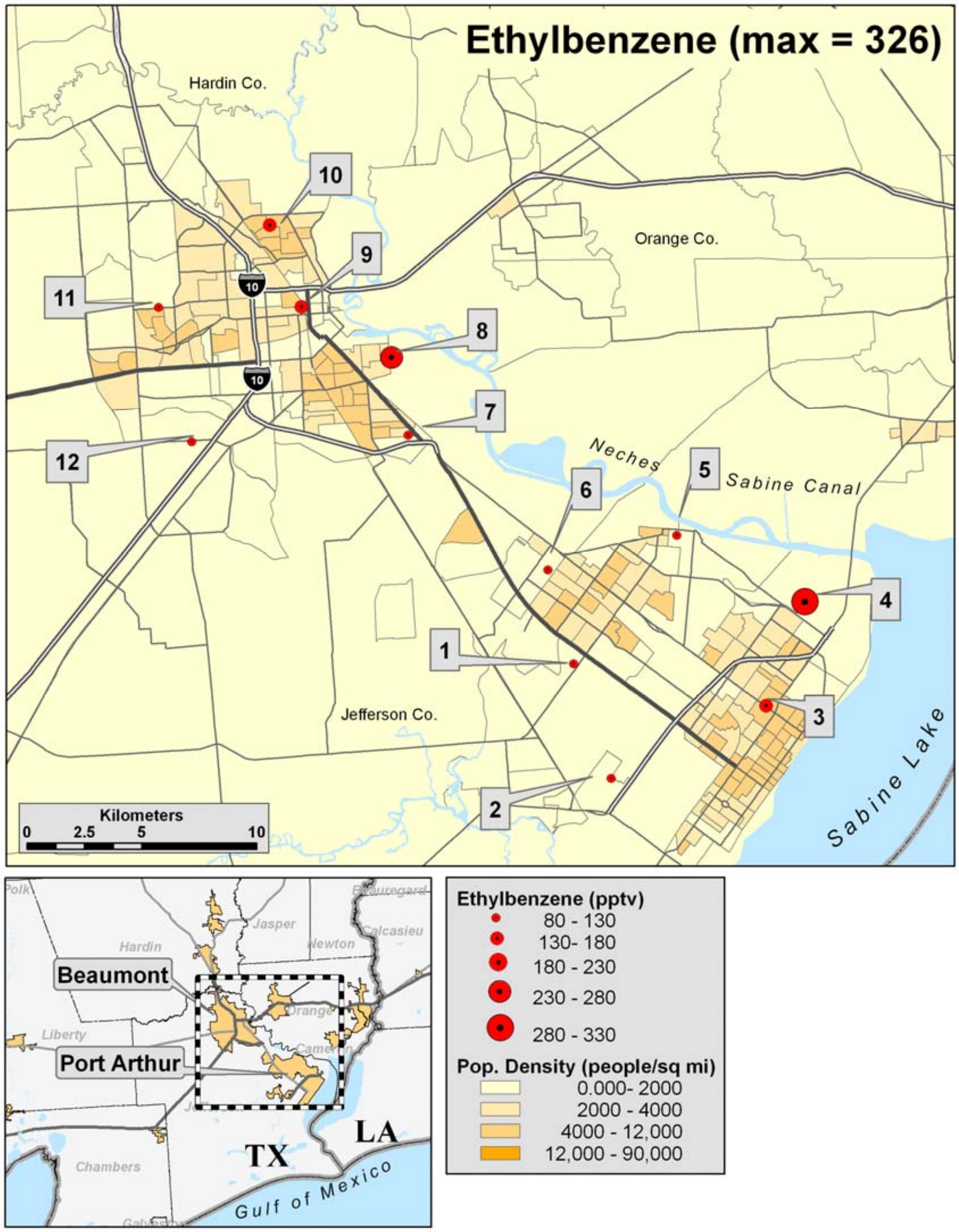

Figure 4. Average Monitored Ethylbenzene Concentration.

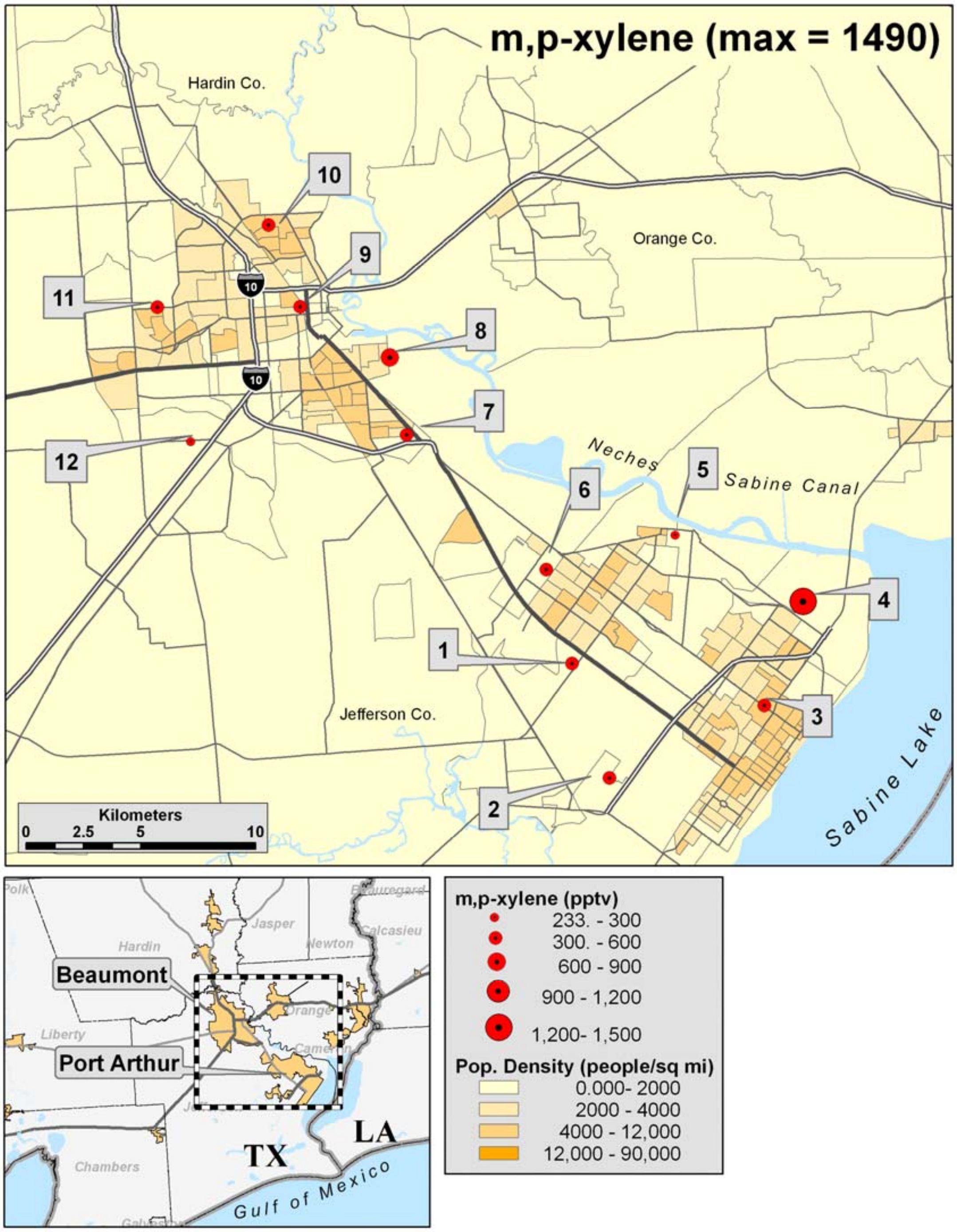

Figure 5. Average Monitored *m,p*-xylene Concentration.

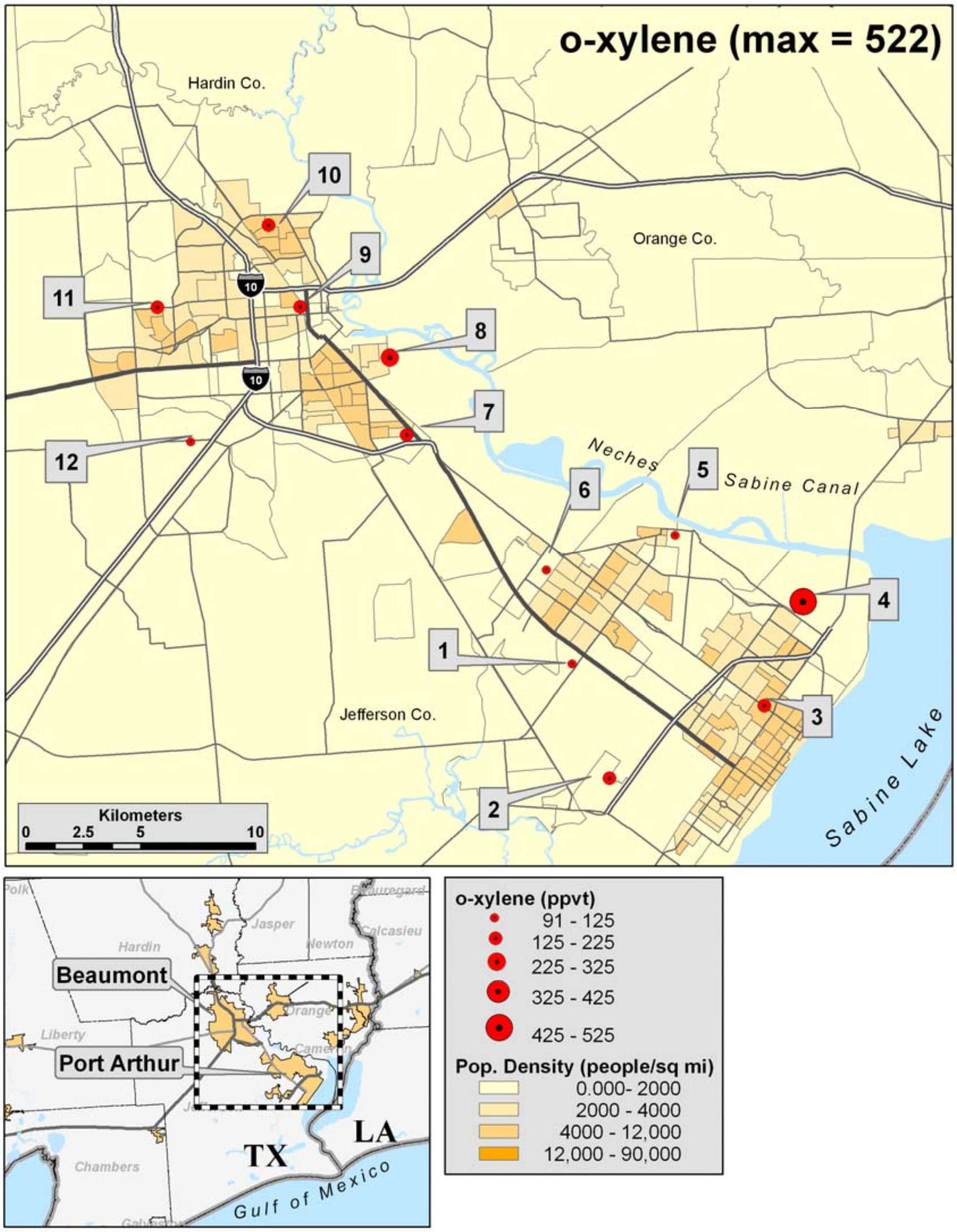

Figure 6. Average Monitored *o*-xylene Concentration.

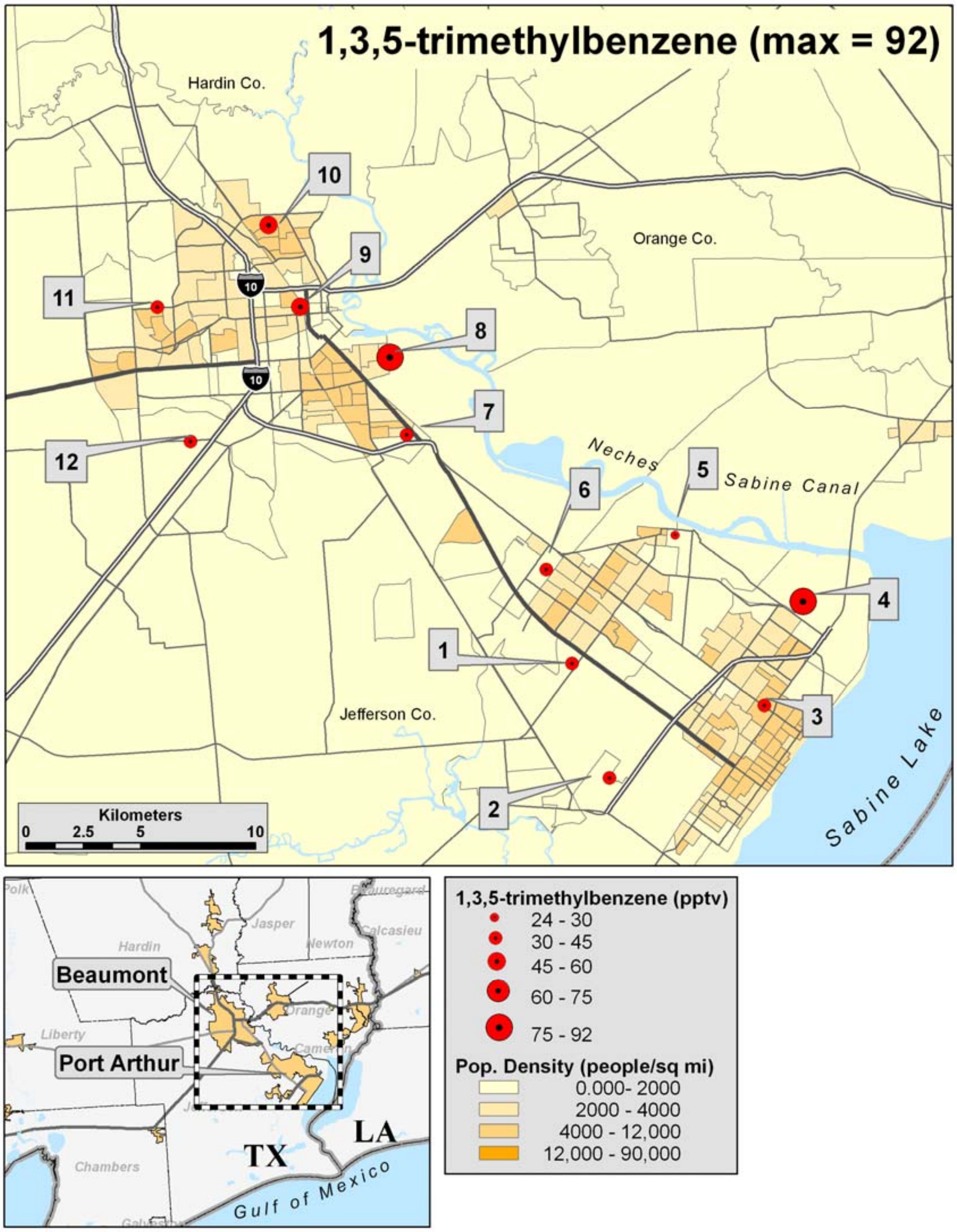

Figure 7. Average Monitored 1,3,5-trimethylbenzene Concentration.

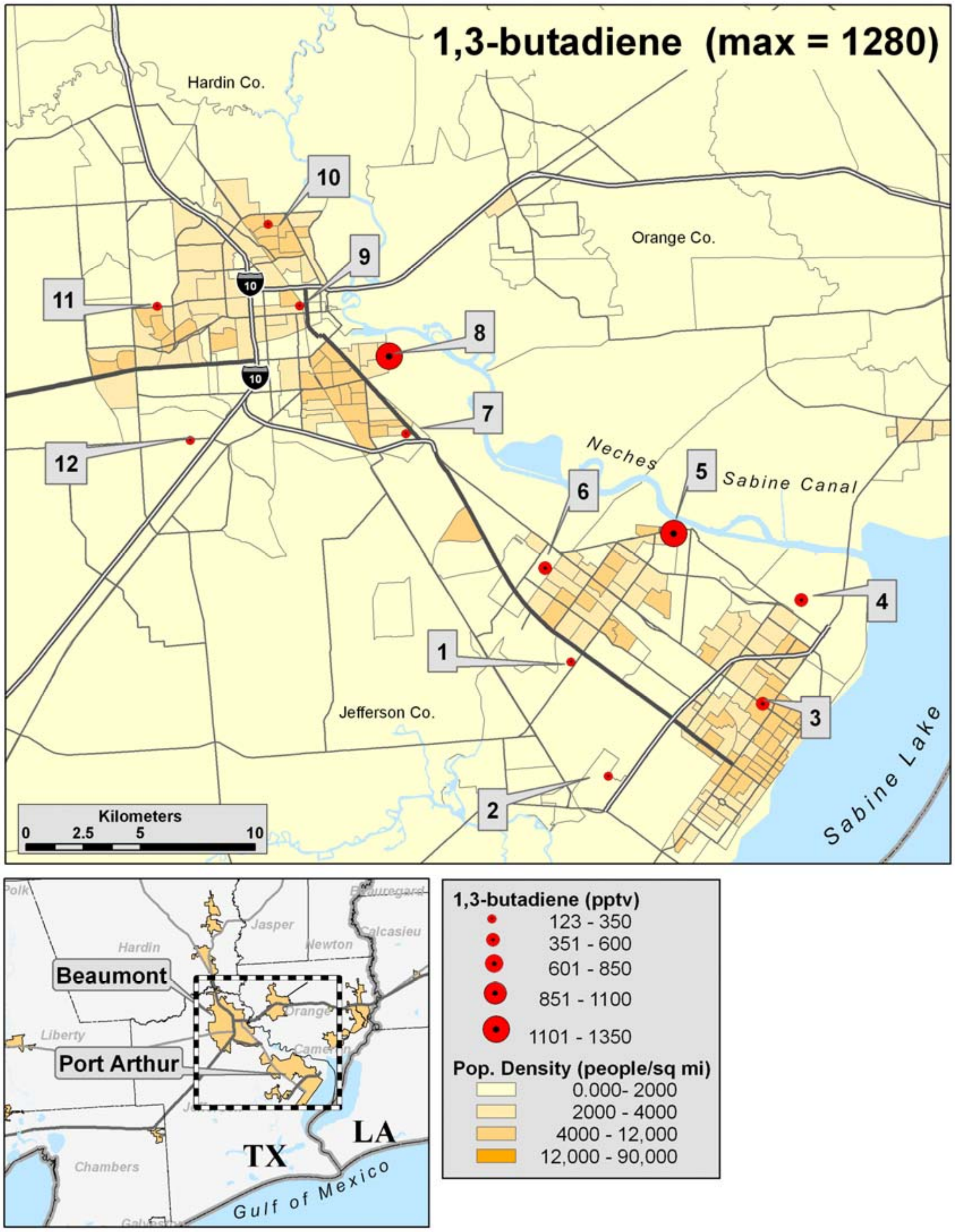

Figure 8. Average Monitored 1,3-butadiene Concentration.

Note in Figure 1 that relatively large emissions sources are located very near sites 4 and 8. These emissions result from ports on the Neches Sabine Canal where tankers offload petroleum for delivery to refineries. (In the case of site 4, the petroleum is delivered directly via pipeline to a facility near the monitoring site.) Site 5 is also near a port, but the role of the port near site 5 could not be determined with certainty.

Based on these considerations, levels of the chemicals were compared between sites. For comparative purposes, sites 4 and 8 were grouped together as "port sites" and compared to the group formed by the remaining ten sites. The comparisons were conducted using the Wilcoxon rank sum test (Hollander and Wolfe, 1999). Because of the relatively small number of sites, the exact form of the test was used; testing was programmed in SAS.

Table 5 displays the results of these comparisons in terms of two-sided p-values; boldface in the table indicates statistical significance at the 5% level. The testing was conducted based on the averages over the five weeks of sampling (the ALL column in Table 5) and separately for each week.

The results of the comparisons were that all the BTEX species, 4-ethyltoluene, and 1,3,5-trimethylbenzene exhibited significantly (at the 5% level) higher concentrations at the port sites over the full length of the project and in both of the first two weeks individually; benzene was higher at the port sites in the last two weeks as well. Toluene, 4-ethyltoluene, and 1,3,5-trimethylbenzene showed higher levels in week 3 at the port sites. Thus, during the sampling conducted for this project, these chemicals exhibited statistically significantly higher concentrations at the port sites (4 and 8) than at the other sites.

The only other statistically significant results at the 5% level were for 1,3-butadiene in week 4 and Freon 113 in week 2, with each chemical being higher at the port sites than the others. It is difficult to gauge the importance these two somewhat anomalous results. It is possible that they are simply statistical artifacts; note that these two significant results occupy 2 of 60 (3.3%) of the cells in the last 10 rows of Table 5.

Table 5. Significance Testing Results: Sites 4 and 8 (Port Sites) vs. Others.

COMPOUND	Two-sided p-value					
	ALL	WK_1	WK_2	WK_3	WK_4	WK_5
Benzene	**0.03**	**0.03**	**0.03**	0.606	**0.03**	**0.03**
Toluene	**0.03**	**0.03**	**0.03**	**0.03**	0.061	0.061
Ethylbenzene	**0.03**	**0.03**	**0.03**	0.061	0.061	0.182
m,p-xylene	**0.03**	**0.03**	**0.03**	0.061	0.061	0.121
o-xylene	**0.03**	**0.03**	**0.03**	0.061	0.061	0.121
4-ethyltoluene	**0.03**	**0.03**	**0.03**	**0.015**	0.106	0.182
1,3,5-trimethylbenzene	**0.03**	**0.03**	**0.03**	**0.015**	0.061	0.182
p-dichlorobenzene	0.485	0.727	0.182	1	0.909	0.258
Styrene	0.485	0.364	0.939	0.591	0.909	0.97
1,2-dichloroethane	0.121	0.167	0.818	0.621	0.152	0.333
1,1-dichloroethene	0.667	0.515	0.546	0.318	0.894	1
Tetrachloroethene	1	0.424	0.273	0.939	0.546	0.409
1,1,1-trichloroethane	0.333	0.106	0.455	0.727	0.227	0.97
Carbon tetrachloride	0.939	0.53	0.742	0.484	0.909	0.909
Freon 113	0.182	0.439	**0.03**	0.591	0.121	0.076
Freon 11	0.273	0.242	0.182	0.909	0.333	0.636
1,3-butadiene	0.121	0.121	0.061	0.121	**0.03**	0.218

References

Alion Science and Technology, 2007, Quality Assurance Project Plan: Passive Sampling of Ambient Concentrations of Volatile Organic Compounds in the Beaumont-Port Arthur Area of Texas prepared for Multimedia Planning and Permitting Division, Region 6, U. S. Environmental Protection Agency.

Hollander, M. and D. A. Wolfe, 1999, *Nonparametric Statistical Methods*, Wiley, New York.

AppendixA

Time Series Plots

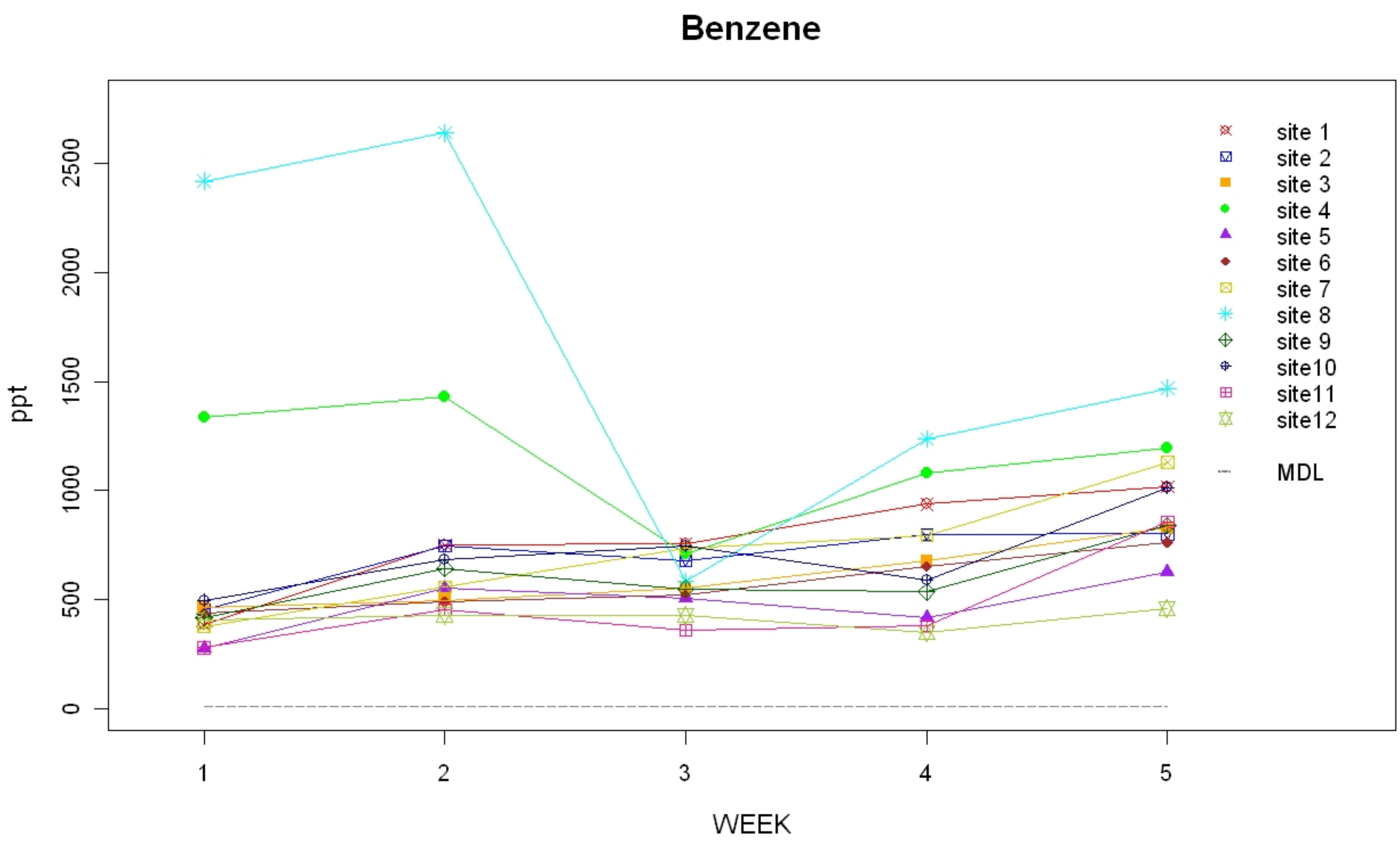

Figure A1. Benzene.

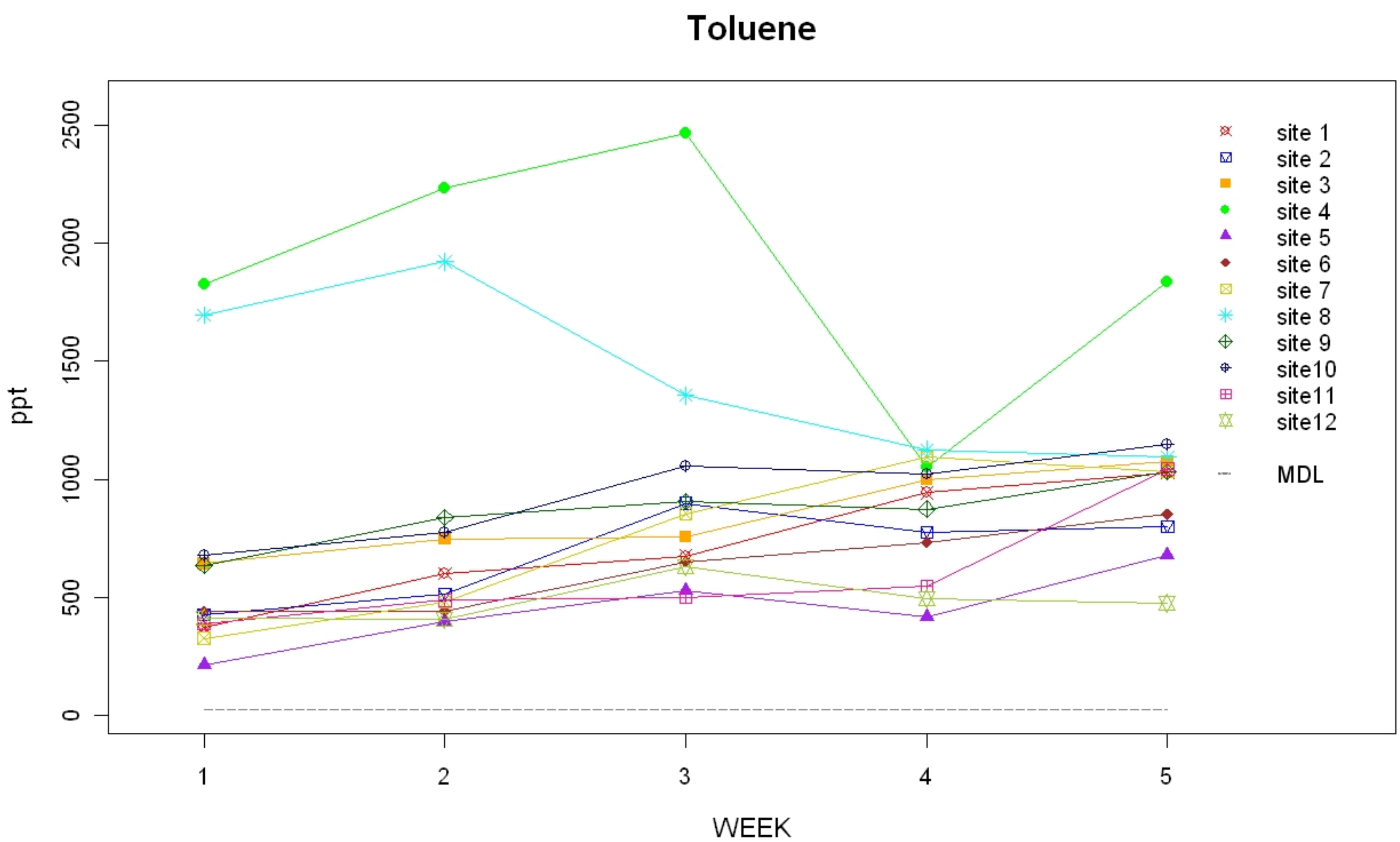

Figure A2. Toluene.

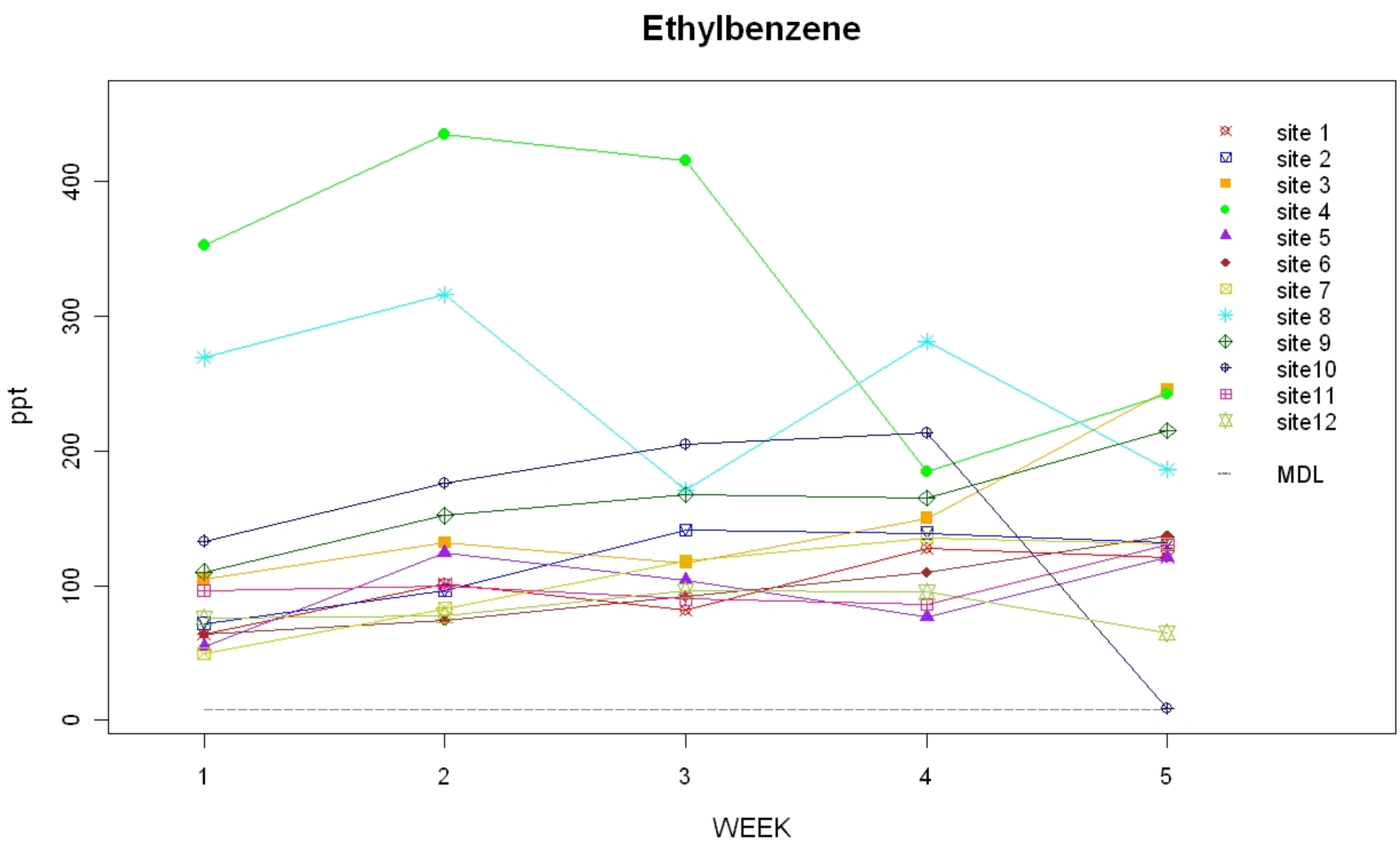

Figure A3. Ethylbenzene.

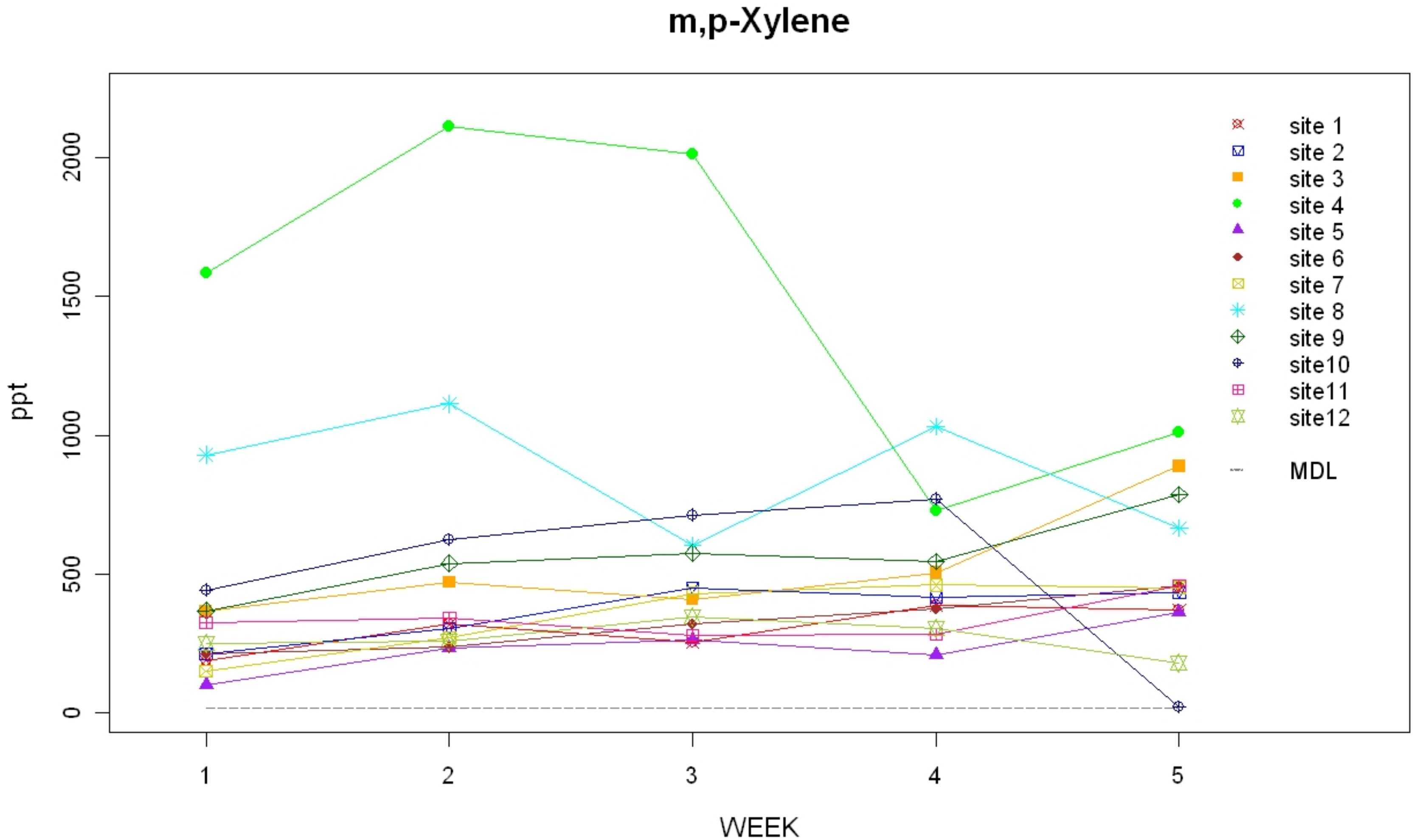

Figure A4. *m,p*-xylene.

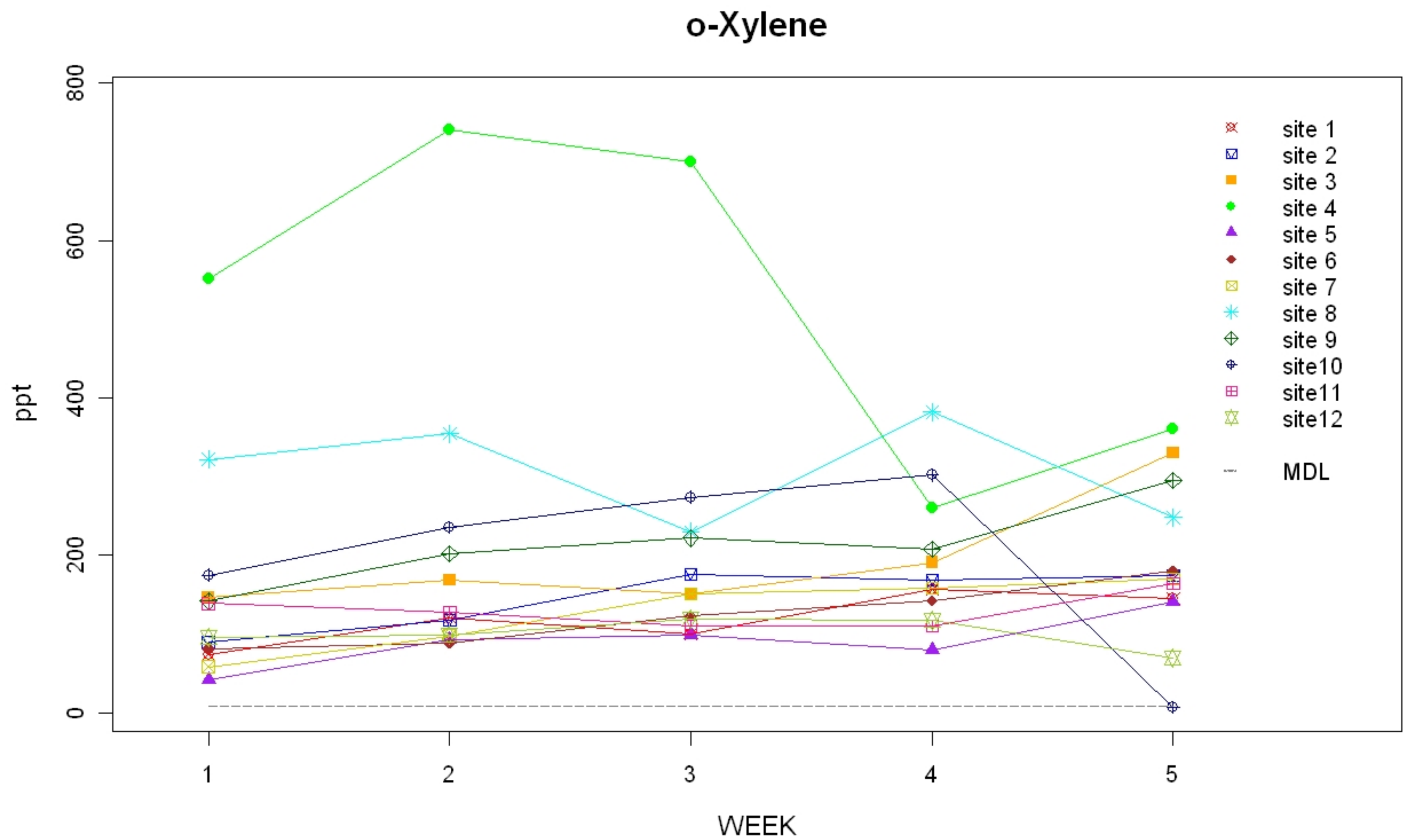

Figure A5. *o*-xylene.

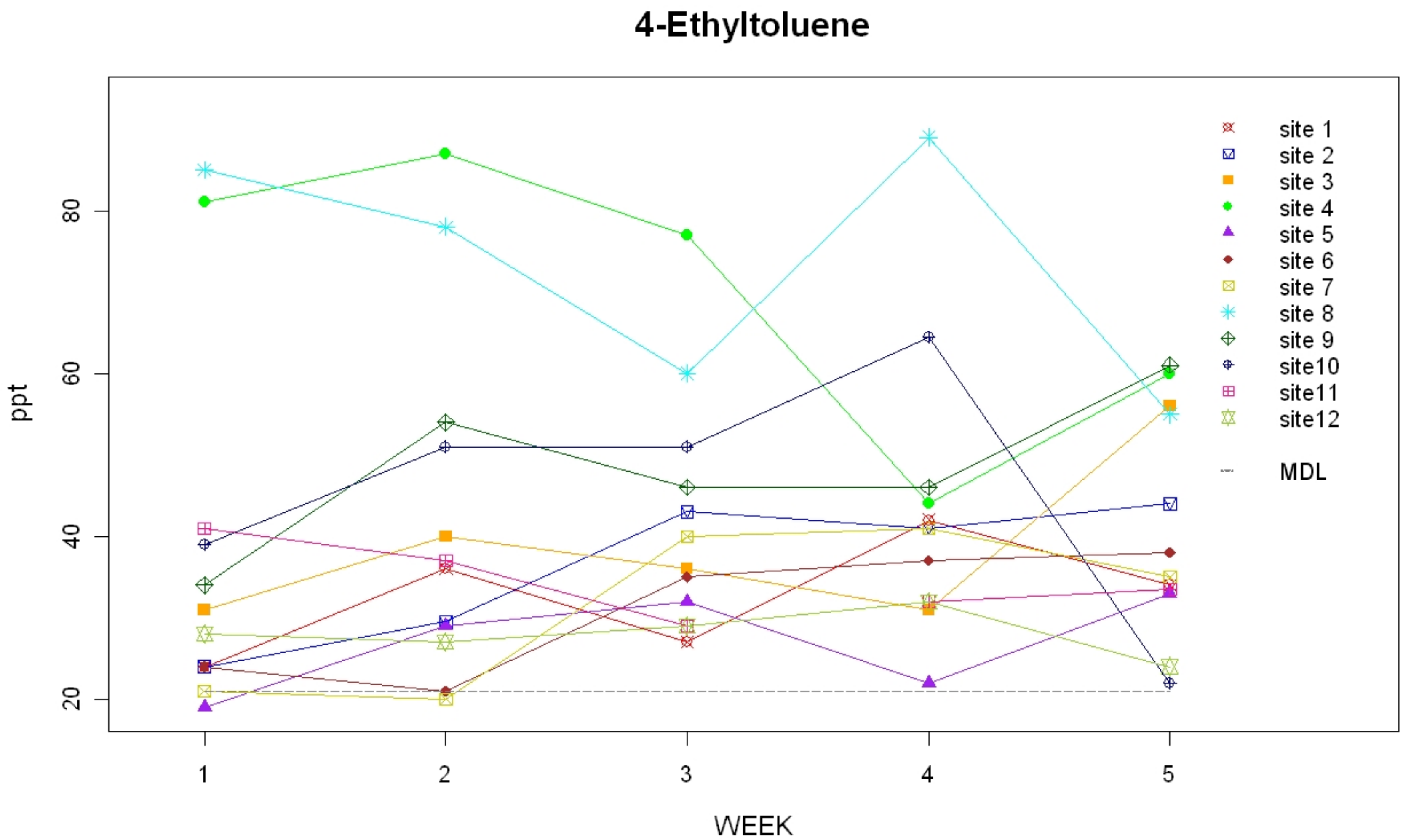

Figure A6. 4-ethyltoluene.

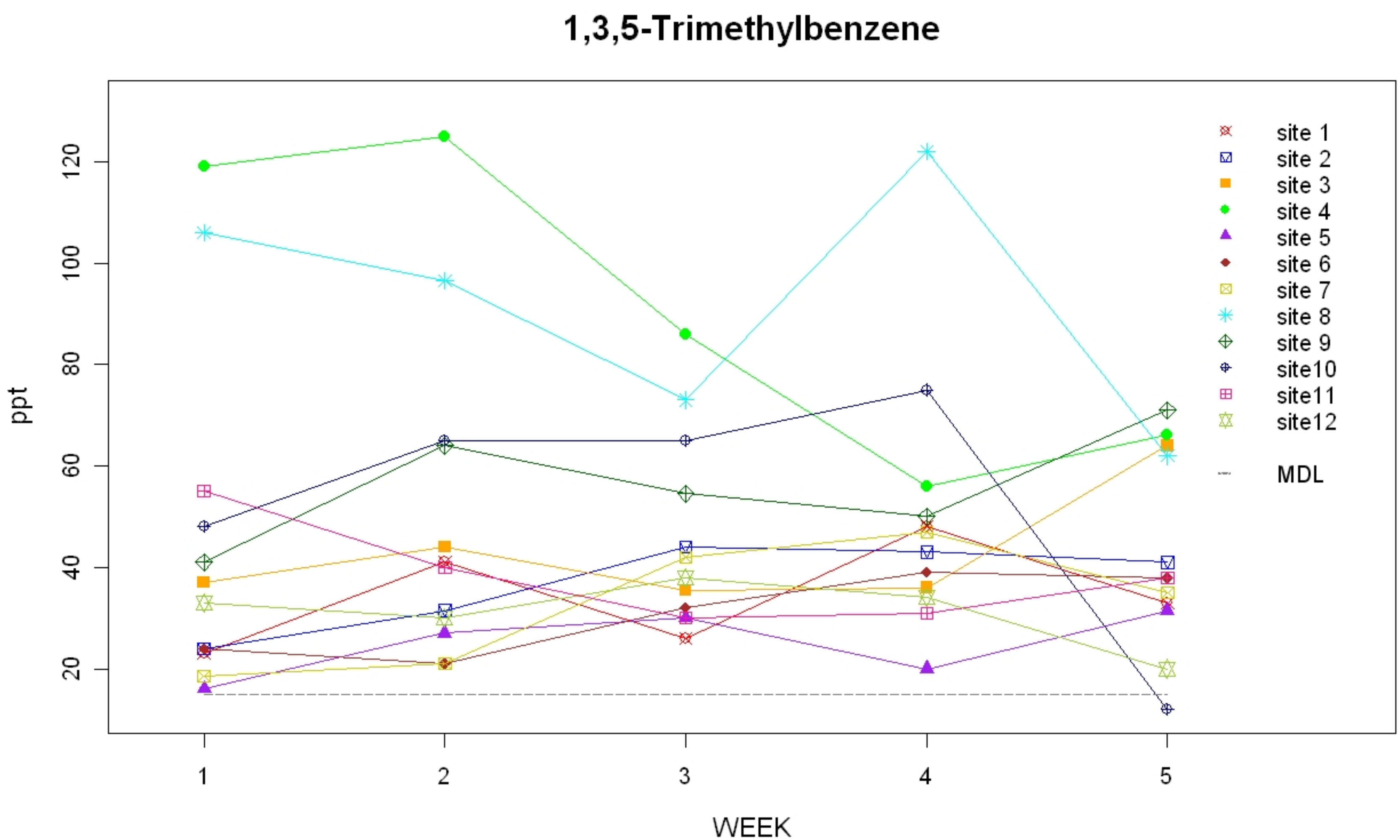

Figure A7. 1,3,5-trimethylbenzene.

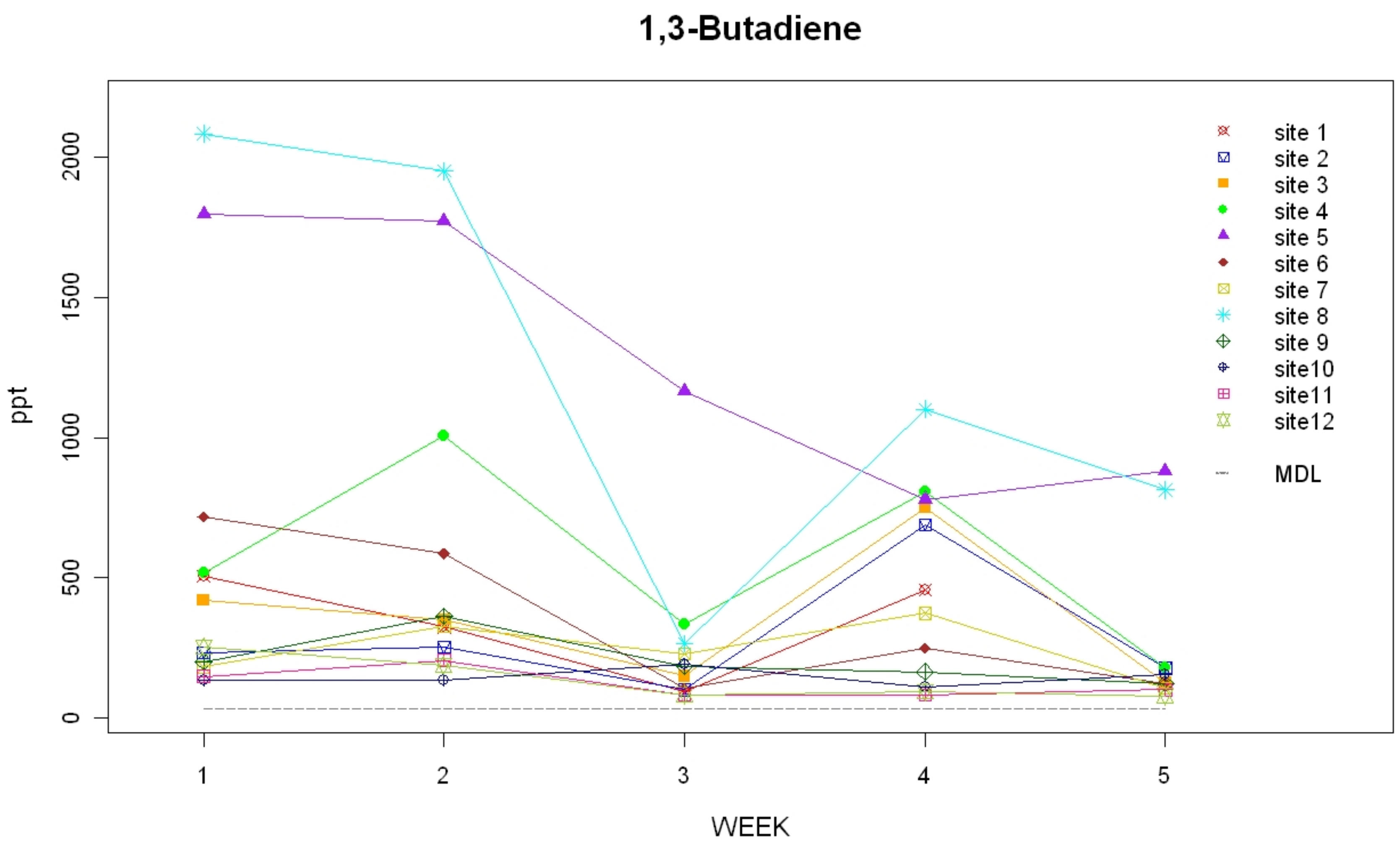

Figure A8. 1,3-butadiene.

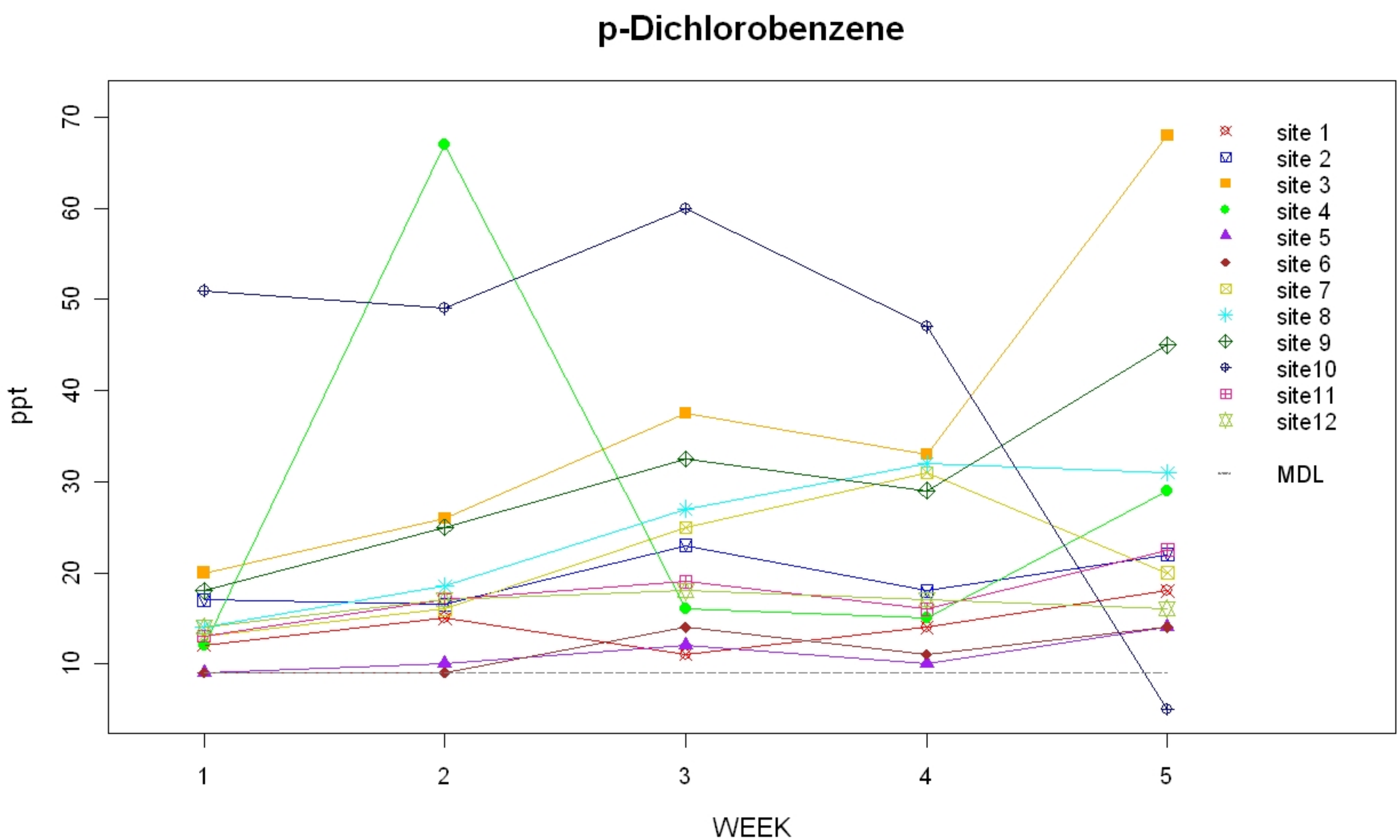

Figure A9. *p*-dichlorobenzene.

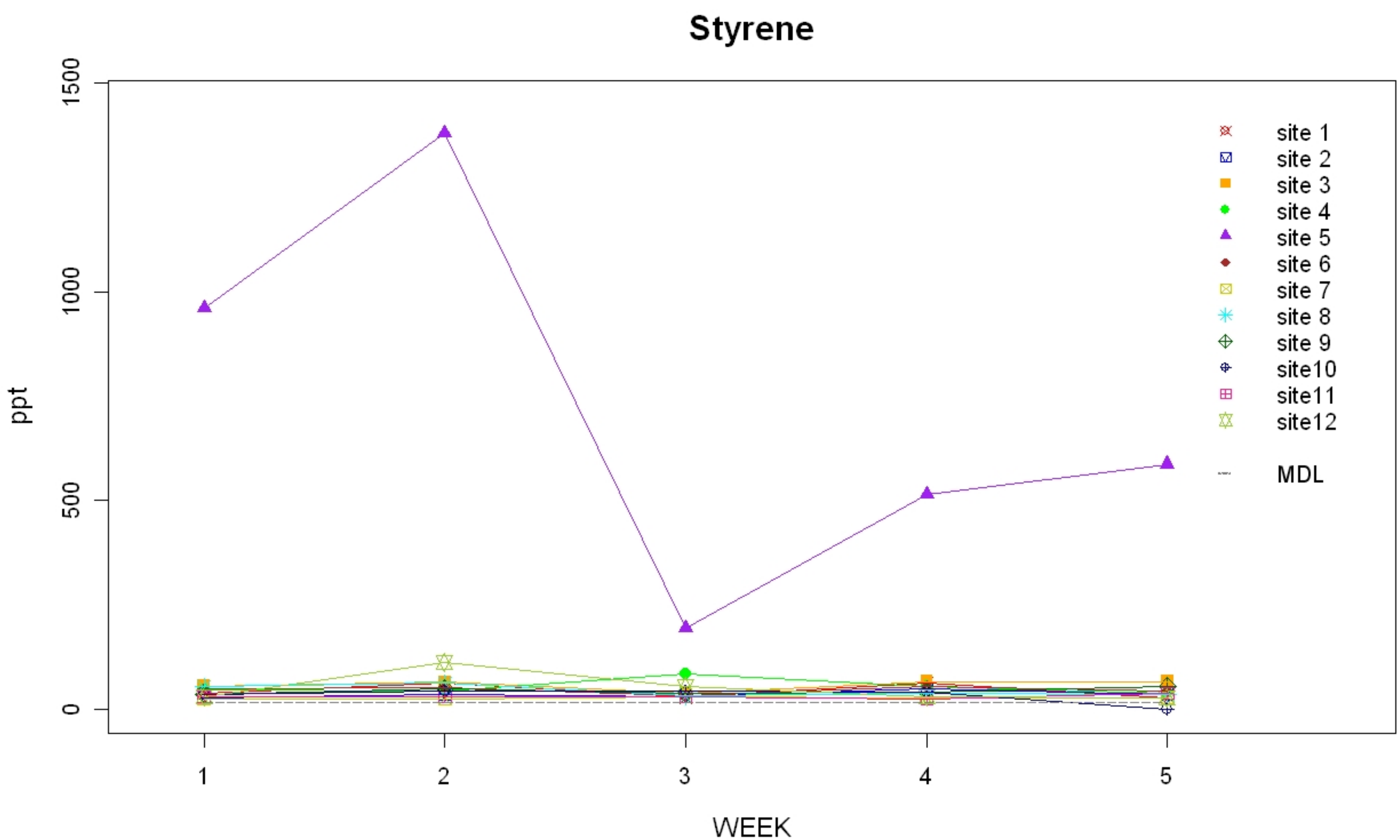

Figure A10. Styrene.

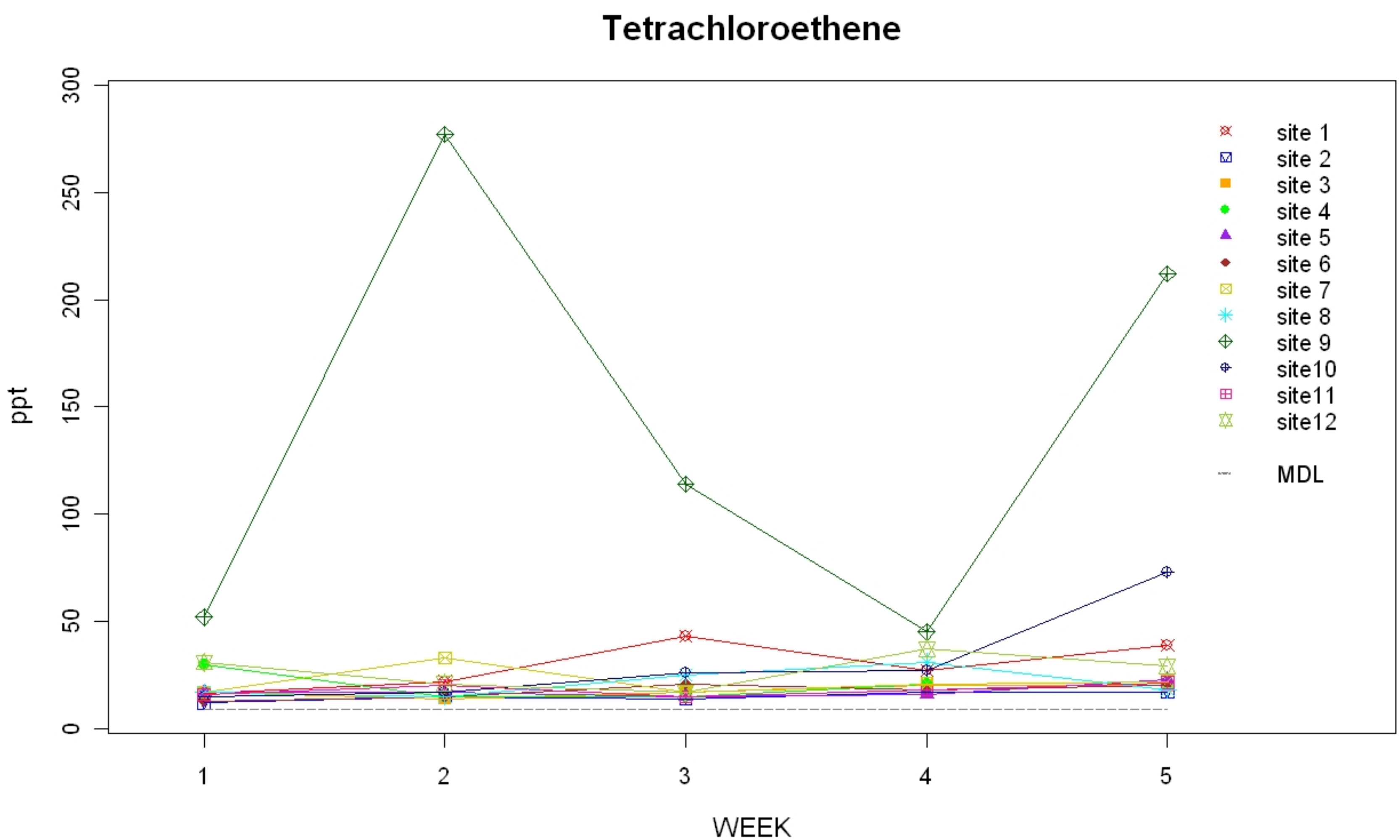

Figure A11. Tetrachloroethene.

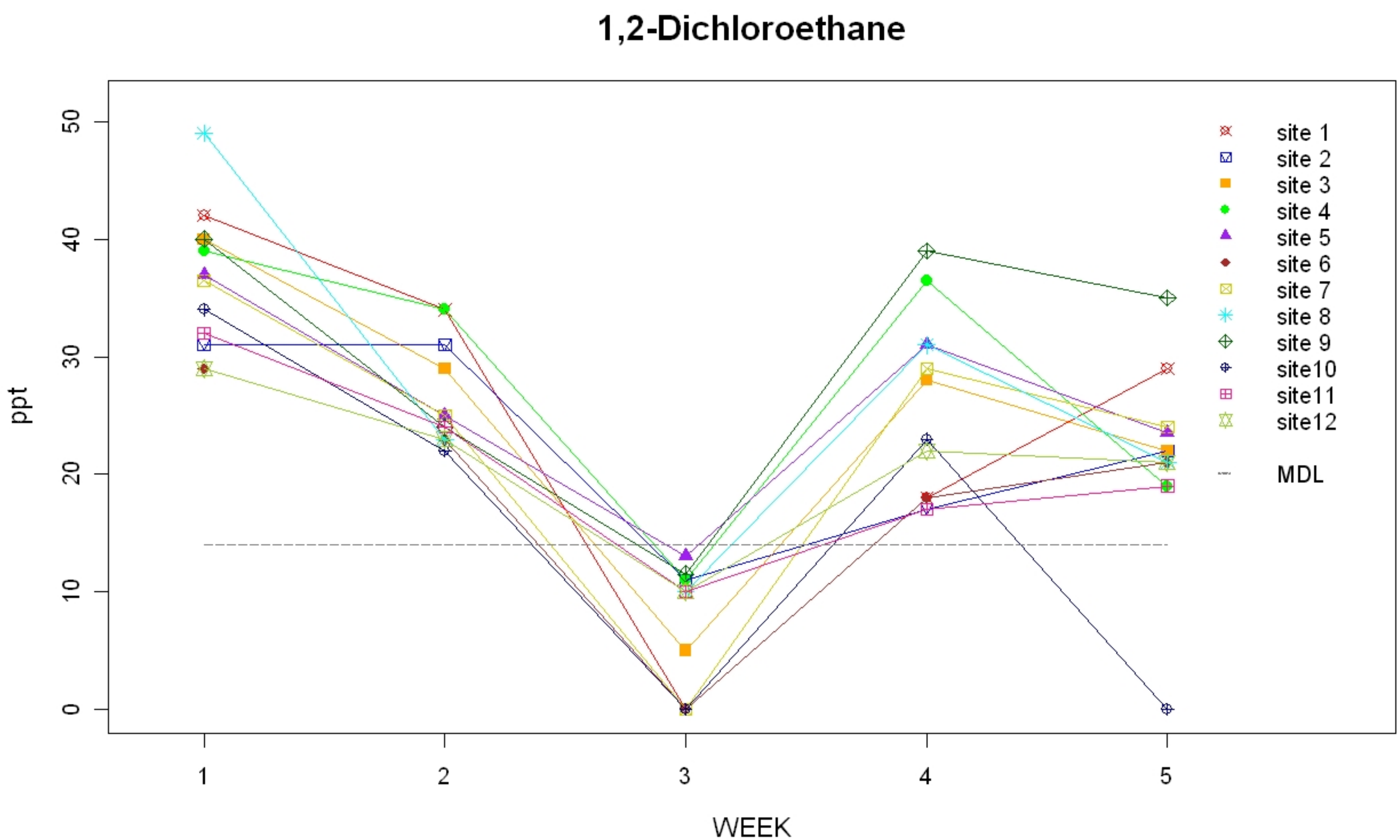

Figure A12. 1,2-dichloroethane.

AppendixB

Additional Time Series Plots

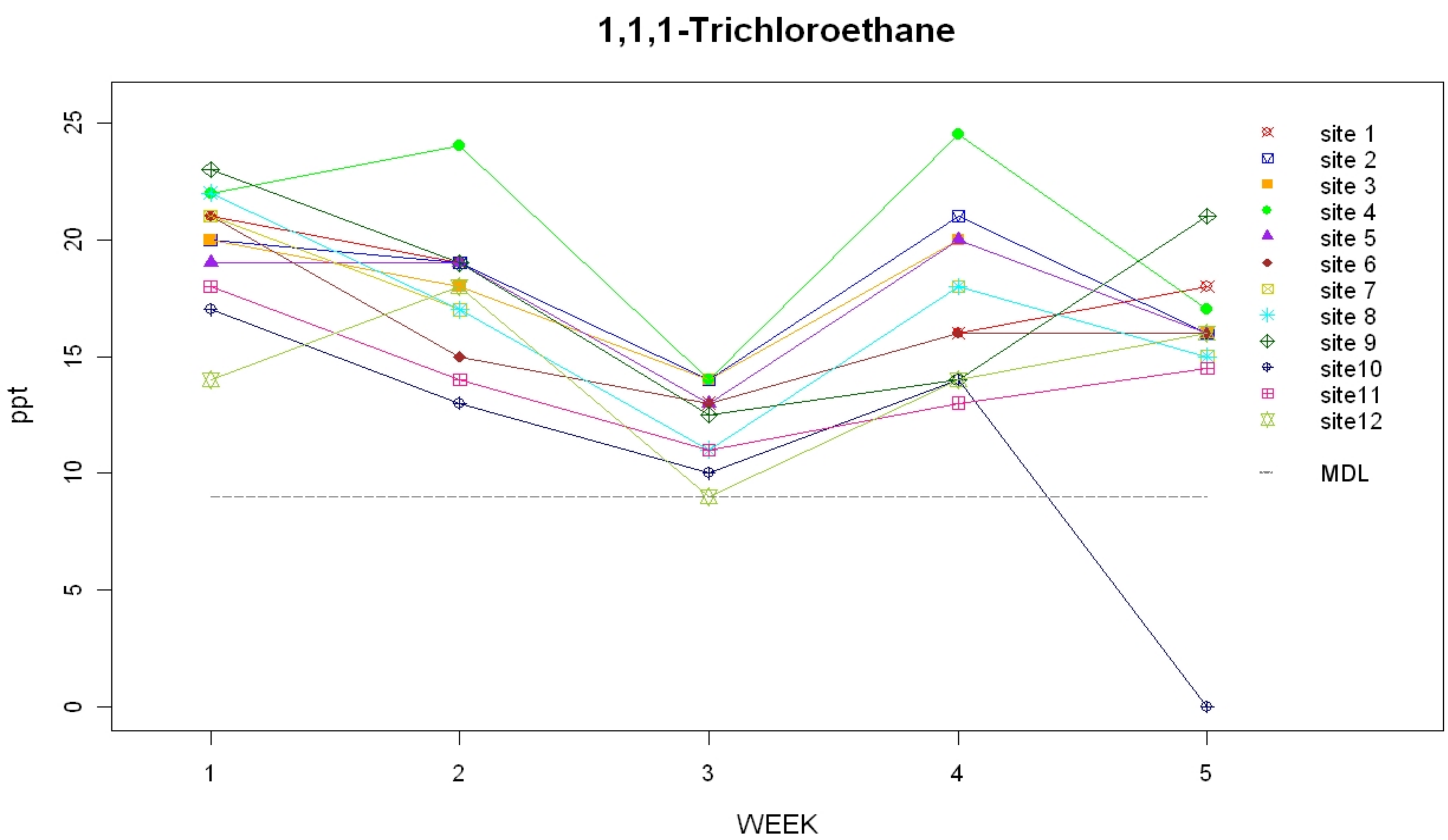

Figure B1. 1,1,1-trichloroethane.

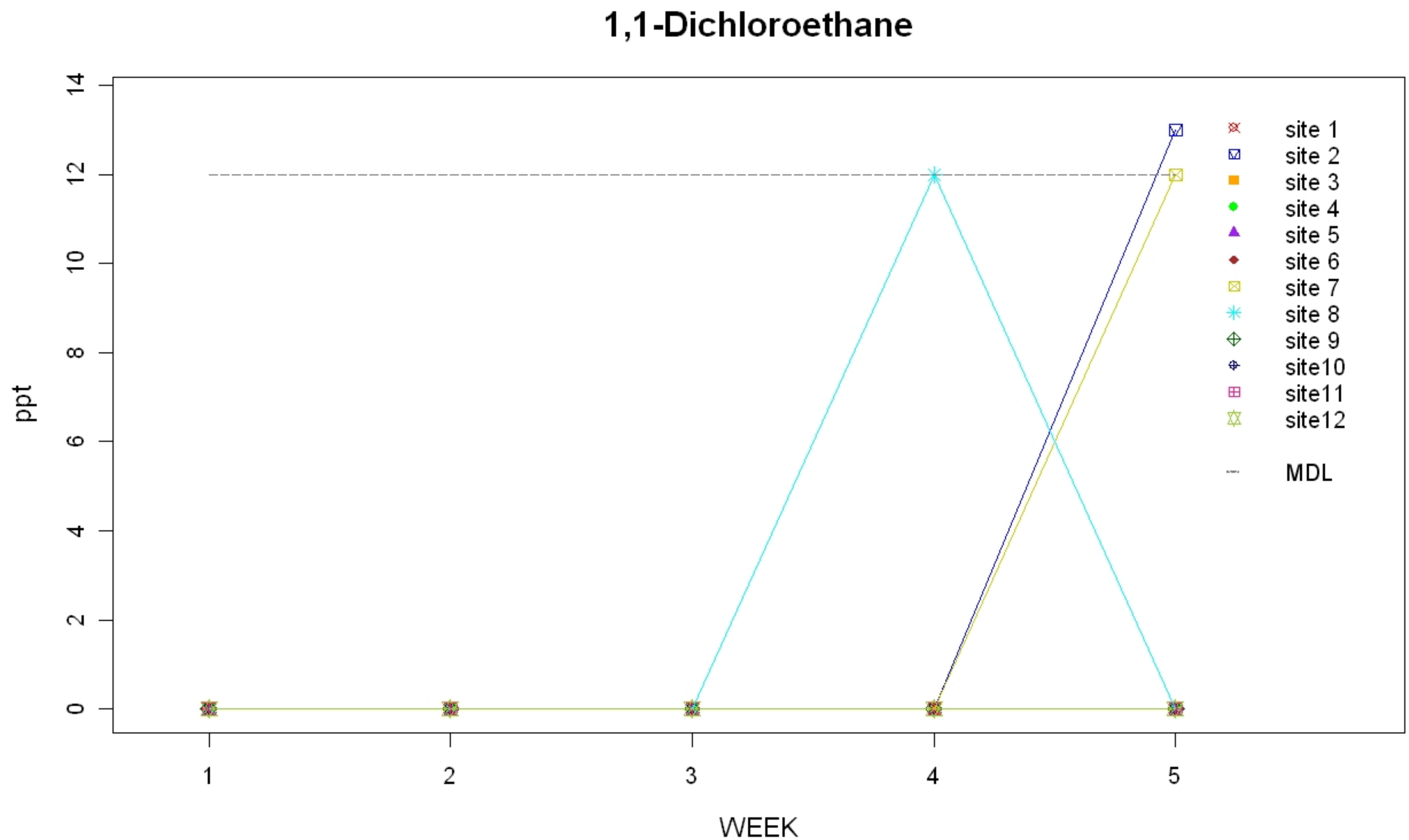

Figure B2. 1,1-dichloroethane.

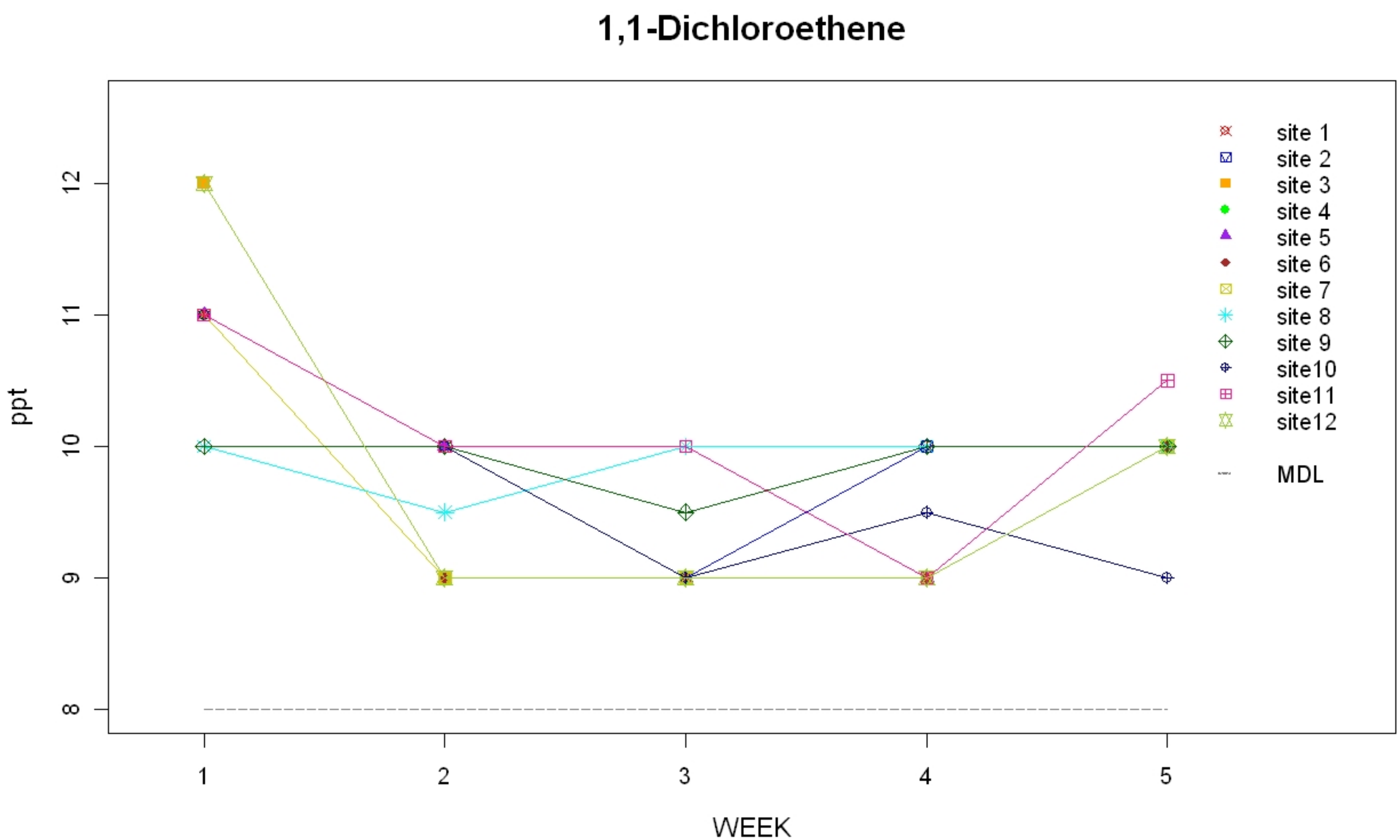

Figure B3. 1,1-dichloroethene.

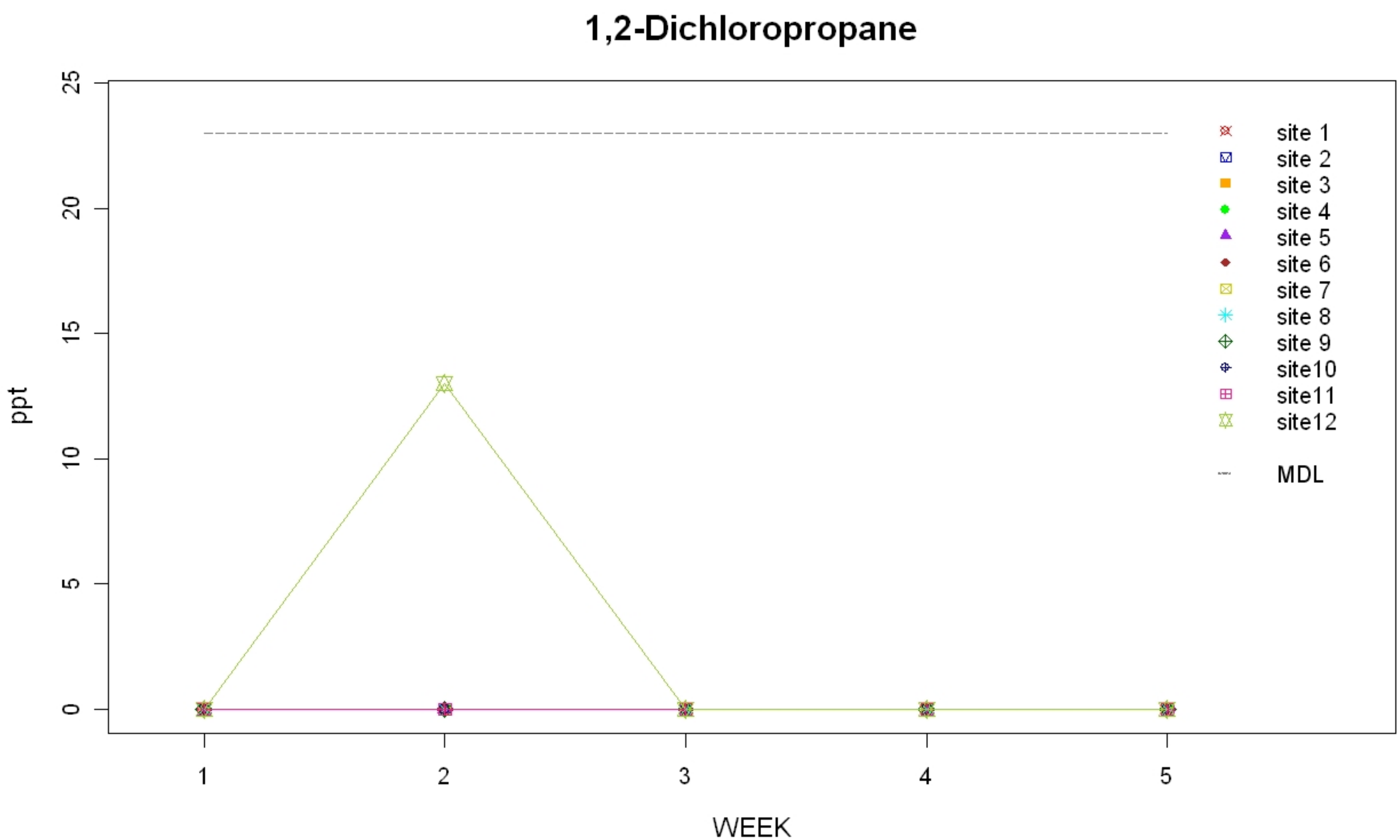

Figure B4. 1,2-dichloropropane.

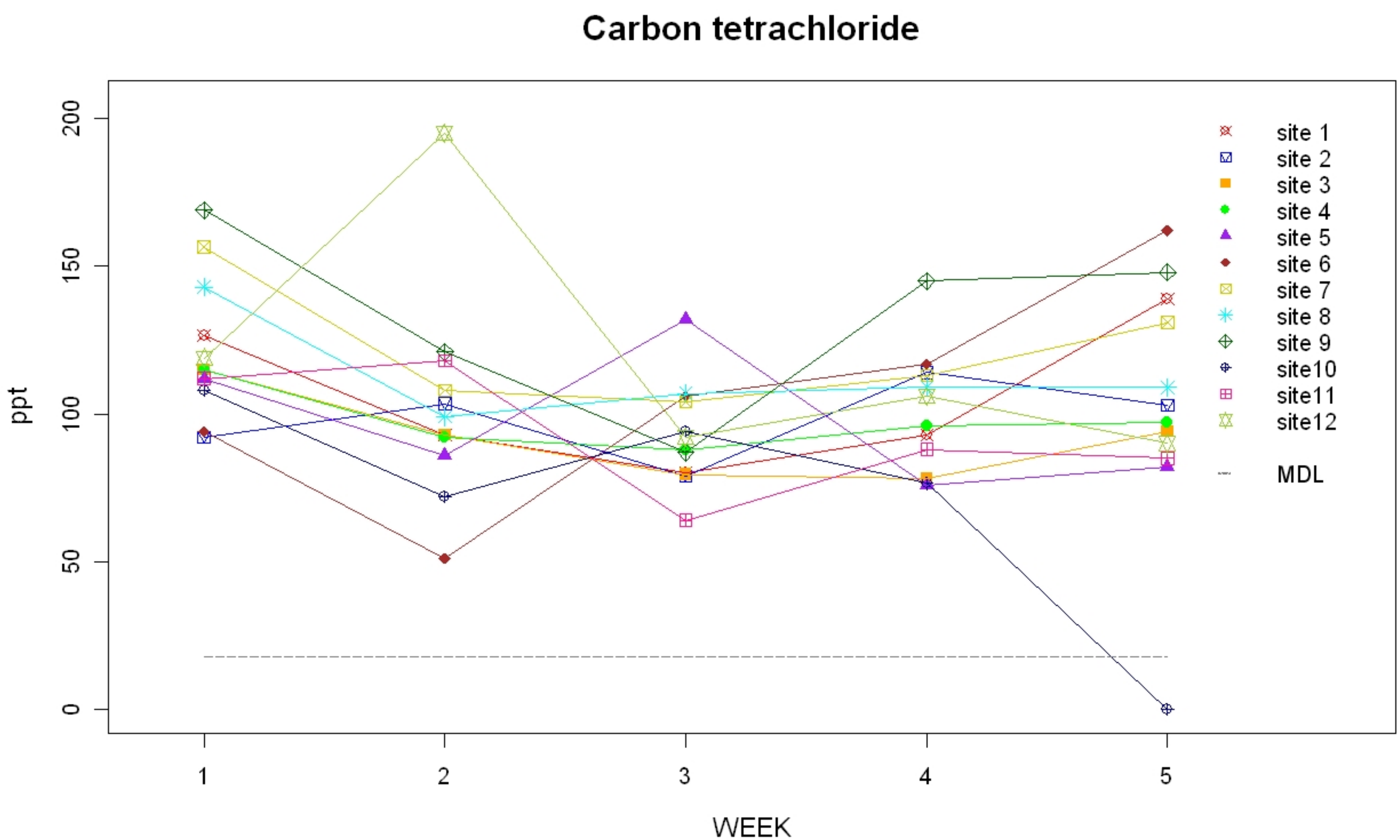

Figure B5. Carbon tetrachloride.

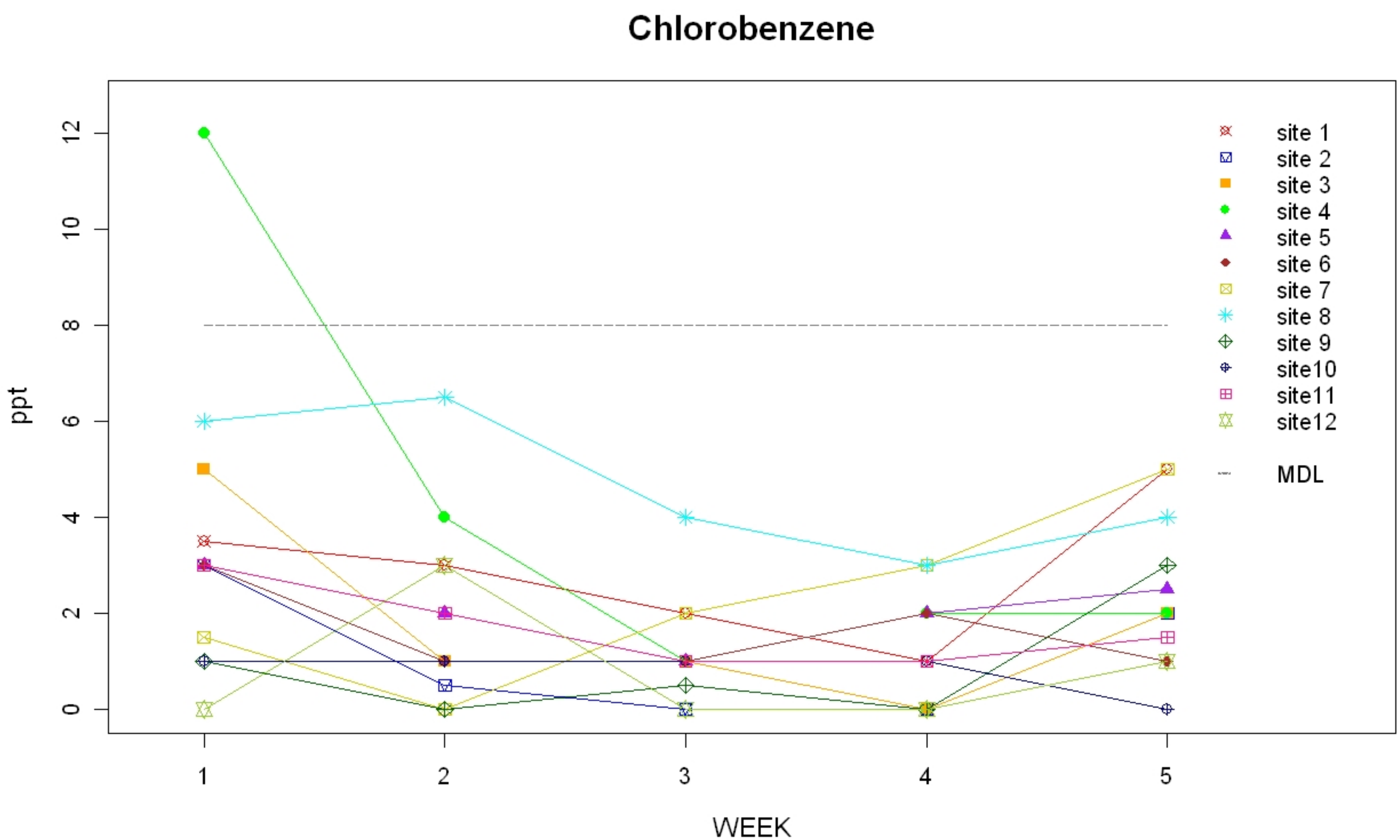

Figure B6. Chlorobenzene.

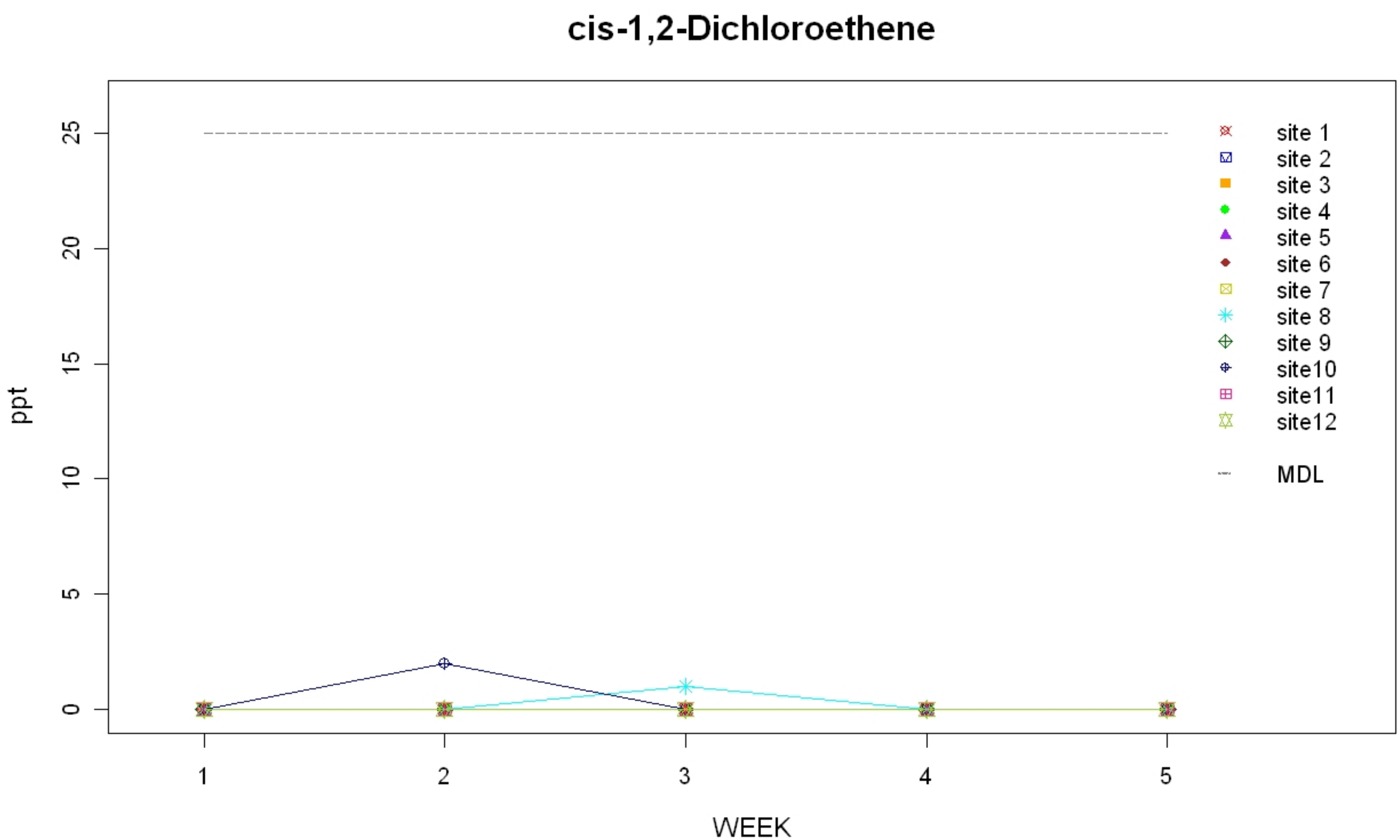

Figure B7. *cis*-1,2-dichloroethene.

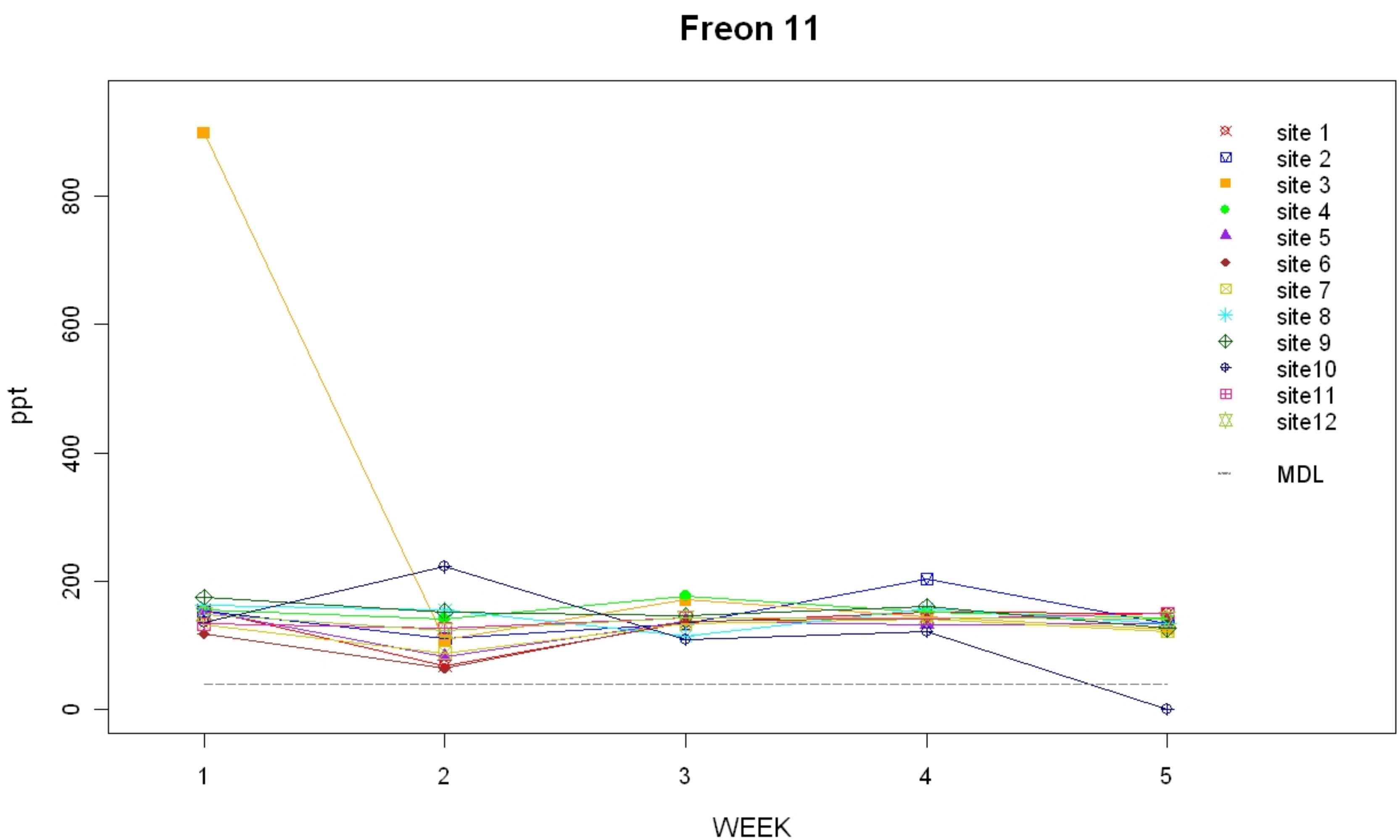

Figure B8. Freon 11.

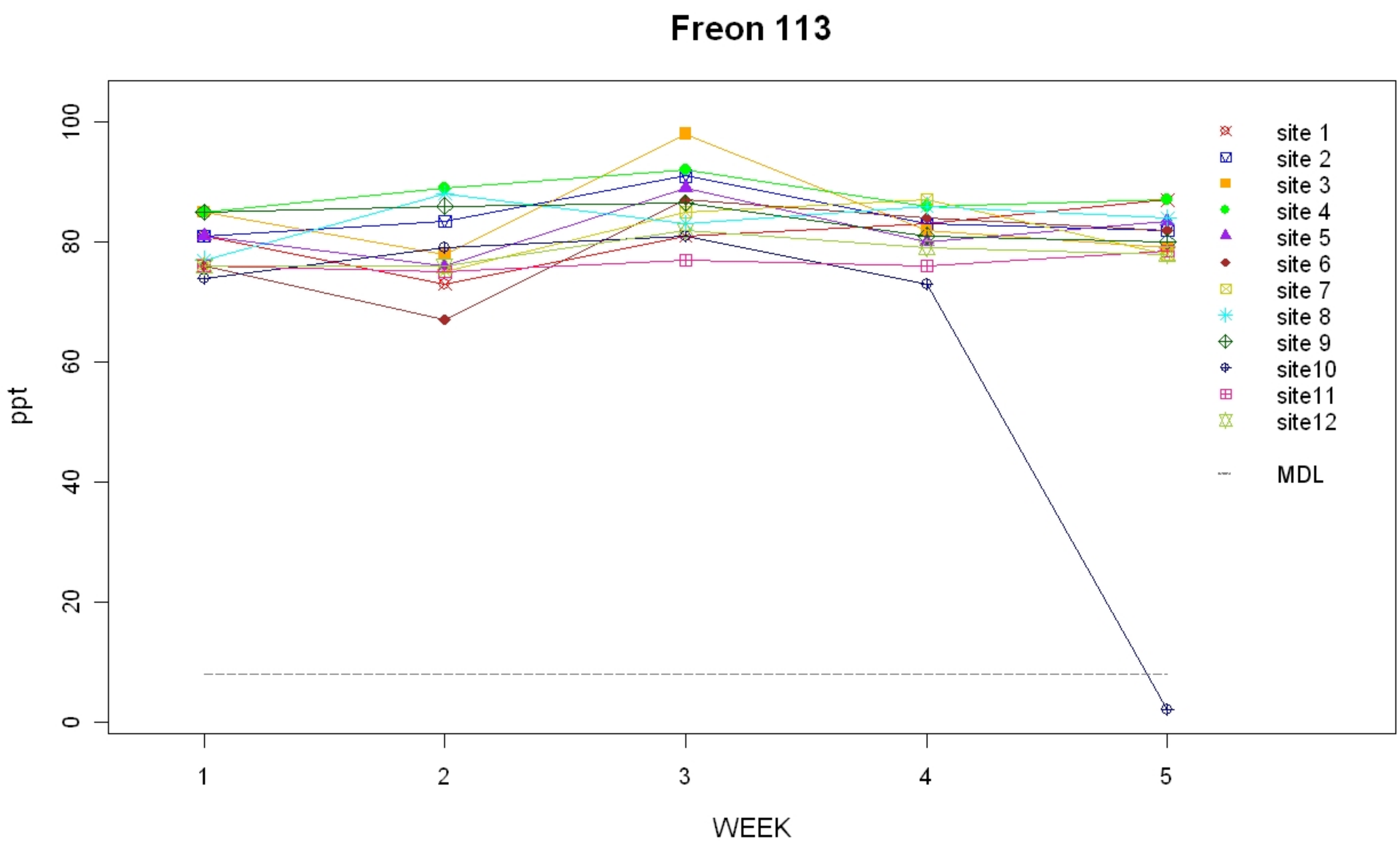

Figure B9. Freon 113.

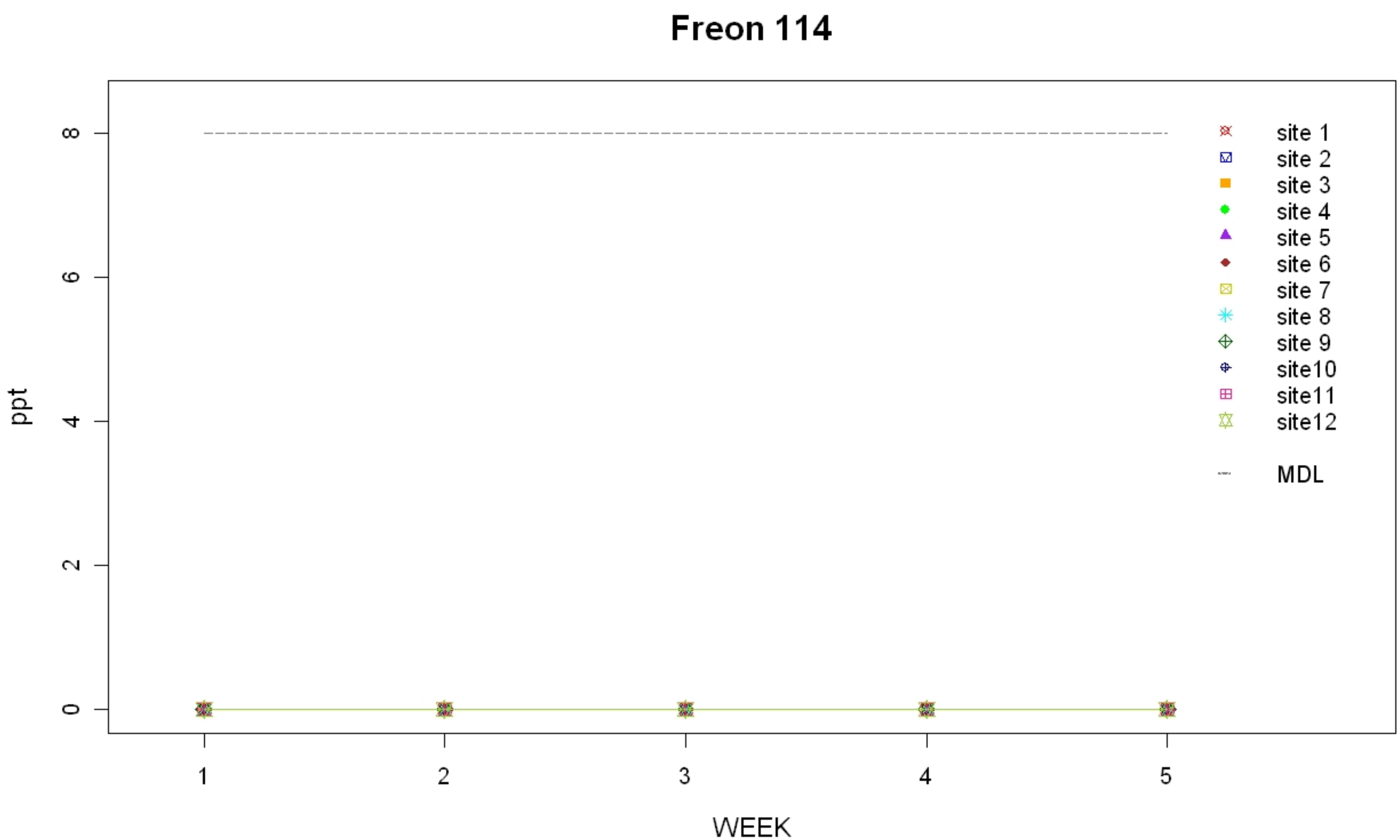

Figure B10. Freon 114.

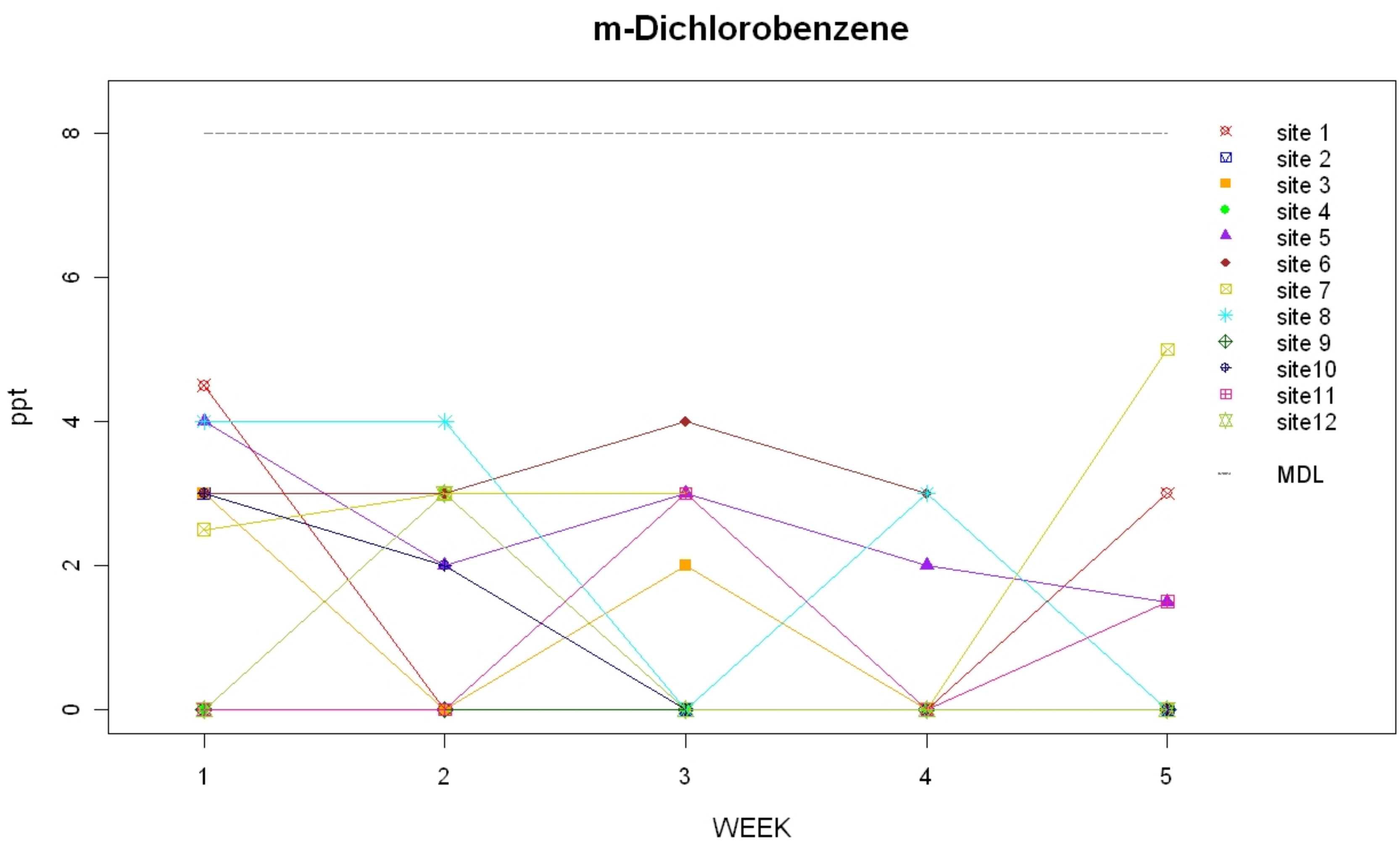

Figure B11. *m*-dichlorobenzene.

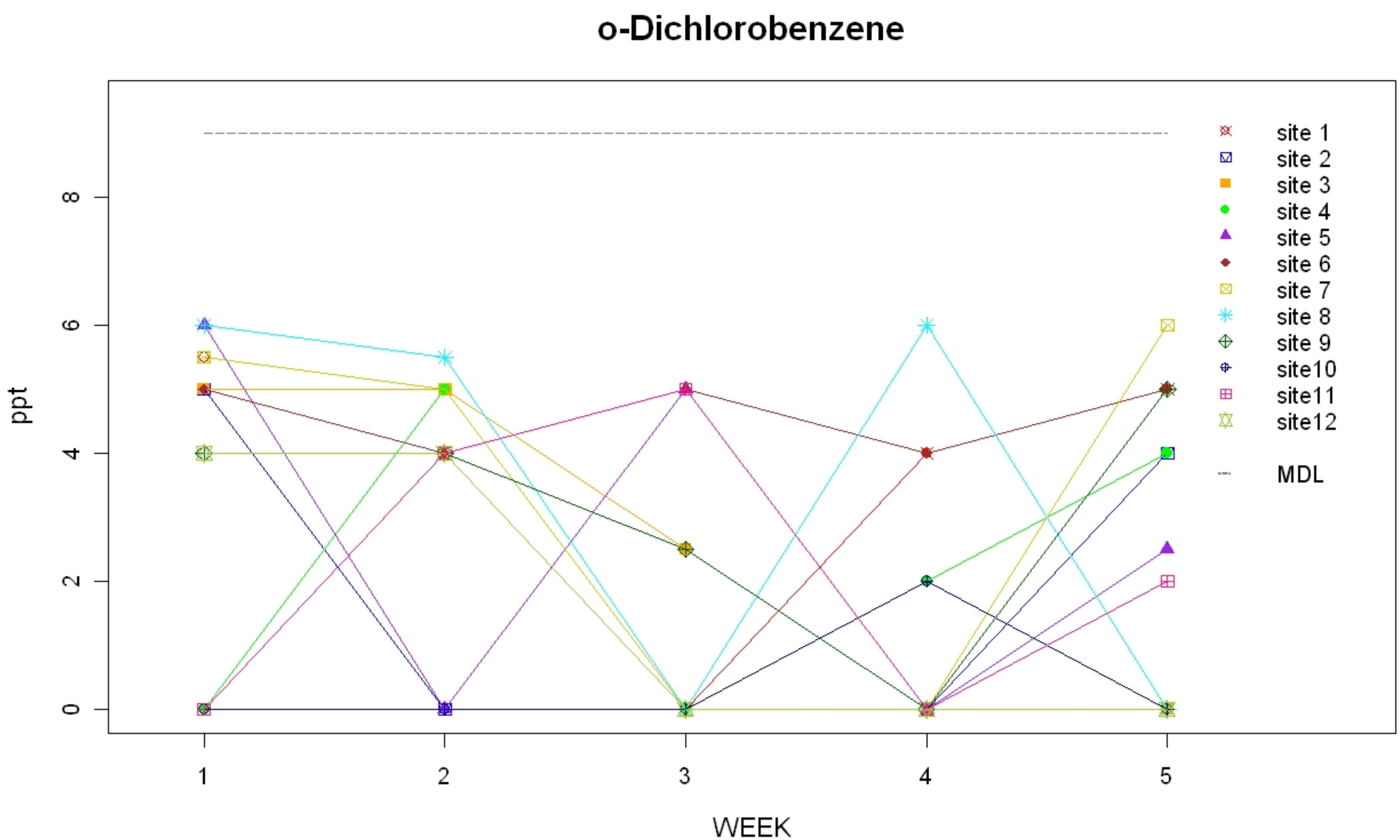

Figure B12. *o*-dichlorobenzene.

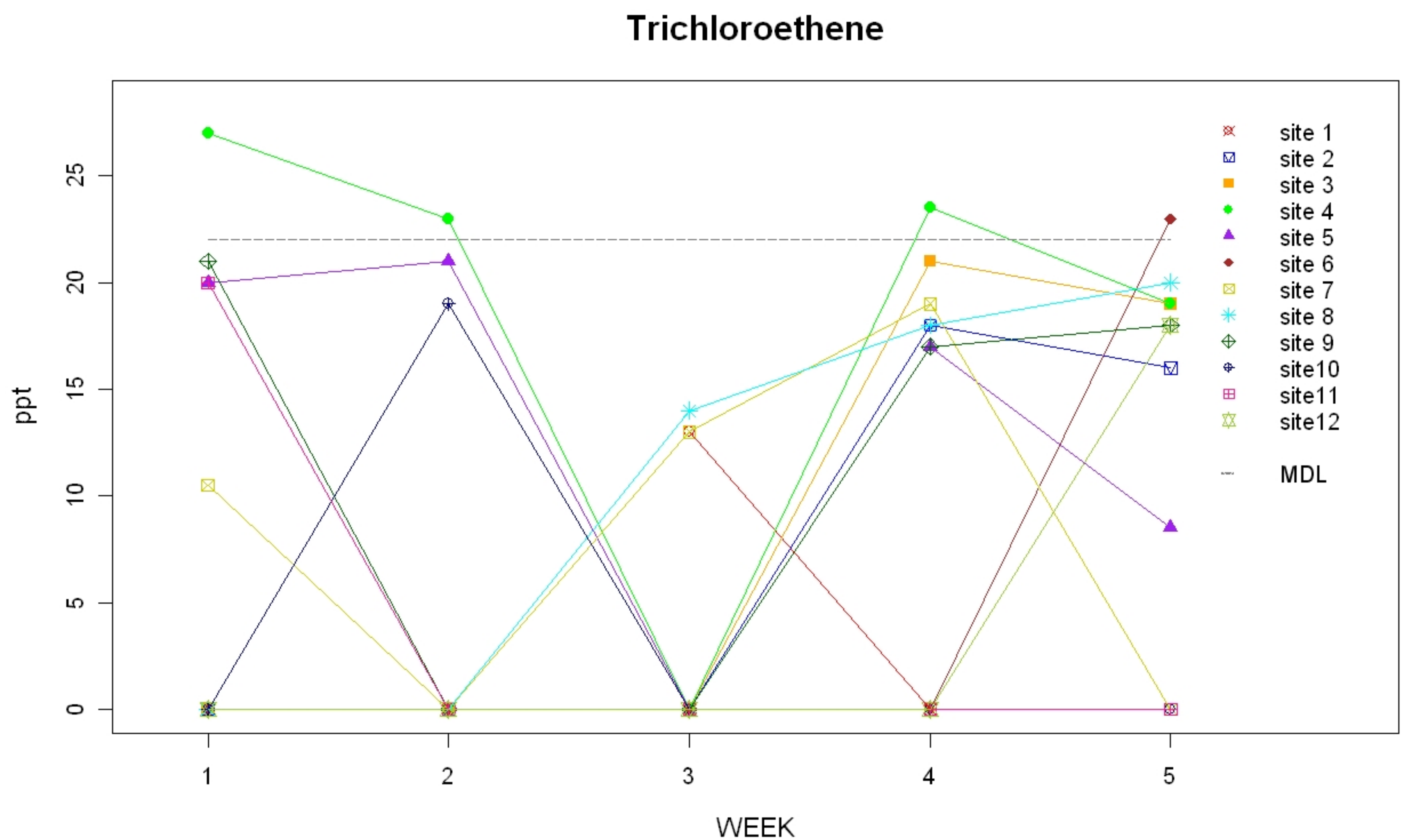

Figure B13. Trichloroethene.