**Supporting Information:**

# Photochemically-induced Changes in Dissolved Organic Matter Identified by Ultrahigh Resolution Fourier Transform - Ion Cyclotron Resonance - Mass Spectrometry

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***Dissolved Organic Carbon Analysis***. Small aliquots from all four water samples (dark controls as well as irradiated samples) were acidified and their DOC content measured using a Shimadzu TOC 5000 total organic carbon analyzer.

***UV/Vis-Absorbance***. A Cary Varian 100 dual beam UV/Vis spectrophotometer and a 5 cm path length quartz cell were used to determine the UV/Vis absorbance between 280-700 nm. The spectra were baseline corrected with Milli-Q water as a blank. The raw optical density A (absorbance) was normalized to the pathlength (L) of the cuvette and converted into a CDOM absorption coefficient ($a_{CDOM}(\lambda)$):

$$a_{CDOM}(\lambda)=2.303 \times A(\lambda) \times L^{-1} \tag{1}$$

The spectral slope *S* was determined across the wavelength range 280 - 700 nm as described elsewhere (1). The extent of photodegradation across the entire wavelength range (280-700 nm) was quantified for specific wavelengths ($\lambda$) using the absolute decrease in the absorption coefficient ($\Delta a_{CDOM}(\lambda)$). Additionally, the value of $a_{CDOM}(\lambda)$ at 355 nm ($a_{CDOM}(355)$) was normalized to the DOC content.

***Excitation emission matrix fluorescence (EEM) spectroscopy***. EEM fluorescence was measured using a Jobin Yvon SPEX FluoroMax-3 fluorescence spectrometer. The emission was recorded between 280 and 600 nm for excitation wavelengths at 5 nm intervals ranging from 250-500 nm. The EEM spectra collected in the present study were calibrated to quinine sulfate units (QSU) and corrected for Raleigh and Raman scattering peaks using a collection of software tools incorporated into a MATLAB

toolbox "FLToolbox 1.91" (2). The total EEM fluorescence ($EEM_{TOTAL}$) was calculated using the entire integral of the spectrum and does not have a unit.

### *Additional Method Description: ESI-FT-ICR-MS Analysis.*

The sample solution was injected at a flow rate of 0.5 µL $min^{-1}$ into a single spray source to which a needle voltage of -2.3 kV was applied to generate negative molecular ions. Octopole frequencies were set to 1.6 MHz to maximize the data set distribution (<1000 m/z) for each experiment. After ion accumulation in the octopoles, the ions were transferred into the cylindrical ion cell (ICR cell), where they were separated by their unique cyclotron frequencies for analysis. A Fourier Transformation is then applied to the data to give a spectrum of the relative abundance of each ion as a function of its m/z ratio. Mass spectra were calibrated using the exact masses of internal calibrant ions that showed high relative abundances. These calibrant ions were also part of Kendrick series and have been observed in previous DOM mass spectra. The mass accuracy achieved using the above calibration procedure was < 0.2 ppm.

A spectrum of the m/z ions present in one DOM sample can contain several thousand peaks and so data analysis begins with setting a signal to noise threshold (in this study: 5) and generating corresponding peak lists. To sort through thousands of peaks, each m/z ratio or peak location is assigned a new Kendrick Mass, which rescales each peak from the IUPAC atomic mass of $^{12}C$ = 12.00000 Dalton (Da) to the Kendrick mass scale where $CH_2$ = 14.00000 Da (3-5). The deviation of the Kendrick mass (KM) from the

nominal mass (NM) is referred to as the Kendrick mass defect (KMD). All members of a homologous series of molecules differing only in the number of $CH_2$ groups can be identified because they will all share the same KMD value.

References:

(1)    Gonsior, M.; Peake, B. M.; Jaffé, R.; Cooper, W. J.; Kahn, A.; Young, H.; Kowalczuk, P. Spectral characterization of chromophoric dissolved organic matter (CDOM) in a fjord (Doubtful Sound, New Zealand). *Aqua. Sci.* **2008**, *xxx*, xxx.

(2)    Zepp, R. G.; Sheldon, W. M.; Moran, M. A. Dissolved organic fluorophores in southeastern US coastal waters: correction method for eliminating Rayleigh and Raman scattering peaks in excitation-emission matrices. *Mar. Chem.* **2004**, *89*, 15-36.

(3)    Kendrick, E. A mass scale based on CH2=14.0000 for high resolution mass spectrometry of organic compounds. *Anal. Chem.* **1963**, *35*, 2146.

(4)    Stenson, A. C.; Marshall, A. G.; Cooper, W. T. Exact Masses and Chemical Formulas of Individual Suwannee River Fulvic Acids from Ultrahigh Resolution Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectra. *Anal. Chem.* **2003**, *75*, 1275-1284.

(5)    Kujawinski, E. B.; Hatcher, P. G.; Freitas, M. A. High-Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry of Humic and Fulvic Acids: Improvements and Comparisons. *Anal. Chem.* **2002**, *74*, 413-419.

**A**                         **B**
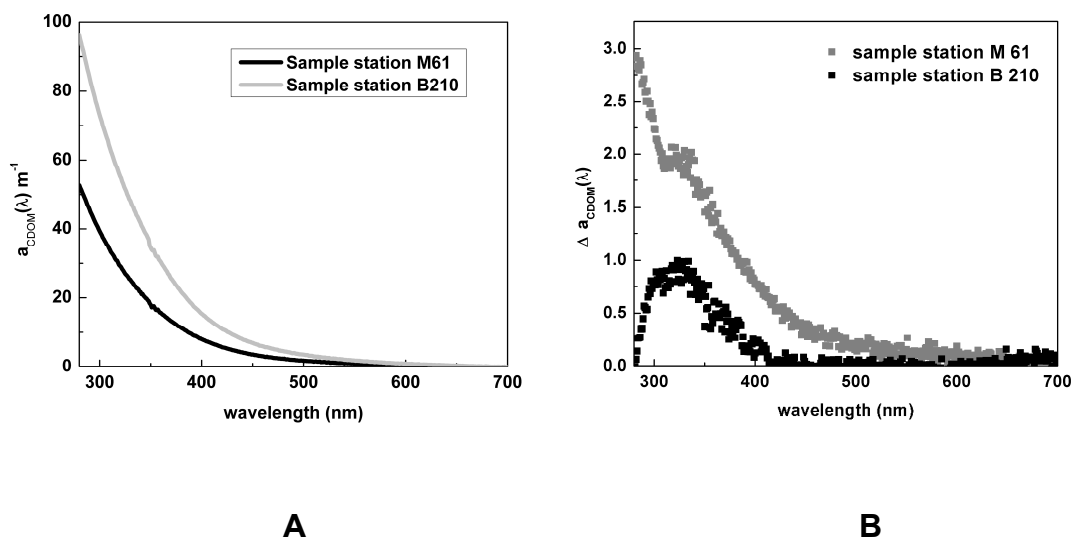
**Figure S1.** $a_{CDOM}$ ($\lambda$) values before irradiation (A) and difference plot of the absolute changes in $a_{CDOM}$ ($\lambda$) after simulated sunlight exposure (B) in sample M61 and B210.
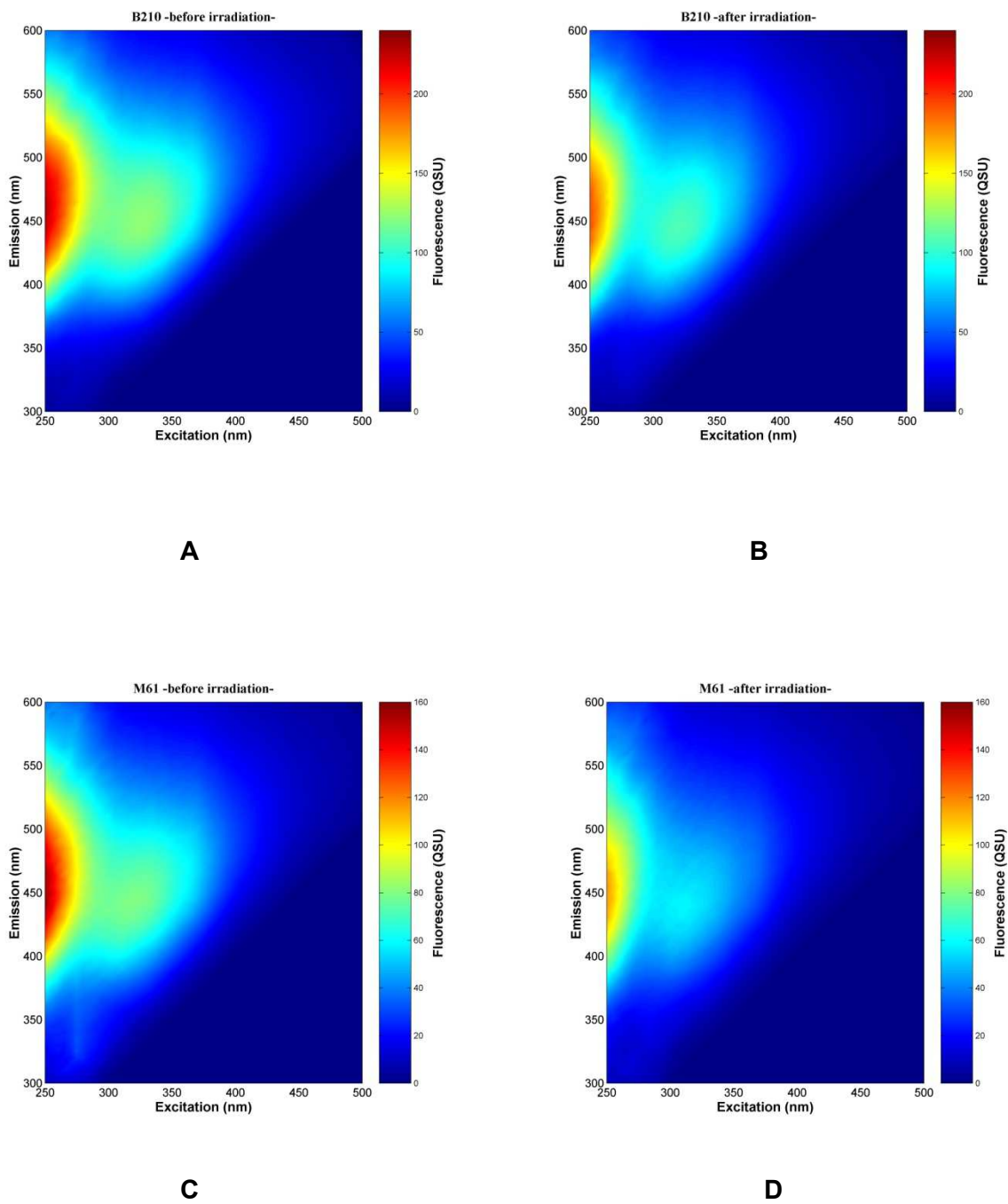
**Figure S2:** Excitation emission matrix (EEM) fluorescence spectra of sample B210 before (A) and after (B) irradiation and sample M61 before (C) and after (D) irradiation.

**Figure S3.** Van Krevelen plots before (A) and after (B) irradiation of sample B210 and before (C) and after (D) irradiation of sample M61 (lines separate areas with aromaticity indices (AI) of AI > 0.5; AI = 0.3-0.5 and AI < 0.3).

**Table S1:** One hundred most abundant photo-degraded compounds in sample M61

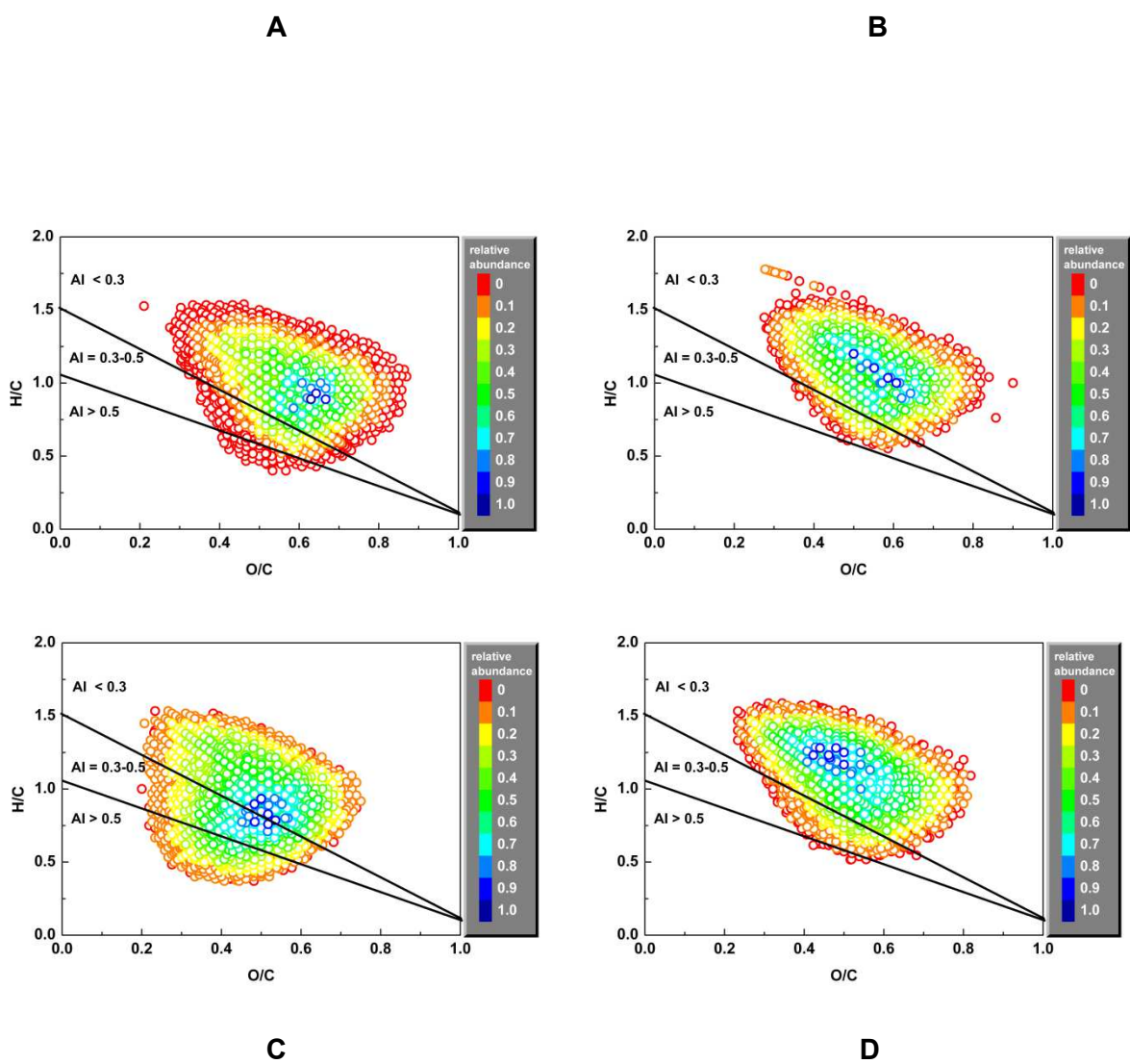| 100 most abundant, completely photo-degraded compounds in sample M61 | | | | | |
|---|---|---|---|---|---|
| Formulas sorted from highest to lowest relative abundance | carbon | hydrogen | oxygen | DBE-O | molecular mass (Da) |
| 1 | 27 | 18 | 11 | 8 | 518.08492 |
| 2 | 28 | 20 | 11 | 8 | 532.10056 |
| 3 | 27 | 20 | 10 | 8 | 504.10565 |
| 4 | 27 | 16 | 12 | 8 | 532.06418 |
| 5 | 30 | 20 | 12 | 9 | 572.09548 |
| 6 | 28 | 18 | 12 | 8 | 546.07983 |
| 7 | 29 | 20 | 11 | 9 | 544.10056 |
| 8 | 29 | 22 | 11 | 8 | 546.11622 |
| 9 | 32 | 22 | 12 | 10 | 598.11113 |
| 10 | 26 | 18 | 11 | 7 | 506.08492 |
| 11 | 26 | 18 | 10 | 8 | 490.0900 |
| 12 | 28 | 22 | 10 | 8 | 518.1213 |
| 13 | 28 | 16 | 12 | 9 | 544.06418 |
| 14 | 31 | 18 | 13 | 10 | 598.07475 |
| 15 | 29 | 18 | 11 | 10 | 542.08492 |
| 16 | 25 | 18 | 11 | 6 | 494.08492 |
| 17 | 28 | 18 | 11 | 9 | 530.08492 |
| 18 | 31 | 20 | 13 | 9 | 600.09039 |
| 19 | 24 | 16 | 10 | 7 | 464.07435 |
| 20 | 29 | 24 | 10 | 8 | 532.13695 |
| 21 | 30 | 18 | 12 | 10 | 570.07983 |
| 22 | 32 | 20 | 13 | 10 | 612.09039 |
| 23 | 27 | 18 | 10 | 9 | 502.0900 |
| 24 | 29 | 18 | 12 | 9 | 558.0798 |
| 25 | 28 | 18 | 10 | 10 | 514.0900 |
| 26 | 25 | 18 | 10 | 7 | 478.0900 |
| 27 | 26 | 16 | 10 | 9 | 488.07435 |
| 28 | 24 | 18 | 9 | 7 | 450.09508 |
| 29 | 32 | 24 | 12 | 9 | 600.12678 |
| 30 | 33 | 22 | 14 | 9 | 642.10096 |
| 31 | 33 | 20 | 15 | 9 | 656.08023 |
| 32 | 25 | 16 | 10 | 8 | 476.07435 |
| 33 | 29 | 16 | 13 | 9 | 572.05909 |
| 34 | 27 | 16 | 10 | 10 | 500.07435 |
| 35 | 25 | 14 | 11 | 8 | 490.05361 |
| 36 | 25 | 18 | 9 | 8 | 462.09508 |
| 37 | 28 | 16 | 11 | 10 | 528.06926 |
| 38 | 31 | 22 | 11 | 10 | 570.11622 |
| 39 | 26 | 14 | 12 | 8 | 518.04853 |
| 40 | 23 | 16 | 10 | 6 | 452.07435 |

| 41 | 27 | 22 | 10 | 7 | 506.1213 |
|----|----|----|----|----|----|
| 42 | 31 | 24 | 11 | 9 | 572.13186 |
| 43 | 34 | 28 | 12 | 9 | 628.15808 |
| 44 | 31 | 22 | 12 | 9 | 586.11113 |
| 45 | 33 | 24 | 12 | 10 | 612.12678 |
| 46 | 30 | 20 | 11 | 10 | 556.10056 |
| 47 | 29 | 22 | 10 | 9 | 530.1213 |
| 48 | 28 | 20 | 10 | 9 | 516.10565 |
| 49 | 30 | 22 | 10 | 10 | 542.1213 |
| 50 | 23 | 14 | 10 | 7 | 450.0587 |
| 51 | 27 | 16 | 11 | 9 | 516.06926 |
| 52 | 22 | 16 | 10 | 5 | 440.07435 |
| 53 | 32 | 20 | 12 | 11 | 596.09548 |
| 54 | 30 | 18 | 13 | 9 | 586.07475 |
| 55 | 23 | 14 | 11 | 6 | 466.05361 |
| 56 | 29 | 18 | 10 | 11 | 526.0900 |
| 57 | 29 | 16 | 12 | 10 | 556.06418 |
| 58 | 29 | 20 | 10 | 10 | 528.10565 |
| 59 | 27 | 14 | 11 | 10 | 514.05362 |
| 60 | 32 | 18 | 13 | 11 | 610.07475 |
| 61 | 33 | 22 | 12 | 11 | 610.11113 |
| 62 | 25 | 20 | 9 | 7 | 464.11073 |
| 63 | 31 | 20 | 12 | 10 | 584.09548 |
| 64 | 31 | 20 | 11 | 11 | 568.10056 |
| 65 | 25 | 16 | 9 | 9 | 460.07943 |
| 66 | 27 | 22 | 9 | 8 | 490.12639 |
| 67 | 34 | 26 | 13 | 9 | 642.13734 |
| 68 | 30 | 22 | 11 | 9 | 558.11622 |
| 69 | 30 | 26 | 10 | 8 | 546.1526 |
| 70 | 33 | 26 | 11 | 10 | 598.14752 |
| 71 | 31 | 16 | 15 | 9 | 628.04893 |
| 72 | 25 | 14 | 12 | 7 | 506.04853 |
| 73 | 25 | 22 | 9 | 6 | 466.12639 |
| 74 | 22 | 14 | 11 | 5 | 454.05361 |
| 75 | 30 | 24 | 10 | 9 | 544.13695 |
| 76 | 28 | 24 | 9 | 8 | 504.14204 |
| 77 | 30 | 18 | 14 | 8 | 602.06966 |
| 78 | 26 | 14 | 11 | 9 | 502.05361 |
| 79 | 28 | 16 | 13 | 8 | 560.05909 |
| 80 | 35 | 28 | 13 | 9 | 656.15300 |
| 81 | 24 | 14 | 10 | 8 | 462.05870 |
| 82 | 27 | 24 | 9 | 7 | 492.14204 |
| 83 | 27 | 20 | 9 | 9 | 488.11073 |
| 84 | 34 | 20 | 13 | 12 | 636.09039 |
| 85 | 26 | 20 | 9 | 8 | 476.11073 |
| 86 | 31 | 16 | 13 | 11 | 596.05909 |
| 87 | 33 | 26 | 12 | 9 | 614.14243 |

| 88 | 28 | 14 | 12 | 10 | 542.04853 |
| 89 | 27 | 14 | 12 | 9 | 530.04853 |
| 90 | 34 | 30 | 12 | 8 | 630.17373 |
| 91 | 28 | 14 | 11 | 11 | 526.05362 |
| 92 | 24 | 14 | 11 | 7 | 478.05361 |
| 93 | 30 | 16 | 12 | 11 | 568.06418 |
| 94 | 26 | 14 | 13 | 7 | 534.04345 |
| 95 | 28 | 20 | 9 | 10 | 500.11073 |
| 96 | 30 | 16 | 14 | 9 | 600.05401 |
| 97 | 31 | 18 | 14 | 9 | 614.06966 |
| 98 | 28 | 22 | 9 | 9 | 502.12639 |
| 99 | 24 | 14 | 12 | 6 | 494.04853 |
| 100 | 26 | 22 | 9 | 7 | 478.12639 |

**Table S2:** One hundred most abundant photo-produced compounds in sample M61

| 100 most abundant, newly formed, photo-produced compounds in sample M61 | | | | | |
|---|---|---|---|---|---|
| Formulas sorted from highest to lowest relative abundance | carbon | hydrogen | oxygen | DBE-O | molecular mass (Da) |
| 1 | 23 | 30 | 14 | -5 | 530.16356 |
| 2 | 22 | 26 | 15 | -5 | 530.12717 |
| 3 | 24 | 32 | 14 | -5 | 544.17921 |
| 4 | 22 | 28 | 14 | -5 | 516.14791 |
| 5 | 27 | 28 | 19 | -5 | 656.12248 |
| 6 | 33 | 28 | 18 | 2 | 712.12757 |
| 7 | 25 | 36 | 12 | -4 | 528.22068 |
| 8 | 27 | 32 | 18 | -6 | 644.15887 |
| 9 | 26 | 36 | 14 | -5 | 572.21051 |
| 10 | 20 | 26 | 12 | -4 | 458.14243 |
| 11 | 27 | 38 | 14 | -5 | 586.22616 |
| 12 | 25 | 34 | 14 | -5 | 558.19486 |
| 13 | 21 | 24 | 15 | -5 | 516.11153 |
| 14 | 20 | 20 | 15 | -4 | 500.08022 |
| 15 | 21 | 26 | 14 | -5 | 502.13226 |
| 16 | 26 | 30 | 18 | -6 | 630.14322 |
| 17 | 27 | 34 | 17 | -6 | 630.17961 |
| 18 | 28 | 34 | 16 | -4 | 626.18469 |
| 19 | 28 | 36 | 17 | -6 | 644.19525 |
| 20 | 21 | 20 | 16 | -4 | 528.07514 |
| 21 | 24 | 34 | 13 | -5 | 530.19994 |
| 22 | 25 | 24 | 19 | -5 | 628.09119 |
| 23 | 19 | 20 | 14 | -4 | 472.08531 |
| 24 | 26 | 26 | 19 | -5 | 642.10684 |
| 25 | 28 | 40 | 14 | -5 | 600.24181 |
| 26 | 19 | 22 | 13 | -4 | 458.10604 |
| 27 | 19 | 24 | 12 | -4 | 444.12678 |
| 28 | 27 | 40 | 12 | -4 | 556.25198 |
| 29 | 31 | 44 | 15 | -5 | 656.26802 |
| 30 | 23 | 32 | 13 | -5 | 516.1843 |
| 31 | 21 | 22 | 16 | -5 | 530.09079 |
| 32 | 32 | 44 | 15 | -4 | 668.26802 |
| 33 | 29 | 42 | 14 | -5 | 614.25746 |
| 34 | 30 | 38 | 13 | -1 | 606.23124 |
| 35 | 20 | 24 | 14 | -5 | 488.11661 |
| 36 | 28 | 32 | 19 | -6 | 672.15378 |
| 37 | 28 | 38 | 16 | -6 | 630.21599 |
| 38 | 24 | 30 | 16 | -6 | 574.15339 |
| 39 | 21 | 28 | 13 | -5 | 488.15299 |
| 40 | 28 | 42 | 12 | -4 | 570.26763 |

| 41 | 26 | 28 | 19 | -6 | 644.12248 |
|----|----|----|----|----|-----------|
| 42 | 21 | 18 | 16 | -3 | 526.05949 |
| 43 | 29 | 38 | 15 | -4 | 626.22108 |
| 44 | 30 | 42 | 15 | -5 | 642.25238 |
| 45 | 24 | 20 | 18 | -3 | 596.06497 |
| 46 | 20 | 22 | 15 | -5 | 502.09587 |
| 47 | 31 | 44 | 11 | -1 | 592.28837 |
| 48 | 20 | 18 | 15 | -3 | 498.06457 |
| 49 | 36 | 48 | 16 | -3 | 736.29424 |
| 50 | 23 | 26 | 17 | -6 | 574.117 |
| 51 | 22 | 28 | 15 | -6 | 532.14283 |
| 52 | 31 | 42 | 15 | -4 | 654.25238 |
| 53 | 30 | 44 | 14 | -5 | 628.27311 |
| 54 | 23 | 30 | 15 | -6 | 546.15847 |
| 55 | 33 | 46 | 15 | -4 | 682.28368 |
| 56 | 25 | 30 | 17 | -6 | 602.14831 |
| 57 | 22 | 30 | 13 | -5 | 502.16865 |
| 58 | 25 | 36 | 13 | -5 | 544.2156 |
| 59 | 30 | 46 | 10 | -2 | 566.3091 |
| 60 | 29 | 40 | 16 | -6 | 644.23164 |
| 61 | 23 | 34 | 10 | -3 | 470.2152 |
| 62 | 28 | 42 | 10 | -2 | 538.2778 |
| 63 | 19 | 18 | 14 | -3 | 470.06966 |
| 64 | 27 | 40 | 13 | -5 | 572.24689 |
| 65 | 24 | 26 | 18 | -6 | 602.11192 |
| 66 | 29 | 36 | 18 | -6 | 672.19017 |
| 67 | 22 | 26 | 16 | -6 | 546.12209 |
| 68 | 31 | 28 | 18 | 0 | 688.12757 |
| 69 | 24 | 32 | 15 | -6 | 560.17413 |
| 70 | 23 | 34 | 11 | -4 | 486.21011 |
| 71 | 26 | 34 | 16 | -6 | 602.18469 |
| 72 | 23 | 28 | 16 | -6 | 560.13774 |
| 73 | 24 | 24 | 18 | -5 | 600.09627 |
| 74 | 21 | 24 | 16 | -6 | 532.10644 |
| 75 | 35 | 48 | 15 | -3 | 708.29932 |
| 76 | 22 | 18 | 16 | -2 | 538.05949 |
| 77 | 34 | 42 | 15 | -1 | 690.25238 |
| 78 | 25 | 34 | 15 | -6 | 574.18978 |
| 79 | 25 | 26 | 19 | -6 | 630.10684 |
| 80 | 21 | 26 | 15 | -6 | 518.12717 |
| 81 | 29 | 44 | 10 | -2 | 552.29345 |
| 82 | 22 | 22 | 17 | -5 | 558.0857 |
| 83 | 26 | 38 | 13 | -5 | 558.23124 |
| 84 | 29 | 44 | 12 | -4 | 584.28328 |
| 85 | 35 | 48 | 16 | -4 | 724.29424 |

| | | | | | |
|---|---|---|---|---|---|
| 86 | 20 | 28 | 11 | -4 | 444.16316 |
| 87 | 33 | 40 | 18 | -4 | 724.22147 |
| 88 | 21 | 28 | 14 | -6 | 504.14791 |
| 89 | 31 | 46 | 11 | -2 | 594.30402 |
| 90 | 18 | 22 | 11 | -3 | 414.11622 |
| 91 | 22 | 32 | 11 | -4 | 472.19446 |
| 92 | 33 | 38 | 20 | -5 | 754.19565 |
| 93 | 22 | 20 | 17 | -4 | 556.07006 |
| 94 | 20 | 18 | 16 | -4 | 514.05949 |
| 95 | 31 | 28 | 20 | -2 | 720.1174 |
| 96 | 20 | 24 | 15 | -6 | 504.11152 |
| 97 | 22 | 30 | 14 | -6 | 518.16356 |
| 98 | 18 | 20 | 13 | -4 | 444.0904 |
| 99 | 26 | 20 | 19 | -2 | 636.05989 |
| 100 | 25 | 38 | 11 | -4 | 514.24141 |