RESPONSE to Reviewers

Manuscript Ref. No: **acp-2021-553, Roman et al., Atmos. Chem. Phys. Discuss**

Title: **Investigations on the gas-phase photolysis and OH radical kinetics of nitrocatechols: Implications of intramolecular interactions on their atmospheric behavior**

Special Issue: Simulation chambers as tools in atmospheric research (AMT/ACP/GMD inter-journal SI)

On behalf of all authors of the above-mentioned paper, I want to thank you and to Professor Cornelius Zetzsch for your careful reading of our revised manuscript and for all the comments and suggestions as well. In the attached file, we are pleased to present our response to all comments and suggestions raised by the reviewer. The original comments from the Professor Cornelius Zetzsch are shown in black and our responses are marked in blue. Changes made in the body of the article are marked in red in this document as well as in the second revised manuscript and in the supplementary material. Lines indications refer to the positions where the text has been amended in the article body.

R1: The second version of the manuscript has improved by adding more graphics to the manuscript and to the supplementary material and the information about another detailed study by Roman et al. (2021) on the IR spectra and further fundamental properties of the nitrocatechols of the present study.

Response from authors: We are glade to notes that our improvements satisfy the reviewer requirement's and appreciate the new comments and suggestions on the articles to complete the final form to publication.

R1: The abstract might mention the two reference compounds for the relative rate technique and to add the upper limits of photolysis (and lower limits of photolytic lifetimes) for the two catechols with isolated nitro groups (4NCat and 4M5NCat) at 365 nm and the photolytic rate constants of these compounds at 254 nm of this excellent photochemical study.

Response from authors: The suggestions from reviewer have been added into the abstract. The following sentences have been added to abstract body accordingly:

Changes in the manuscript:

L 9-16: ..... Employing relative rate techniques at a temperature of 298 ± 2 K and a total air pressure of 1 atm, the obtained rate coefficients (in 10^{-12} $cm^3 \times s^{-1}$) were as follows: k_{3NCAT} = (3.41 ± 0.37) for 3-nitrocatechol and $k_{5M3NCAT}$ = (5.55 ± 0.45) for 5-methyl-3-nitrocatechol at 365 nm using CH_3ONO photolysis as OH radicals source and dimethyl ether and cyclohexane as reference compounds, and k_{4NCAT} = (1.27 ± 0.19) for 4-nitrocatechol and $k_{4M5NCAT}$ = (0.92 ± 0.14) for 4-methyl-5-nitrocatechol at 254 nm using H_2O_2 as OH radicals source and dimethyl ether and methanol as reference compounds. The photolysis rates in the actinic region, scaled to atmospheric relevant conditions by NO_2 photolysis, were evaluated for 3-nitrocatechol and 5-methyl-3-nitrocatechol: J_{3NCAT} = (3.06 ± 0.16) $\times 10^{-4}$ s^{-1} and $J_{5M3NCAT}$ = (2.14 ± 0.18) $\times 10^{-4}$ s^{-1}, respectively. The photolysis rate constants at 254 nm were measured for 4-nitrocatechol and 4-methyl-5-nitrocatechol and the obtained values are J_{4NCAT} = (6.7 ± 0.1) × 10^{-5} s^{-1} and $J_{4M5NCAT}$ = (3.2 ± 0.3) × 10^{-5} s^{-1}.....

R1: The estimated quantum yields should be treated with caution: The charge transfer band of nitroaromatics is known to undergo a considerable redshift by the change from gas-phase to solution

and in thin film; water is expected to provide largest shifts, see Reichardt, C., Solvents and solvent effects in organic chemistry, 2nd ed., VCH-Verlagsgesellschaft, Weinheim (1999). There might also be an influence on the oscillator strength.

Response from authors: In the supplement material we specified that the proposed quantum yields and absorption cross sections should be treated carefully, as many assumptions have been made prior to the data provision, with the most evident being the experimental method for cross section evaluation.

Suggested further corrections:

R1: L. 10: => insert "at Iasi" here and possibly omit "for the first time"

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 12: => and a total

Response from authors: Authors have considered the reviewer suggestion.

R1: L.12: you might wish to mention the two photolytic sources of OH radicals and the two reference compounds here

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 14: omit "For the investigated compounds" but start the sentence with The photolysis…

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 29: put references into chronological order

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 31: => ring opening and fragmentation.

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 34: put references into chronological order

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 35: dimethylphenols …. trimethylphenols

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 37: to the Master

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 50, 52-55, 62: put cumulated references into chronological order

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 61: aerosols, the

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 65: seem to => may

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 80: from => at

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 84: Gas-phase..

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 87: and a temperature

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 90: a stream

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 92: Teflon-blade

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 104: the ozone formation might be explained by adding the reaction:
$2\ NO_2 + O_2 + h\nu \longrightarrow 2\ NO + O_3$

Response from authors: Authors have considered the reviewer suggestion, by amending the text.

Changes in the manuscript:

L. 100: ….in R.1.1-R.1.5 reactions…..

L 104-105: $NO_2 + O_2 + h\nu \rightarrow O_3 + NO$ (R1.4)

$O_3 + NO \rightarrow NO_2 + O_2$ (R.1.5)

R1: L. 107: → 2 OH

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 108: photodissociate

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 115: time with respect

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 119, 120: referent => reference

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 131: nitrocatechols, their

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 140: nitrocatechols were

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 145: have => has

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 150-154: use subscripts

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 159: have => has

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 175: has => have

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 179: omit about in the first place and replace it by "it was" in the second one

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 184: The four digits of precision are not justified; I would suggest errors of 0.7 and 0.5

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 188: give wavenumber here

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 193-208: Such a discussion of collision theory is not required nor useful without information about size distribution and particle number density and aerosol surface area, including the geometric surface area of the chamber. How the loss of OH might affect the relative rate and photolysis constants remains unclear. The precision of the OH velocity (L. 196) as an average of a broad distribution and even more so the discussion of Henry's law constants appear to be meaningless in view of the linearity and the zero intercept of figure 1-4 and the small intercept of the photolysis results in figure S1 and S2. The wall reaction k_4 might be an appropriate topic here - and how the numbers in L. 199 are calculated. To which experiment/figure do they refer? L. 212 of?

Response from authors: The authors are very thankful for the reviewer comment. Considering the less importance of the discussion on the OH deactivation the authors agreed to remove part of the paragraph and reconsider the context.

Changes in the manuscript:

L191-207: The rate coefficients obtained from the kinetic investigations of a series of nitrocatechols with OH radicals are reported for the first time in this study. No significant differences have been observed between the two reference compounds that have been employed to achieve the quality of the rate coefficient values. Based on collision theory and the standard gas kinetic theory, Sørensen et al. (2002) showed that the presence of inorganic aerosols does not influence the value of the OH radicals rate coefficients when relative kinetic technique is used. The OH radicals deactivation from collisions with surfaces, both with aerosols and chamber respectively, were found to be negligible for all nitrocatechols. However, even if such process occurs at higher rate, using of the relative kinetic technique, where the k_1/k_2 ratio is experimentally determined independent of the OH radical

concentration, no systematic errors rising up from the OH radical concentration would influence the kinetic data.

R1: L. 220: atoms

Response from authors: Authors have considered the reviewer suggestion.

R1: L221: reveals a H-bond between

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 224: H-bonds

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 230-231: change color of text to black

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 233: structures

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 234: This suggest that

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 239: To the first one => position(?).

Response from authors: Authors have considered the reviewer suggestion by removing "in -*ortho* to the first one".

Changes in the manuscript:

L 233-234: This suggest that for 1,2-dihydroxybenzenes the E+ effect is less diminished through the presence of the vicinal OH groups.

R1: L. 240: group to its

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 243: reactivities

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 246: orders

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 254: radicals

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 255: that the H-atom …than the abstraction.

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 2r57: gas-phase

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 279: radicals

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 283: If the OH group

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 290: considered to be

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 294: analysis, that

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 296: reaction pathways

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 328: τ => σ

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 363: behavior

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 369: using the Kwok

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 370: observations, revisions for the

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 372: presents such a correlation

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 373: presents…..substituent interactions

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 376-378: reflects…for the nitrophenols……reduced…..spread…..the correlation lines of interest.

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 383: H-bond on the rate coefficient values….rising from r =

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 385: …we believe…

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 392: nitronaphthalenes… methylnitronaphthalenes…

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 395: area might…

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 401 and 403: 3-nitroctechol compounds

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 404: in 4-nitr- or 5-nitrocatechols, the…..while in the 3-nitrocatechols case..

Response from authors: Authors have considered the reviewer suggestion.

R1: L. 408: atmospheric degradation process

Response from authors: Authors have considered the reviewer suggestion.

R1: L.631-645: The sum k3 + k4 forces the straight lines through the origin and should be given in the figure captions of figs. 1-4; this should be the case for the photolysis experiments in figures S1 and S2 as well, where k4 could be given, neglecting any wall loss of the reference compounds.

Response from authors: Authors have considered the reviewer suggestions and modify the figure captions accordingly.

R1: L. 666-669: Legend 8A => Figure 8A (and so on)

Response from authors: Authors have considered the reviewer suggestion.

R1: A space should be added between the Σ and the σ in fig 8A and fig. 8B. Minor ticks might be more useful on the ordinate axes (see below) instead of half orders of magnitude.

Response from authors: Authors have considered the reviewer suggestion.

R1: Fig. 8D: electrofilic => electrophilic

Response from authors: Authors have considered the reviewer suggestion.

R1: The linear scales of figures 8C and 8D do not provide an overview about the present limitations of SAR calculation. This led me to provide the data of 8C in a double logarithmic diagram (using e.g. Sigmaplot) with compound names, where deviations by a factor of two are marked by dashed lines.

Response from authors: figures 8C and 8D changed as reference suggested, to provide an overview about the present limitations of SAR calculation.

Changes in the manuscript:

L381-382: ...the Pearson coefficient value rising from r = 0.321 for the original estimates to r = 0.843 for…

L667:

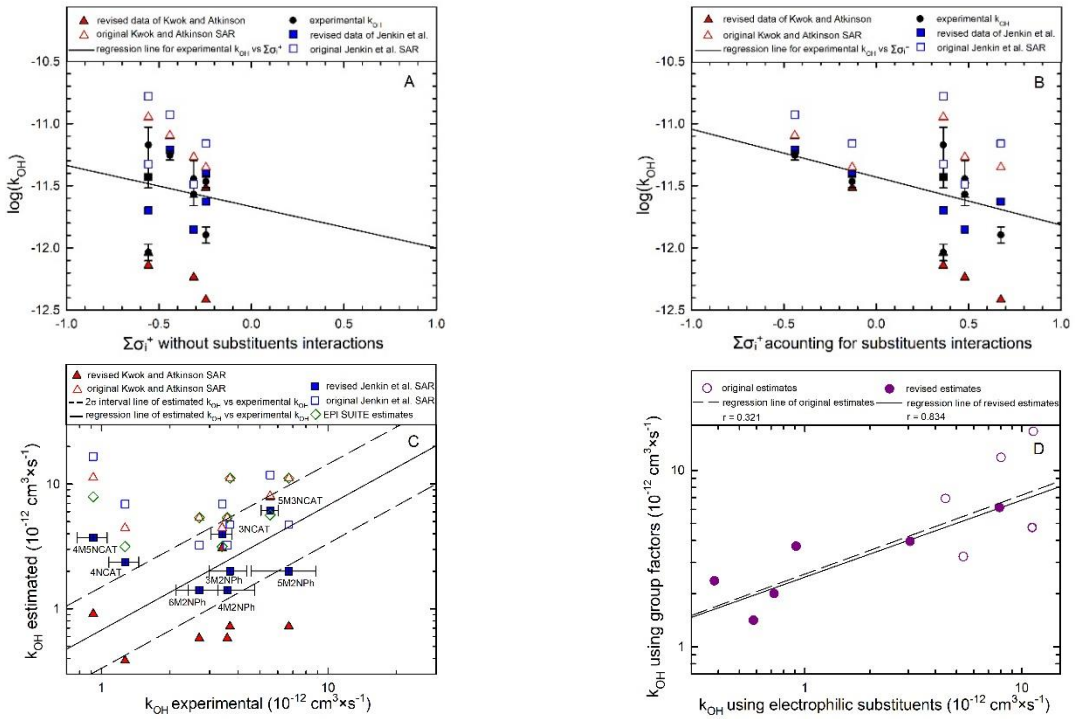

Figure 8: Correlation analyses between the experimental, the original estimated and the revised estimated OH gas-phase rate coefficients of nitrophenols and nitrocatechols

R1: Table 1: Referent => Reference

Response from authors: Authors have considered the reviewer suggestion.

R1: The precision of the stated lifetimes is unreasonable, and the very simple formula (an oversimplification for good reasons) used for its calculation should be given in the footnote

Response from authors: Authors have considered the reviewer suggestion by adding in the table 1 footnote the lifetime formula derived from the kinetic theory. Also, we approximate the values to the units of hour.

Changes in the manuscript:

L671 Table 1 footnote: [a] calculated by applying $\tau = 1/(k_1 \times [\overline{OH}])$ and considering the average daytime OH radical concentration ($[\overline{OH}]$) of 1.6 ×10^6 cm^{-3} (Prinn et al., 1995).

R1: Table 2: Unreasonable precision of lifetimes, which are simply the inverse of the rate constants here in still inconvenient units. These are different for daylight hours and nighttime and for different seasons and latitudes.

Response from authors: Authors have considered the reviewer suggestion by adding in table 2 footnote the lifetime formula and additional information about the calculations.

Changes in the manuscript:

L 675 Table 2 footnote: [a]Calculated by applying $\tau = 1/J_{NCAT}$, where J_{NCAT} at 365 nm has been estimated from the experimental determined $J_{NCAT,exp}$ and using a scaled factor derived from the NO_2 photolysis frequency for the atmospheric conditions (Klotz et al., 1997) (see in text).

Supplementary material

R1: The UV-VIS absorbance spectra of 3NCAT and 5M3NCAT in aqueous solution are a valuable

information about the absorption bands responsible for photolysis. It might be more instructive to use a logarithmic scale for the absorbance and to display them in separate diagrams together with the spectrum of the lamps. The conversion of the molar extinction into molecular absorption cross sections on the right ordinate is misleading and should be restricted to table TS1, where the conversion factor could be given as a footnote. That table should extend to 500 nm in order to cover the full range of the measurements. This will unravel the band shapes and demonstrate the proper background subtraction/purity of the compounds. A reference to tabulated data of the emission spectrum over the same spectral range would be useful.

Response from authors: The changes have been performed to the supplementary material and the references in the text of the manuscript have been updated according to reviewer suggestions.

L185**: …**spectra recording (see Figure **S3A for 3NCAT and S3B for 5M3NCAT** from SM)…

Figure S3 has been divided into two figures S3A and S3B, for each investigated compound (3NCAT and 5M3NCAT), and the figure caption has been revised.

Changes in the supplementary material:

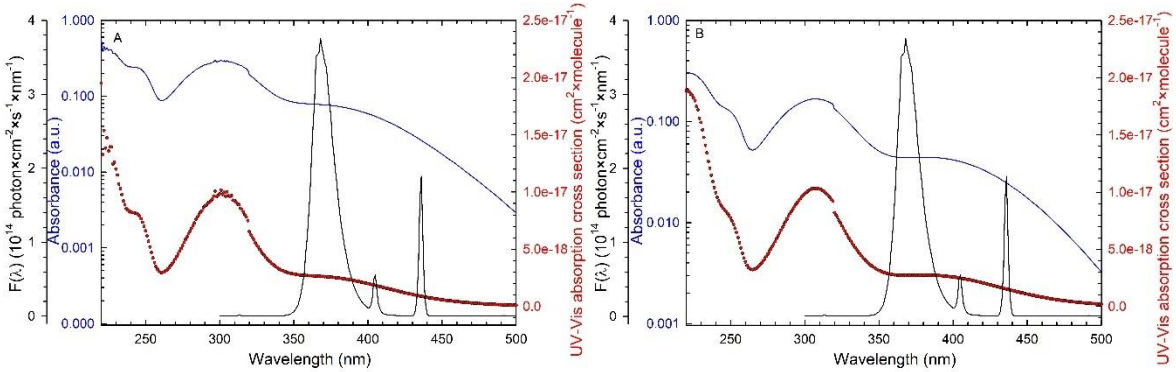

Figure S3: UV-Vis absorbance spectra of (A) 3NCAT and (B) 5M3NCAT in aqueous solution with the corresponding UV-Vis absorption cross sections (base 10) for 3NCAT and 5M3NCAT in the 220-500 nm range, along with the emission spectrum in the range of 300-500 nm of the Philips TL-DK 36W lamps.

Table TS1 data and table caption have been also revised according to the reviewer suggestions for 350-500 nm cross section values and mean irradiance values of the Philips TL-DK 36W lamps measured inside the reactor.

Table TS1: UV-Vis absorption cross sections of 3NCAT and 5M3NCAT in aqueous solution in the 350-500 nm spectral range (base 10) and the mean irradiance values of the actinic lamps (2π sr solid angle acquisition mode) inside the ESC-Q-UAIC reactor.

λ (nm)	$\sigma_{3NCAT}\times10^{18}$ ($cm^2\times molecule^{-1}$)	$\sigma_{5M3NCAT}\times10^{18}$ ($cm^2\times molecule^{-1}$)	$E\times10^{-11}$ ($photon\times cm^{-2}\times nm^{-1}\times s^{-1}$)	λ(nm)	$\sigma_{3NCAT}\times10^{18}$ ($cm^2\times molecule^{-1}$)	$\sigma_{5M3NCAT}\times10^{18}$ ($cm^2\times molecule^{-1}$)	$E\times10^{-11}$ ($photon\times cm^{-2}\times nm^{-1}\times s^{-1}$)
350	2.82	3.16	1.30	426	1.16	1.87	3.19
351	2.80	3.10	0.82	427	1.13	1.83	3.43
352	2.78	3.04	1.22	428	1.10	1.80	3.26

353	2.76	3.00	1.01	429	1.08	1.77	3.25
354	2.74	2.95	1.58	430	1.05	1.73	3.35
355	2.73	2.91	0.73	431	1.02	1.70	7.84
356	2.72	2.88	0.88	432	0.99	1.67	38.13
357	2.71	2.85	0.49	433	0.97	1.63	122.32
358	2.70	2.82	0.78	434	0.94	1.60	327.30
359	2.69	2.80	0.27	435	0.91	1.56	773.47
360	2.68	2.78	0.72	436	0.89	1.53	946.83
361	2.67	2.77	1.51	437	0.86	1.49	564.43
362	2.67	2.75	4.57	438	0.83	1.46	209.74
363	2.66	2.74	8.52	439	0.81	1.42	71.36
364	2.66	2.73	6.50	440	0.79	1.39	14.72
365	2.65	2.73	2.49	441	0.76	1.36	3.00
366	2.64	2.73	1.22	442	0.74	1.33	2.34
367	2.63	2.72	0.57	443	0.72	1.30	2.13
368	2.63	2.72	0.87	444	0.70	1.27	2.30
369	2.62	2.72	0.77	445	0.68	1.24	2.16
370	2.61	2.72	0.54	446	0.66	1.21	2.22
371	2.60	2.73	0.37	447	0.64	1.18	1.98
372	2.59	2.73	0.51	448	0.62	1.15	1.99
373	2.58	2.73	0.85	449	0.60	1.11	1.97
374	2.57	2.73	0.82	450	0.58	1.08	1.96
375	2.56	2.74	0.48	451	0.56	1.05	2.01
376	2.54	2.74	0.75	452	0.54	1.03	1.96
377	2.53	2.74	0.87	453	0.53	1.00	1.79
378	2.51	2.74	0.57	454	0.51	0.97	1.89
379	2.50	2.74	0.43	455	0.49	0.94	1.75
380	2.48	2.74	0.59	456	0.48	0.92	1.78
381	2.46	2.74	1.04	457	0.47	0.90	1.79
382	2.45	2.74	1.06	458	0.45	0.87	1.84
383	2.43	2.74	1.58	459	0.44	0.85	1.80
384	2.41	2.74	2.23	460	0.42	0.82	1.78
385	2.38	2.74	2.16	461	0.41	0.80	1.77
386	2.36	2.73	1.59	462	0.39	0.77	1.70
387	2.34	2.73	0.74	463	0.38	0.75	1.84
388	2.32	2.73	1.38	464	0.37	0.72	1.75
389	2.30	2.72	1.58	465	0.36	0.70	1.84
390	2.27	2.71	1.70	466	0.34	0.68	1.78
391	2.25	2.71	2.11	467	0.33	0.66	1.78
392	2.22	2.70	2.45	468	0.32	0.64	1.65
393	2.19	2.69	2.91	469	0.31	0.62	1.74
394	2.16	2.68	5.53	470	0.30	0.60	1.74
395	2.14	2.66	6.90	471	0.29	0.58	1.69
396	2.11	2.65	9.17	472	0.28	0.56	1.80
397	2.08	2.64	11.65	473	0.27	0.54	1.67
398	2.05	2.62	14.77	474	0.26	0.52	1.77
399	2.02	2.61	25.67	475	0.25	0.51	1.63
400	1.99	2.59	28.78	476	0.24	0.49	1.61
401	1.96	2.56	44.73	477	0.23	0.47	1.73
402	1.93	2.55	60.73	478	0.23	0.46	1.70
403	1.90	2.53	80.00	479	0.22	0.44	1.73
404	1.87	2.51	120.45	480	0.21	0.42	1.62
405	1.84	2.48	165.19	481	0.20	0.41	1.68
406	1.80	2.46	223.60	482	0.19	0.40	1.64
407	1.77	2.44	289.32	483	0.19	0.38	1.76
408	1.74	2.41	423.36	484	0.18	0.37	1.69
409	1.70	2.39	535.28	485	0.17	0.36	1.77
410	1.67	2.36	681.85	486	0.17	0.34	1.73
411	1.64	2.33	838.44	487	0.16	0.33	1.83
412	1.60	2.30	1090.00	488	0.16	0.32	1.92
413	1.57	2.28	1289.25	489	0.15	0.31	2.42
414	1.54	2.25	1458.40	490	0.14	0.30	3.16
415	1.51	2.22	1754.08	491	0.14	0.28	4.95
416	1.48	2.19	1768.50	492	0.13	0.27	5.23
417	1.45	2.16	1781.33	493	0.13	0.26	3.52
418	1.41	2.13	1876.48	494	0.12	0.25	2.41

419	1.38	2.10	1809.75	495	0.12	0.24	1.90
420	1.35	2.07	1767.25	496	0.11	0.23	1.76
421	1.32	2.03	1712.93	497	0.11	0.23	1.61
422	1.28	2.00	1680.45	498	0.11	0.22	1.61
423	1.25	1.97	1556.10	499	0.10	0.21	1.64
424	1.22	1.93	1439.23	500	0.10	0.20	1.66
425	1.19	1.90	1358.03				