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N-Nitrosamine Formation Kinetics in Wastewater Effluents and Surface Waters

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Supplementary Information

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Text S1: NDMA formation pathways in chloramination. NAs could be formed from primary amines through a nitrosation pathway, these NAs are not stable and decay rapidly.[1] Secondary amines which form stable secondary NAs have been studied in greater detail.[2-6] Tertiary amines were also found to be important precursors. Some tertiary amines (e.g. trimethylamine (TMA)) decay nearly instantaneously and quantitatively in presence of chlorine to release a secondary amine which forms the nitrosamine upon chloramination.[7] Mechanistic studies found that nitrosamine yields from most secondary amines and tertiary amines are similar (i.e., ~0-2%). Some other tertiary amines (e.g. where one of the alkyl substituents contained an aromatic group in the β-position to the dimethylamine (DMA) nitrogen such as a benzyl functional group, or those alkyl substituents containing branched alkyl groups next to the nitrogen of DMA) have much higher yields of NDMA in chloramination.[8-10] In particular, ranitidine, a widely used amine-based pharmaceutical, forms NDMA at yields higher than 80%. It suggests that these tertiary amines form nitrosamines through different pathways.

NDMA is thought to be produced in chloraminated drinking waters through three pathways. Two pathways assume unprotonated DMA undergoes nucleophilic substitution with either mono- or dichloramine, yielding unsymmetrical dimethylhydrazine (UDMH) (NH_2Cl) in or chlorinated UDMH intermediate (Cl-UDMH) ($NHCl_2$).[2,5] UDMH is then oxidized by monochloramine to produce NDMA or Cl-UDMH is oxidized by oxygen to produce NDMA. Based upon competition kinetics, it has been suggested that monochloramine pathway is negligible compared with dichloramine pathway. The importance of the two reaction mechanisms remains debated, with dichloramine producing NDMA concentrations orders of magnitude higher than monochloramine when reacted with amine-containing model compounds.[6] However, research on suspected NDMA precursors found that compounds with electron withdrawing groups react preferentially with monochloramine while compounds with electron donating groups react preferentially with dichloramine.[11] As the molar yield of NDMA from DMA is low (i.e., <5%), it was suspected that a third pathway, not through DMA, existed. Recently it was shown that compounds such as ranitidine follow a different series of reactions involving nucleophilic attack of the amine group in organic amines. Further reaction involving dissolved O_2 allows for the direct formation of NDMA and a resulting sister carbocation.[8] When the requisite β-aryl tertiary amine is present on a parent compound, molar yields of NDMA are always in excess of 20%.[11] Other NDMA-forming compounds typically have molar conversion of <5% and therefore β-aryl tertiary amine containing compounds are thought to be of great importance.

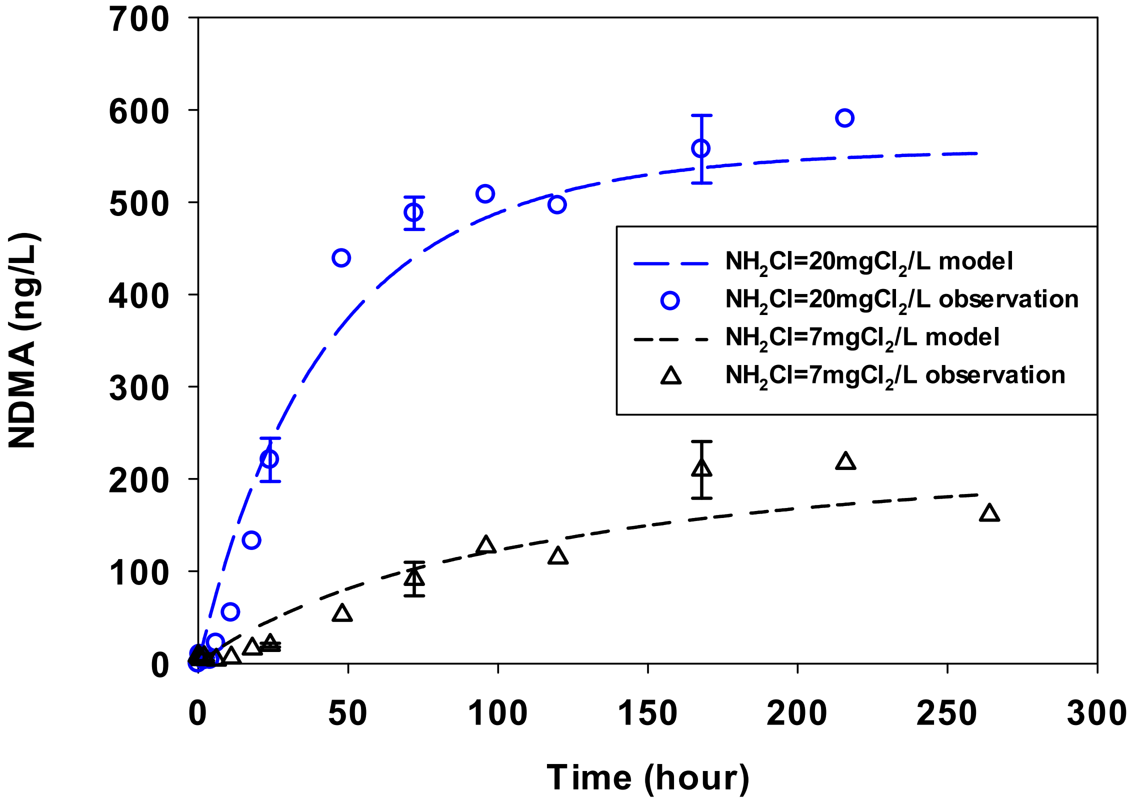

Fig S1. NDMA formation observed (symbols) and fitted by Equations 2&3 (line) in WW2 at two initial monochloramine doses. (pH=8.0, 20°C)

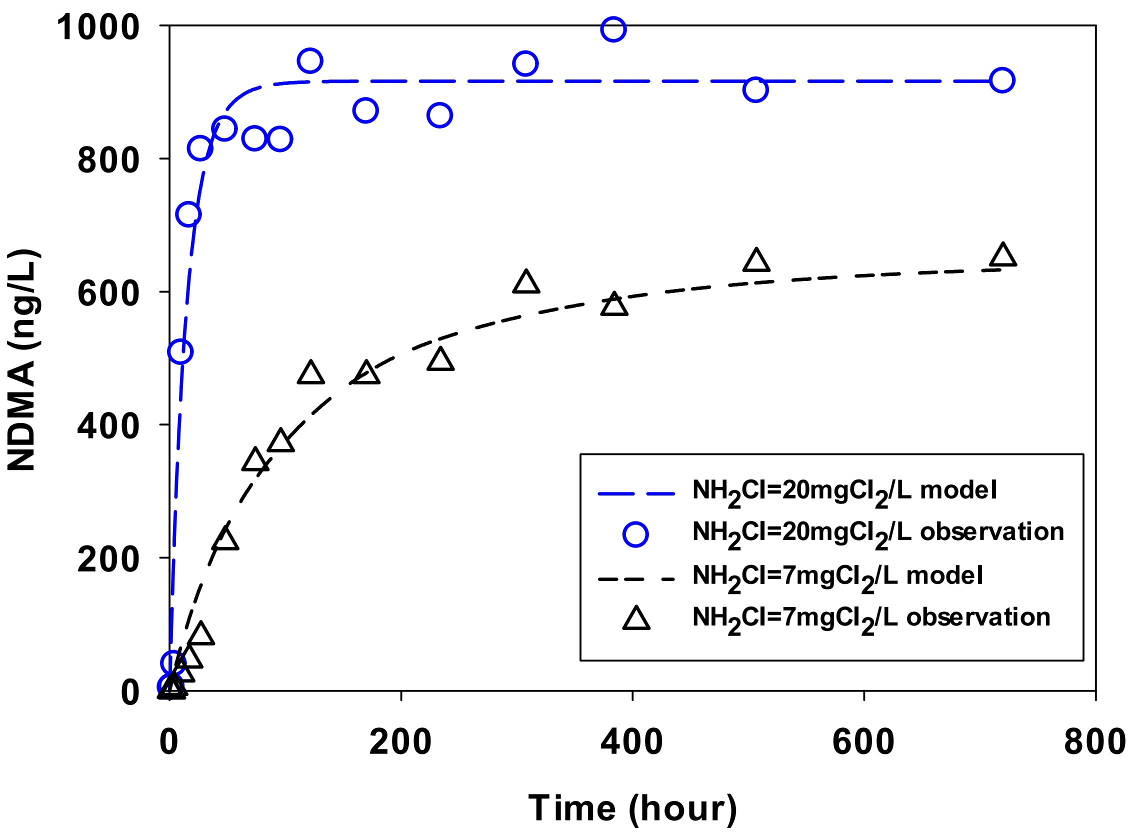

Fig S2. NDMA formation observed (symbols) and fitted by Equations 2&3 (line) in WW3 at two initial monochloramine doses. (pH=8.0, 20°C)

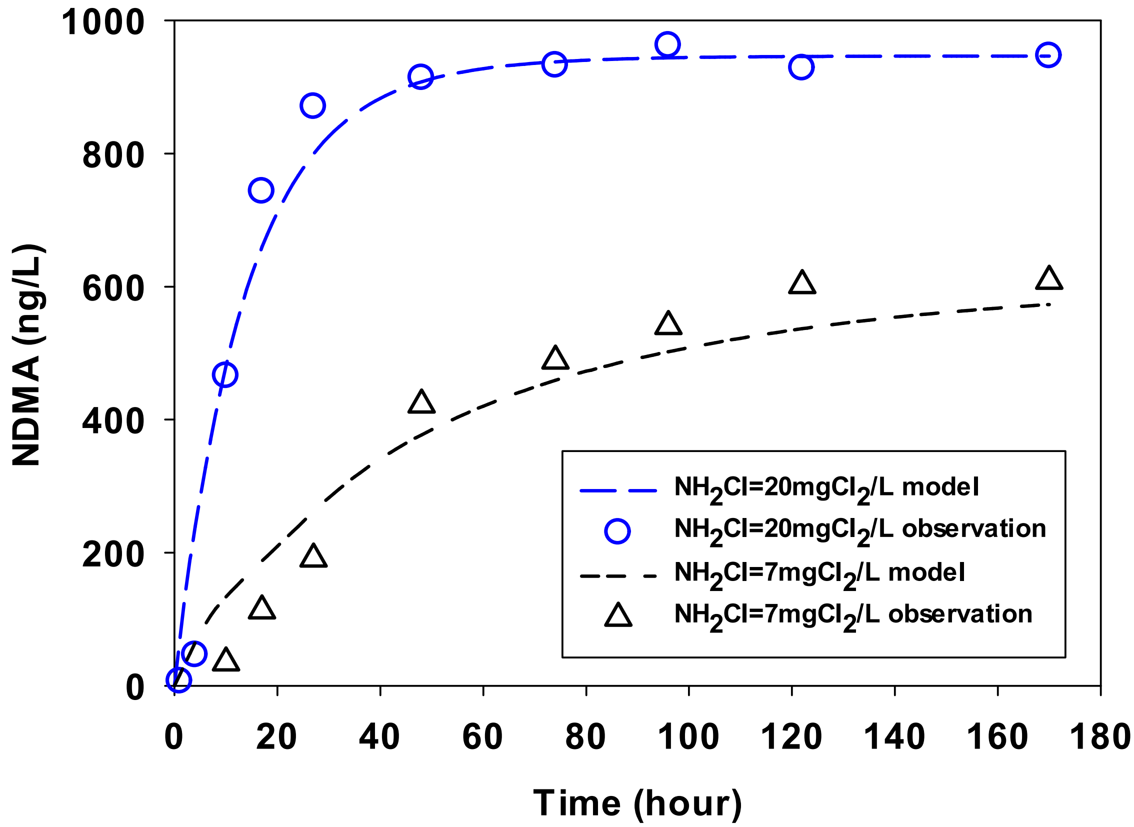

Fig S3. NDMA formation observed (symbols) and fitted by Equations 2&3 (line) in WW4 at two initial monochloramine doses. (pH=8.0, 20°C)

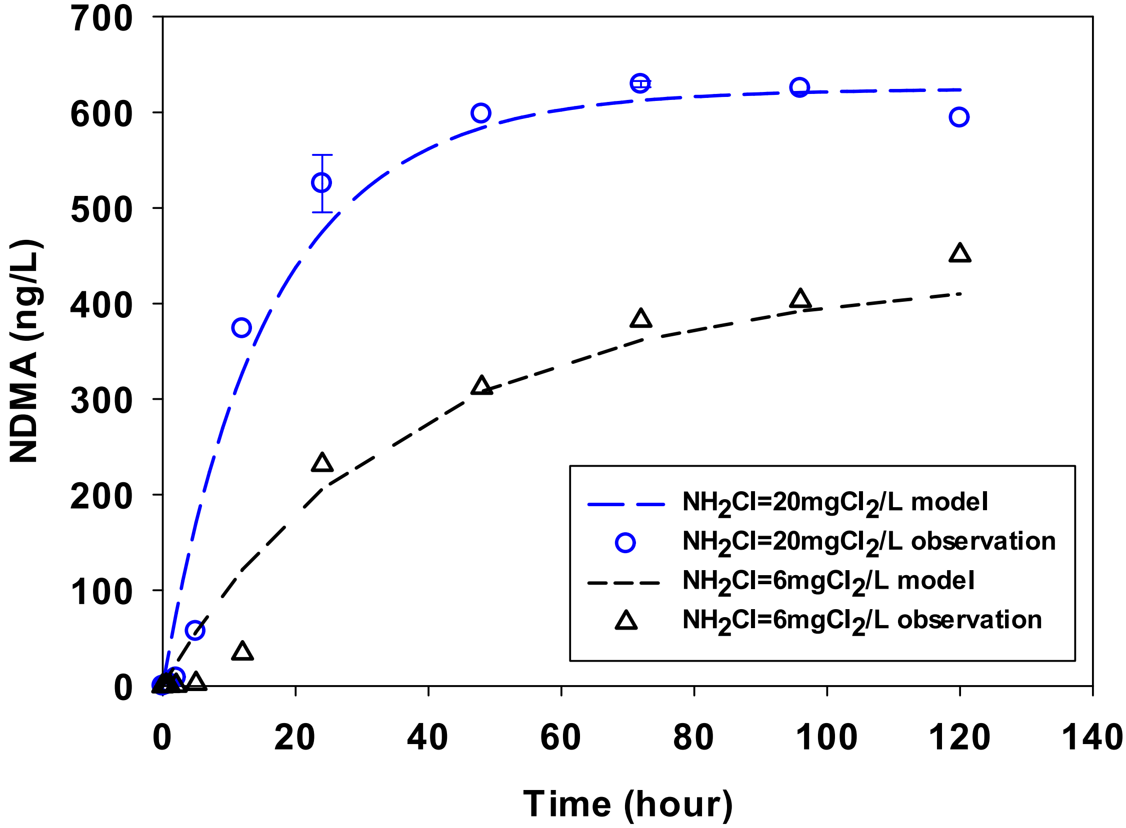

Fig S4. NDMA formation observed (symbols) and fitted by Equations 2&3 (line) in WW5 at two initial monochloramine doses. (pH=8.0, 20°C)

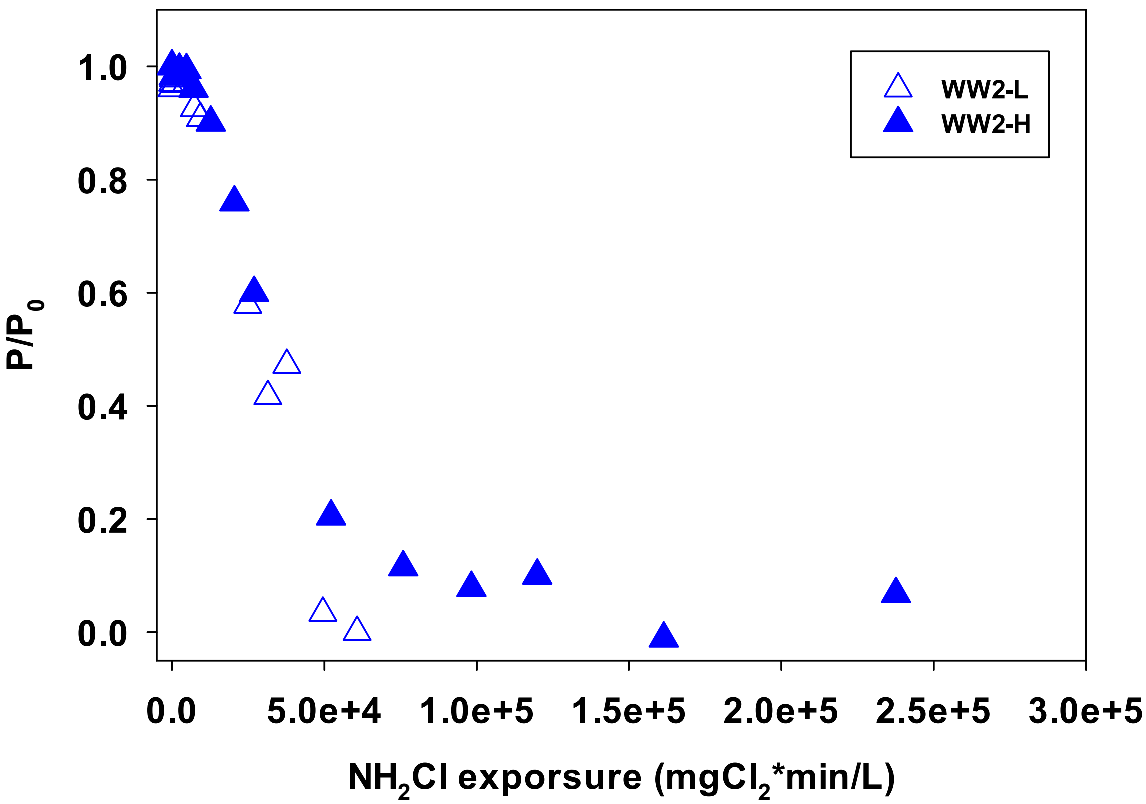

Fig S5: Plots of P/P_0 verses monochloramine exposure for water samples WW2, L= lower, H= higher, represent samples with lower or higher NH_2Cl concentration.

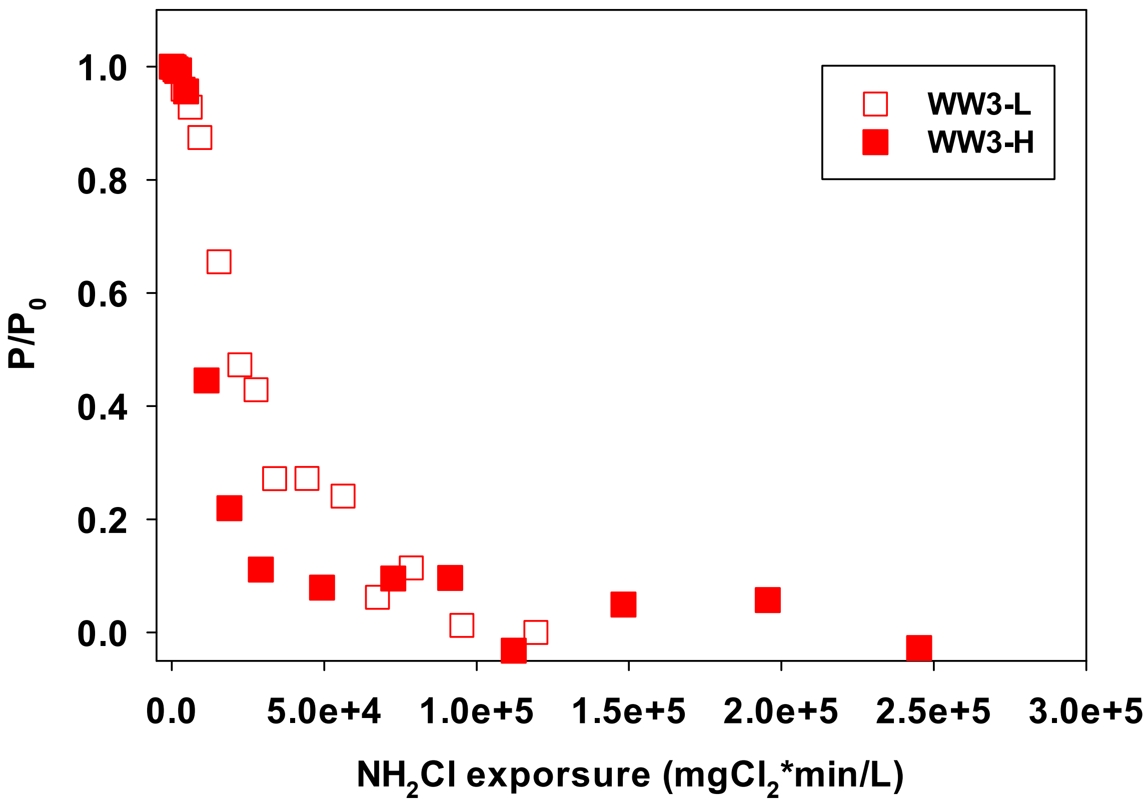

Fig S6: Plots of P/P_0 verses monochloramine exposure for water samples WW3, L= lower, H= higher, represent samples with lower or higher NH_2Cl concentration.

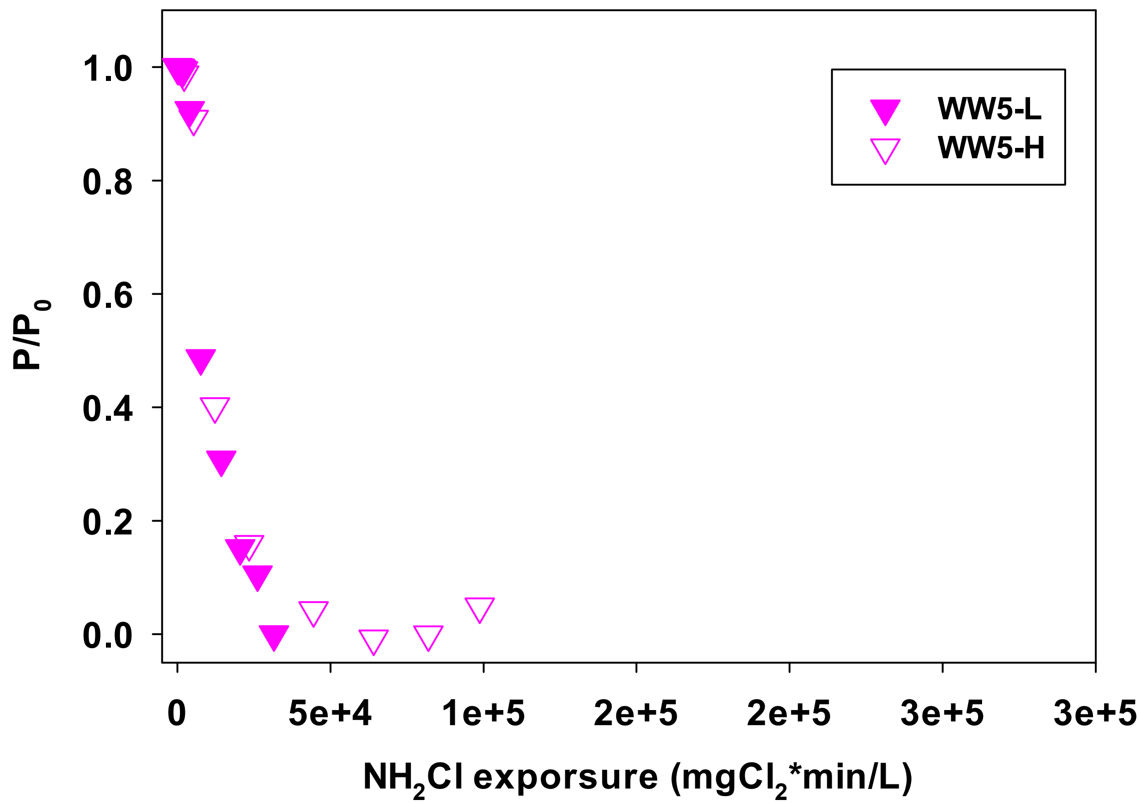

Fig S5: Plots of P/P_0 verses monochloramine exposure for water samples WW5, L= lower, H= higher, represent samples with lower or higher NH_2Cl concentration.

Table S1: Dose-response curve model parameters

Sample ID	Upon Monochloramine Addition				
	Monochloramine dose ($mgCl_2/L$)	pH	$NDMA_{max}$ (nM) [ng/L]	k(h^{-1})	R^2
WW1	18	8.2	6 [450]	0.03	0.99
	6		4 [280]	0.02	0.91
WW2	20	8	7 [520]	0.05	0.98
	7		2 [200]	0.01	0.96
WW3	20	8	12[920]	0.17	0.97
	7		9[620]	0.02	0.96
WW4	20	8	12[920]	0.13	0.99
	7		8[580]	0.03	0.98
WW5	20	8	8[600]	0.18	0.99
	6		5.5[380]	0.04	0.98
SW1	36	8	0.7[53]	0.01	0.98
	12		0.4[35]	0.01	0.93
GW1	20	8	0.2[16]	0.04	0.93
	7		0.2[11]	0.07	0.95

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