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# Fast Analysis of 140 Environmental Compounds by GC/MS/MS

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## Introduction

Pesticides, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) are persistent environmental pollutants with the potential for bioaccumulation.[1] Previously, these compound classes have been analyzed using gas chromatography with an electron capture detector (GC-ECD), but this requires full chromatographic separation of all analytes for confident chemical identification. With a triple quadrupole detector (QQQ), analysis time significantly drops due to mass identification eliminating the need to chromatographically separate all components. Further, multiple reaction monitoring (MRM) mode on the QQQ provides a higher confidence in peak identification than analysis by scan or selected ion monitoring (SIM) mode. Combining chromatographic separation and MS/MS analysis is especially useful for PAHs and PCBs where multiple analytes may have the same m/z value.

| PAH | Conc. (ppb) |
|---|---|
| Acenaphthene | 200 |
| Acenaphthylene | 200 |
| Anthracene | 200 |
| Benz[a]anthracene | 200 |
| Benzo[b]fluoranthene | 200 |
| Benzo[k]fluoranthene | 200 |
| Benzo[g,h,i]perylene | 200 |
| Benzo[a]pyrene | 200 |
| Benzo[e]pyrene | 200 |
| Chrysene | 200 |
| Coronene | 200 |
| Dibenz[a,h]anthracene | 200 |
| Fluoranthene | 200 |
| Fluorene | 200 |
| Indeno[1,2,3-cd]pyrene | 200 |
| Naphthalene | 200 |
| Phenanthrene | 200 |
| Pyrene | 200 |
| Retene | 200 |
| Perylene-$d_{12}$ | 200 |
| Benz[a]anthracene-$d_{12}$ | 200 |
| Anthracene-$d_{10}$ | 200 |
| Phenanthrene-$d_{10}$ | 200 |
| Pyrene-$d_{10}$ | 200 |

| Pesticide | Conc. (ppb) |
|---|---|
| α-HCH | 20 |
| β-HCH | 20 |
| γ-HCH | 20 |
| δ-HCH | 20 |
| ε-HCH | 20 |
| Heptachloroepoxide | 20 |
| Aldrin | 20 |
| Dieldrin | 20 |
| Endrin | 20 |
| *p,p'*-DDT | 20 |
| *p,p'*-DDD | 20 |
| *p,p'*-DDE | 20 |
| *o,p'*-DDD | 20 |
| *o,p'*-DDT | 20 |
| α-Chlordane | 20 |
| γ-Chlordane | 20 |
| Oxychlordane | 20 |
| *trans* -Nonachlor | 20 |
| Methoxychlor | 20 |
| Endosulfan I | 20 |
| Endosulfan II | 20 |
| Endosulfan sulfate | 20 |
| Hexachlorobenzene | 20 |
| Dibutyl chlorendate | 20 |
| PCB-155 (std) | 20 |
| PCB-65 (std) | 20 |

| PCB | Conc. (ppb) | PCB | Conc. (ppb) | PCB | Conc. (ppb) | PCB | Conc. (ppb) |
|---|---|---|---|---|---|---|---|
| **4+10** | 20 | **45** | 5 | **92+84** | 10 | **163+138** | 10 |
| **7+9** | 20 | **52** | 5 | **89** | 5 | **126** | 5 |
| **6** | 10 | **49** | 5 | **101** | 5 | **166** | 5 |
| **8+5** | 20 | **47** | 5 | **99** | 5 | **128** | 5 |
| **14** | 20 | **48** | 5 | ***trans* -Nonachlor** | 5 | **167** | 5 |
| **19** | 5 | **65** | 5 | **119** | 5 | **174** | 5 |
| **30** | 8 | **44** | 5 | **83** | 5 | **202+171** | 10 |
| **12** | 10 | **37** | 5 | **97** | 5 | **156** | 5 |
| **13** | 10 | **42** | 5 | **81** | 5 | **204** | 6 |
| **18** | 5 | **41+71** | 10 | **87** | 5 | **172** | 5 |
| **15+17** | 15 | **64** | 5 | **85** | 5 | **180** | 5 |
| **16** | 5 | **100** | 5 | **77** | 5 | **199** | 5 |
| **32** | 5 | **Octachlorostyrene** | 5 | **110** | 5 | **169** | 5 |
| **26** | 5 | **74** | 5 | **135+144** | 10 | **170+190** | 10 |
| **31** | 5 | **70+76** | 10 | **123+149** | 10 | **201** | 5 |
| **28** | 5 | **66** | 5 | **118** | 5 | **207** | 5 |
| **33** | 5 | **95** | 5 | **114** | 5 | **194** | 5 |
| **53** | 5 | **91** | 5 | **131** | 5 | **205** | 5 |
| **22** | 5 | **56+60** | 10 | **132+153+105** | 15 | **206** | 5 |

Figure 1. List of compounds present in each standard with the concentration of each analyte (in ppb). Standards contained either PAHs, pesticides, or PCBs.

## Experimental

Samples were collected from both air and precipitation using XAD-2, then fractionated into hexane and a 1:1 mix of hexane and DCM. An Agilent 8890 GC with Agilent 7000D QQQ was used for this analysis. Injections were pulsed in splitless mode on an MMI inlet with a bottom-fritted liner. The final method contained 425 MRMs across 181 MRM groups. Standards were prepared in hexane for all 140 compounds.

Table 1. Agilent 8890 GC Parameters

| **GC and MS Conditions:** | |
|---|---|
| **Injection vol.** | 1µL |
| **Inlet** | MMI @ 280°C pulsed splitless mode<br>25 psi pulse until 0.5 min<br>Purge 30mL/min at 0.75 min |
| **Column** | HP-5MS Column (30m x 250µm, 0.25mm) |
| **Carrier gas** | 1.0 mL/min constant flow (helium) |
| **Oven** | 60°C hold 1.0 min<br>Ramp 40°C/min → 170°C, no hold<br>Ramp 10°C/min → 310°C, hold 3 min |
| **MSD Transfer Line** | 320°C |

Figure 2. Agilent 8890 GC with Agilent 7000D QQQ used for this analysis.

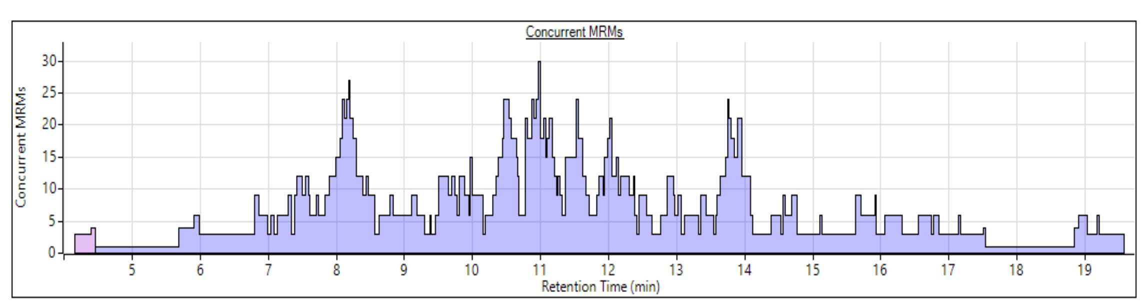


Figure 3. Plot of MRMs set in the acquisition method over time. As many as 30 MRMs occur simultaneously.

## Standards were run to develop a dMRM method.

Standards were prepared for each of the three compound classes (pesticide, PAH, and PCB) and retention times were assigned by running in scan mode and analyzing the data in MassHunter Unknowns Analysis. The Pesticide and Environmental Pollutant (P&EP) Database assisted with identifying the elution order of the compounds. MRM transitions were developed for all compounds of interest to analyze on GC-QQQ by using a combination of the P&EP Database, literature, and Optimizer software. Samples were run in dynamic MRM (dMRM) mode with at least 1 quantifier ion and 1 qualifier ion transition per analyte.

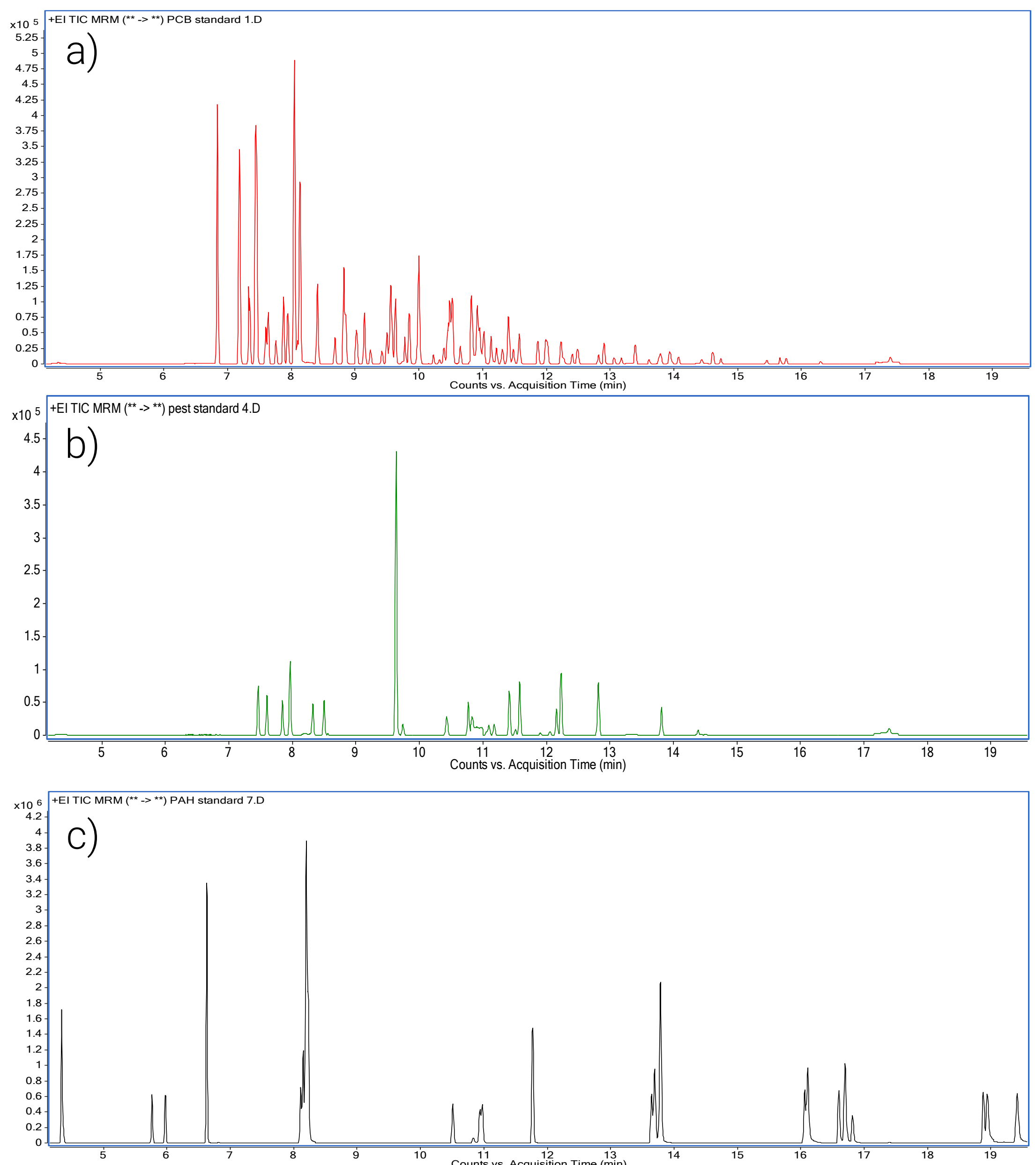


Figure 4. Total ion chromatograms of standards for a) PCBs, b) pesticides, and c) PAHs.

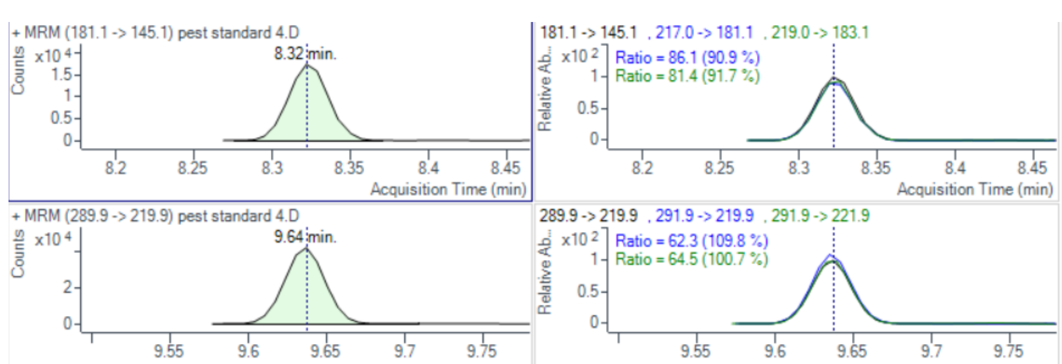


Figure 5. Example extracted ion chromatograms of quantifier and qualifier transitions for the pesticide δ-BHC.

## Sample quantification by GC/MS/MS is comparable to GC-ECD analyses.

Samples containing various mixtures of pesticides, PAHs, and PCBs were analyzed by this GC/MS/MS method, after previously being analyzed by GC-ECD. Quantification of all compounds by GC/MS/MS is comparable to historical data by GC-ECD. Using a single unified acquisition method, 24 PAHs, 24 pesticides, and 92 PCBs have been identified from environmental samples at low ppb levels. Final concentrations of the samples ranged from 3 to 675 ppb.

Table 2. List of samples that were quantified with analyte class of interest, original sample matrix, and fraction.

| Sample Number | Analyte Class of Interest | Original Sample Matrix | Current Solvent | IUB Concentration | IUB Batch | IUB Fraction |
|---|---|---|---|---|---|---|
| 1 | Polychlorinated biphenyls | Air/Vapor Phase (XAD) | Hexane | 500 ng/ul | JU22C | Hexane |
| | Pesticides | Air/Vapor Phase (XAD) | Hexane | 70 ng/ul | JU22C | Hexane:DCM |
| 2 | Pesticides | Precipitation (XAD) | Hexane | 15 ng/ul | M22P | Hexane:DCM |
| 3 | Polychlorinated biphenyls | Precipitation (XAD) | Hexane | 35 ng/ul | JL22P | Hexane |
| 4 | Polychlorinated biphenyls | Matrix Spike (XAD) | Hexane | 675 ng/ul | F2M22C | Hexane |
| | Pesticides | Matrix Spike (XAD) | Hexane | 300 ng/ul | F2M22C | Hexane:DCM |
| 5 | Pesticides | Air/Particle Phase (Filter) | Hexane | 5 ng/ul | J22F | Hexane:DCM |
| 6 | Polychlorinated biphenyls | Lab Blank Vapor (XAD) | Hexane | 3 ng/ul | JL22C | Hexane |
| 7 | Pesticides | Air/Vapor Phase (XAD) | Hexane | 35 ng/ul | M222C | Hexane:DCM |
| | Polychlorinated biphenyls | Air/Vapor Phase (XAD) | Hexane | 13 ng/ul | M222C | Hexane |

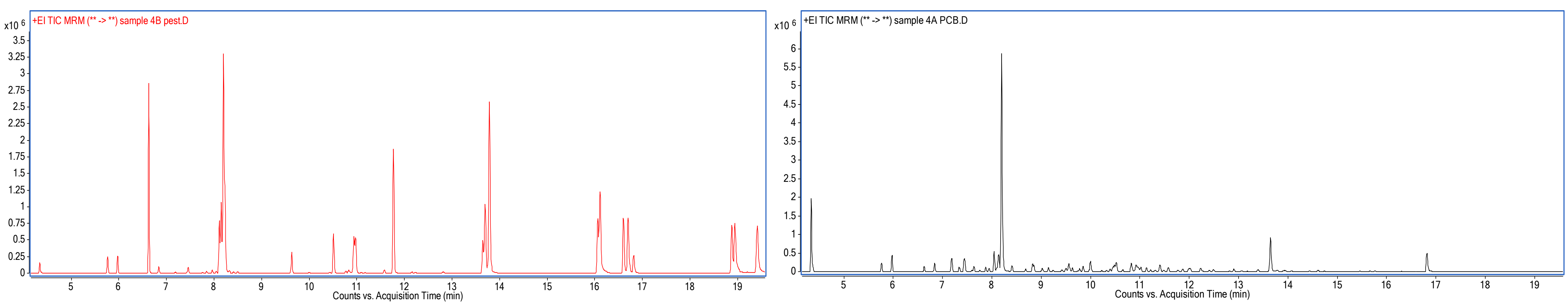


Figure 6. Total ion chromatograms for example pesticide (left) and PCB (right) samples that were quantified by GC/MS/MS.

Table 3. Quantification of pesticides in each sample (concentrations shown in ppb). Retention times and quantifier MRM transition are shown, along with absolute response.

| | | | Sample 1B pest | | Sample 2 pest | | Sample 4B pest | | Sample 7a pest | | Sample 5 pest | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Name | Transition | RT | Resp. | Final Conc. | Resp. | Final Conc. | Resp. | Final Conc. | Resp. | Final Conc. | Resp. | Final Conc. |
| Aldrin | 254.9 -> 220.0 | 9.78 | | | | | 1148 | 3.49 | | | | |
| BHC-alpha (benzene hexachloride) | 216.9 -> 181.0 | 7.47 | 544 | 0.369 | 1264 | 0.755 | 15782 | 10.75 | 46 | 0.019 | 2386 | 1.236 |
| BHC-beta | 181.0 -> 145.0 | 7.85 | 680 | 0.582 | 914 | 0.689 | 14507 | 12.47 | 934 | 0.488 | 582 | 0.38 |
| BHC-delta | 181.1 -> 145.1 | 8.32 | 2560 | 2.213 | 997 | 0.759 | 13521 | 11.75 | | | 6592 | 4.357 |
| BHC-epsilon | 180.9 -> 144.9 | 8.51 | 18368 | 11.257 | 20611 | 11.128 | 19628 | 12.09 | 9369 | 3.504 | 25562 | 11.975 |
| BHC-gamma (Lindane, gamma HCH) | 181.0 -> 145.0 | 7.97 | 555 | 0.436 | 1380 | 0.954 | 12849 | 10.14 | 194 | 0.093 | 225 | 0.135 |
| Chlordane-cis | 271.8 -> 236.9 | 11.18 | | | 2002 | 3.932 | 4334 | 9.62 | | | | |
| Chlordane-oxy | 114.9 -> 51.1 | 10.44 | | | 1346 | 1.865 | 7108 | 11.13 | | | | |
| Chlordane-trans | 271.7 -> 236.9 | 10.84 | 446 | 0.809 | 3545 | 5.674 | 6736 | 12.19 | 701 | 0.78 | 79 | 0.111 |
| DDD-o,p' | 235.0 -> 165.1 | 11.58 | | | | | 64971 | 15.70 | | | | |
| DDD-p,p' | 237.0 -> 165.1 | 12.23 | | | 803 | 0.44 | 6605 | 4.09 | | | | |
| DDE-p,p' | 246.1 -> 176.2 | 11.42 | | | 853 | 0.255 | 1929 | 0.65 | | | | |
| DDT-o,p' | 235.0 -> 165.2 | 12.24 | | | 894 | 0.32 | 10138 | 4.11 | | | | |
| DDT-p,p' | 235.0 -> 165.2 | 12.82 | | | 1805 | 0.65 | 19710 | 8.02 | | | | |
| Dibutyl chlorendate | 237.0 -> 236.5 | 14.39 | 5700 | 17.041 | 3032 | 7.986 | 3634 | 10.82 | 7021 | 12.849 | 4423 | 10.245 |
| Dieldrin | 262.9 -> 193.0 | 11.51 | 970 | 3.616 | 4023 | 13.214 | 2959 | 10.99 | 377 | 0.861 | | |
| Endosulfan I (alpha isomer) | 194.9 -> 160.0 | 11.06 | | | | | 1743 | 11.38 | | | | |
| Endosulfan II (beta isomer) | 206.9 -> 172.0 | 12.06 | | | | | 1695 | 9.87 | | | | |
| Endosulfan sulfate | 271.9 -> 237.0 | 12.81 | | | | | 7841 | 10.01 | | | | |
| Endrin | 262.8 -> 193.0 | 11.91 | | | | | 2188 | 14.00 | | | | |
| Heptachlor exo-epoxide | 352.8 -> 262.9 | 10.42 | | | 1517 | 4.384 | 3740 | 12.34 | | | | |
| Hexachlorobenzene | 283.8 -> 213.9 | 7.6 | | | 50 | 0.031 | 65 | 0.05 | | | 102 | 0.055 |
| Methoxychlor, p,p'- | 227.0 -> 169.1 | 13.81 | | | | | 13119 | 10.90 | | | 754 | 0.488 |
| Nonachlor, trans- | 271.8 -> 236.9 | 11.18 | 16 | 0.038 | 2296 | 4.905 | 4372 | 10.56 | | | 101 | 0.19 |

## Results and Discussion

### Analysis time was shortened significantly by using GC/MS/MS.

The analysis time for 140 pesticides, PAHs, and PCBs has been sped up about 17X. With the original methodology, three injections were needed over multiple hours to quantify all 140 analytes. This initial analysis by GC-ECD took 165 minutes for PCBs, a separate 165 minutes for pesticides, and another 24 minutes for PAHs. Running each sample therefore took about 6 hours to look for all analytes of interest. This new QQQ method allows for one single injection that takes under 21 minutes. GC/MS/MS therefore creates a significant time savings and allows full calibrations to now be completed in hours instead of multiple days.

## Conclusions

### Transitioning methods from GC-ECD to GC/MS/MS is highly beneficial.

By running in MRM mode, we enable the following:

- Significant time-savings
- Increased confidence in hits
- Sample quantification remains the same

## References

[1]Zohair, A., et al. "Residues of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides in organically-farmed vegetables." *Chemosphere* 63.4 (2006): 541-553.

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